Inorganic Chemistry
Article

Inorg. Chem. **2011**, *50*, 1491–1497 **1491**
DOI: 10.1021/ic102074a

Evidence for [18-Crown-6 Na]$_2$[S_2O_4] in Methanol and Dissociation to $Na_2S_2O_4$ and 18-Crown-6 in the Solid State; Accounting for the Scarcity of Simple Oxy Dianion Salts of Alkali Metal Crown Ethers in the Solid State

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Received October 13, 2010

[18-Crown-6 Na]$_2S_2O_4$ complex was prepared in methanol solution but dissociates into 18-Crown-6 $_{(s)}$ and $Na_2S_2O_4$ $_{(s)}$ on removal of the solvent. Evidence for complexation in methanol is supported by a quantitative mass analysis and the dissociation in the solid state by vibrational spectroscopy and powder X-ray diffraction. These observations are accounted for by investigating the energetics of complexation in solution and dissociation in the solid state using calculated density functional theory (DFT) gas phase binding enthalpies and free energies combined with conductor-like screening model (COSMO) solvation energies and lattice enthalpy and free energy terms derived from volume based thermodynamics (VBT). Our calculations show that complexation of alkali metal dianion salts to crown ethers are much less favorable than that of the corresponding monoanion salts in the solid state and that the formation of alkali metal crown complexes of stable simple oxy-dianion (e.g., CO_3^{2-}, SO_4^{2-}) salts is unlikely. The roles of complexation with 18-Crown-6 and ion pair formation in the process of dissolution of $Na_2S_2O_4$ to methanol are discussed.

1. Introduction

Sodium dithionite is an important industrial chemical used as a reductive bleaching agent for pulp and paper,[1] and for the reduction of Vat dyes and sulfur containing dyes.[2] Sodium dithionite is also used widely in research as a reducing agent in organic,[3] organometallic,[4] and inorganic[5] chemistry. The dithionite anion is known to adopt three different conformations depending on the countercation. In the Na^+,[6] Zn^{2+},[7] and Sn^{2+}[8] salts the anion has a *cis*-$[O_2S\text{-}SO_2]^{2-}$ eclipsed structure (nearly C_{2v} symmetry) and in the dihydrate of the Na^+ salt it has a gauche conformation (C_2 symmetry) with a torsion angle of 56° about the S−S bond.[9] In all structures, the S−S bond (2.298−2.39 Å)[6−8] is much longer than that in S_8 (2.04 Å).[1] The dithionite is observed to have a *trans*-$[O_2S\text{-}SO_2]^{2-}$ staggered structure (C_{2h} symmetry) in the salt of the larger tetraethylammonium cation based on solid state Raman studies.[10] The staggered centrosymmetric structure is also observed in aqueous solution.[11] The bonding in the dithionite anion is of continuing interest.[12] It has been compared to the analogous isolobal $Se_2I_4^{2+}$ and can be described by the interaction of the π^* SOMO's of two SO_2^- moieties resulting in an occupied $\pi^*-\pi^*$ bonding combination.[12b]

Simple oxy dianions, for example, O_2^{2-}, CO_3^{2-}, SO_4^{2-}, $S_2O_4^{2-}$, and so forth, are not observed in the gas phase and are thermodynamically unstable with respect to the loss of an electron.[13] They are stabilized in the solid state and solution by lattice and solution energies. As the size of the cation is increased the lattice energy decreases. Only a few of these salts are reported with large cations, particularly two; the tetraethylammonium[14] and 18-Crown-6 sodium[15] salts of dithionite. Salts of this kind are expected to lead to better solubility in solvents of lower dielectric constant, increasing the dianion reactivity. The evidence presented for the former salt in the literature was convincing,[14] the latter less so.

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It is claimed in the literature that the solid 18-Crown-6 sodium dithionite complex softened at 45 °C but never completely melted.[15] This observation is not inconsistent with a mixture of the components rather than a complex of 18-Crown-6 and sodium dithionite. The route to large cation dianion salts by complexation of a simple metal cation in a dianion salt by a suitable crown ether or related complexing agent is potentially very general and therefore very attractive. In this paper we confirm that the 18-Crown-6 sodium dithionite salt is stable in methanol solution, but we found that it dissociates in the solid state to 18-Crown-6 and sodium dithionite, consistent with our estimates of the energetics of the system. A search of the literature shows that there are essentially no examples of isolated metal crown ether complexes of the simple oxy dianions. In contrast, there is extensive knowledge of the corresponding monoanion salts, for example, NO_3^-,[16] ClO_4^-,[17,18] halides.[19,20] We account for these observations by investigating the corresponding energetics of dissociation in solution and in the solid state. We note that although energetics of metal complexation of crown ethers[21] and related species[22] in solution have been extensively investigated, solid state energetics seem to have received much less attention.[21,22]

2. Experimental Section

2.1. General Procedures. All operations were carried out in an MBraun Unilab drybox under a nitrogen atmosphere or using vacuum line techniques. The Monel vacuum line and general techniques have been fully described elsewhere.[23] The reaction vessel used was a two tube (3 cm OD) Pyrex H vessel equipped with two Rotaflo (6 HK) Teflon in glass valves and a medium sintered glass frit (see the Supporting Information, Figure S1A).

FT-IR spectra were recorded on a Thermo Nicolet NEXUS 470 FT-IR. FT-Raman spectra were recorded on a Thermo Nicolet 6700 FT-IR equipped with a Thermo Nicolet NXR FT-Raman accessory at 298 K using a Nd:YVO_4 laser (emission wavelength: 1064 nm; maximum laser power: 65 mW; Resolution: 4 cm^{-1}; 180° excitation) with the solids sealed in melting point tubes. Powder X-ray diffraction patterns were acquired on a Bruker D8 X-ray diffractometer equipped with a monochromator and a vertical goniometer with $\theta-2\theta$ mode using CuKα radiation with a wavelength of $\lambda = 1.5418$ Å at 40 kV and 20 mA and a scanning rate of 0.04deg $2\theta\ s^{-1}$. Scan range was from 5.0°−90° 2θ.

2.2. Materials. Sodium dithionite (Sigma-Aldrich) was used as received. 18-Crown-6 (Fluka) was recrystallized from acetonitrile as described by Perrin et al.[24] and vacuum-dried. Acetonitrile (ACP Chemicals) was dried over CaH_2 in a 500 mL rbf for 24 h and distilled onto fresh CaH_2 in a 500 mL rbf for storage. Methanol was taken from a solvent purification system and degassed. Sulfur dioxide (Canlab) was vacuum distilled and stored over CaH_2 in a 100 mL rbf equipped with a Whitey valve. Sulfur dioxide was freshly distilled into the reaction vessels via the vacuum line.

2.3. Preparation of [18-Crown-6 Na]$_2$S$_2$O$_4$ in Methanol.

$$\begin{array}{c} 2\ \text{18-Crown-6}_{(s)} + Na_2S_2O_{4(s)} \\ \downarrow\ \text{MeOH} \\ 2[\text{18-Crown-6 Na}]^+_{(MeOH)} + S_2O_4^{2-}{}_{(MeOH)} \end{array}$$

18-Crown-6 sodium dithionite complex in methanol solution was prepared by a modification of the procedure given by Mincey and Traylor.[15] A more detailed description of the procedure can be found in the Supporting Information (see section S1.1). 18-Crown-6 (2.185 g, 8.273 mmol) and $Na_2S_2O_4$ (1.534, 8.811 mmol) were added to a dried two tube vessel equipped with Teflon in glass Rotaflo (6 HK) valves. Methanol (15 mL) was syringed into the vessel under a flow of nitrogen, and the mixture was stirred at room temperature for 13.5 h. A pale yellow solution was filtered from 0.861 g of colorless insoluble solid, then methanol was removed under dynamic vacuum to give an off-white solid with a yield of 2.804 g (96% based on eq 1). Both solids were identified by IR (Supporting Information, Figure S2), Raman spectroscopy (Figure 1), and powder X-ray diffraction (Figure 2).

2.4. Quantum Chemical Calculations. All calculations were carried out with the Gaussian 03[25] and Turbomole[26] program packages. B3PW91[27] functional with the 6-311+G(d,p)[28] basis set was employed for geometry optimizations and frequency calculations. Solvation free energies were determined on vacuum optimized geometries using the conductor-like screening model (COSMO)[29] as implemented in Turbomole. Calculations involving dianions (and their ion pairs) were done using the 6-311G(2d) basis set without diffuse basis functions to minimize the non-physical stabilization of the dianion that is due to its inherent instability in the gas phase toward losing an electron while retaining flexibility of the basis set.

3. Results and Discussion

3.1. Evidence for Formation of [18-Crown-6 Na]$_2$S$_2$O$_4$ in Methanol Solution. We found that sodium dithionite has a very low solubility in methanol (0.173 g/100 mL)

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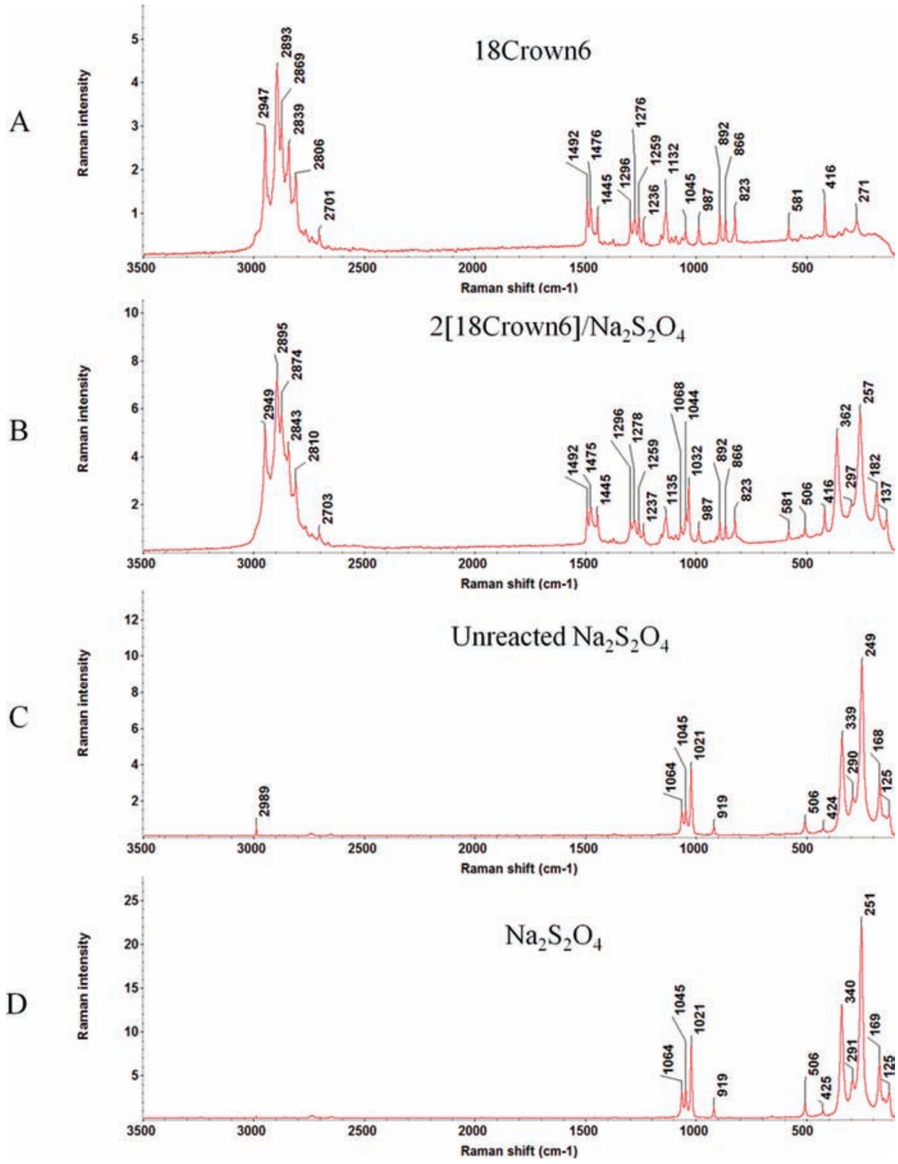

Figure 1. Raman spectra for the [18-Crown-6 Na]$_2$S$_2$O$_4$ reaction in methanol (Reaction 1). (A) 18-Crown-6, (B) soluble solid from reaction 1 (2[18-Crown-6]/Na$_2$S$_2$O$_4$), (C) insoluble solid from reaction 1 (Unreacted Na$_2$S$_2$O$_4$), (D) Na$_2$S$_2$O$_4$ (85% Aldrich). (A)(B) Ge detector with 1024 scans, (C)(D) InGaAs detector with 1000 and 256 scans respectively.

(see Supporting Information section S1.2 for procedure). However when 2.185 g of 18-Crown-6 was added to a mixture of 1.534 g of $Na_2S_2O_4$ and 15 mL of methanol, a solution was formed over some remaining solid. The solution was filtered from the excess $Na_2S_2O_4$ leaving 2.804 g of soluble solid (expected 2.907 g based on eq 1 and identified by Raman and IR Figure 1 and in Supporting Information, Figure S2, respectively). The insoluble solid was collected giving 0.861 g (expected 0.814 g based on eq 1). The difference between collected amounts and calculated weights of products might arise from the impurities in commercial $Na_2S_2O_4$.[30] Thus, we confirm the work of Mincey et al.[15] that [18-Crown-6 Na]$_2$S$_2$O$_4$ is very likely formed in methanol solution. Removal of the methanol gives a solid, which is shown by IR/Raman and X-ray powder diffraction (sections 3.2 and 3.3) to be a mixture of $Na_2S_2O_4$ and 18-Crown-6. Therefore, the complex which is formed in solution dissociates in the solid state according to eq 2.

$$\begin{array}{c} 2[\text{18-Crown-6 Na}]^{+}{}_{(\text{MeOH})} + S_2O_4{}^{2-}{}_{(\text{MeOH})} \\ \Big\downarrow \text{-MeOH} \\ 2\ \text{18-Crown-6}_{(s)} + Na_2S_2O_{4(s)} \end{array}$$

3.2. IR and Raman Analysis of Solid Product. The infrared spectrum of the soluble solid from reaction 1 (Supporting Information, Figure S2B) clearly shows the presence of both 18-Crown-6 and sodium dithionite with distinct peaks at 1106 cm^{-1} and 915 cm^{-1} respectively. The Raman spectrum (Figure 1B) contains peaks that match the peaks of free 18-Crown-6 (Figure 1A) exactly and the peaks assigned to the sodium dithionite match the free sodium dithionite (Figure 1D) although, the dithionite peaks are shifted to higher frequencies by 10−20 cm^{-1}. The infrared spectrum only confirms that there is both 18-Crown-6 and sodium dithionite in the recovered soluble

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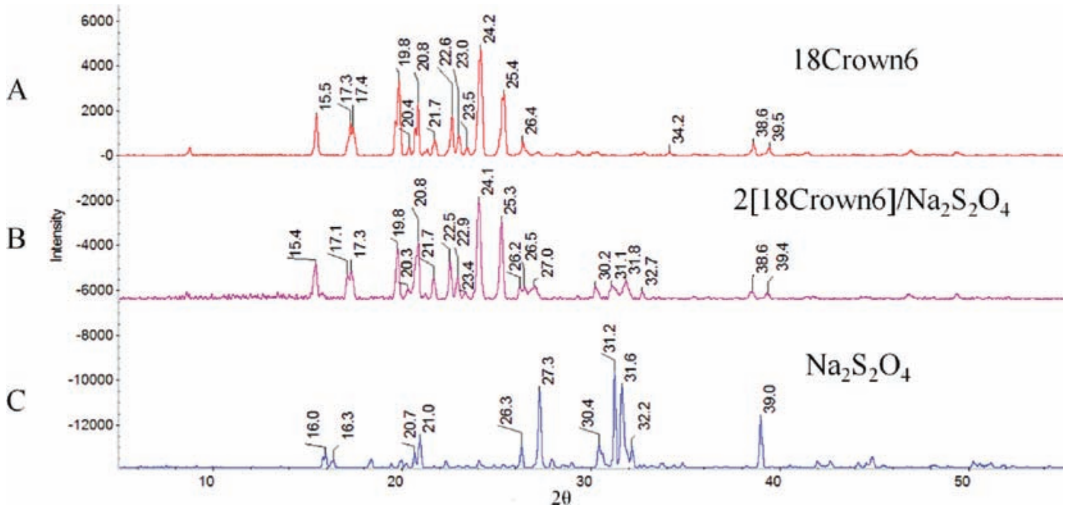

Figure 2. Comparison of Powder XRD from 5 to 55° 2*θ*. (A)18-Crown-6, (B) soluble material from reaction 1, (C) $Na_2S_2O_4$ (85% Aldrich).

solid but does not give evidence whether the solid is a complex. The analysis of the Raman spectrum shows that the 18-Crown-6 peaks match free 18-Crown-6 suggesting that the solid is not a complex but a mixture. The Raman of a complexed 18-Crown-6 is characterized by the appearance of a sharp intense band near 870 cm^{-1} making it different than a free 18-Crown-6 as reported by Sato et al.[31] Although the peaks attributable to $Na_2S_2O_4$ are shifted by 10−20 cm^{-1} compared to literature values the Raman spectrum of a salt of $S_2O_4^{2-}$ with a large cation is expected to be very different from that in $Na_2S_2O_4$ as $S_2O_4^{2-}$ is expected to adopt a staggered C_{2h} conformation with large cations.[32] The observed differences could be due to the surface of the solid, from which the Raman scattering occurs, having a somewhat different structure than that of the bulk $Na_2S_2O_4$.

3.3. Powder X-ray Diffraction Analysis. The powder XRD pattern of the soluble solid from the reaction of 18-Crown-6 and sodium dithionite in methanol (Figure 2B) is almost the same as the superimposition of free 18-Crown-6 (Figure 2A) and free sodium dithionite (Figure 2C). There is some line broadening in the peaks corresponding to the sodium dithionite which could be due to poor crystallinity of the sodium dithionite in the mixture. This is additional evidence that the solid product from the reaction is a mixture of the two starting materials.

3.4. Stability of Crown Ether Complex Salts of Dianions in the Solid State. Different conformers of free crown ethers[33−35] and their metal complexes[34,36−38] have been extensively investigated in computational studies. Albeit the theoretically predicted minimum energy conformations do not always coincide with the experimentally observed structures, the energy differences between the theoretically predicted global minima and the optimized structures corresponding to the experimentally observed conformations are found to be small. We have chosen to use the experimentally observed conformations as a starting point for our calculations. Comparison of our optimized structures with the minimum energy conformations found in previous studies has been presented in the Supporting Information section S2.1.

Enthalpies and free energies for complexation reactions corresponding to Born−Haber cycles shown in Figures 3, 4, and 5 are given in Tables 1 and 2. The calculated gas phase binding energies of crown ethers with lithium and sodium cations are in good agreement with those obtained in earlier experimental[39−41] and theoretical[34,36,37] studies (see Table 1). Calculated gas phase binding energies reproduce the trend that lithium binds more strongly to all crown ethers studied here in the gas phase than sodium. In the gas phase sodium binds most strongly to 18-Crown-6 while lithium favors 15-Crown-5.

The solid phase enthalpies of complex salt formation (e.g., reaction 4) are presented in Table 2.[42] The solid

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(42) Assuming that there is no significant difference between the sum of the molecular volumes of reactants and the molecular volume of the product in the solid state, the solid state free energy of reaction (298 K) (eq 4) can be derived from the enthalpy of reaction by adding +9 kJ mol^{-1} for dianion salts and +4 kJ mol^{-1} for monoanions salts.

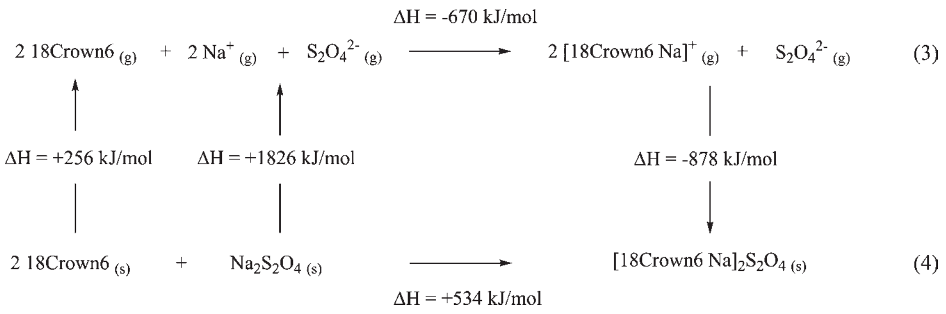

Figure 3. Born–Haber cycle for the complexation of sodium dithionite with 18-Crown-6 in the solid state. See Tables 1, 2, and Supporting Information sections S2.1, and S2.2 for computational details.

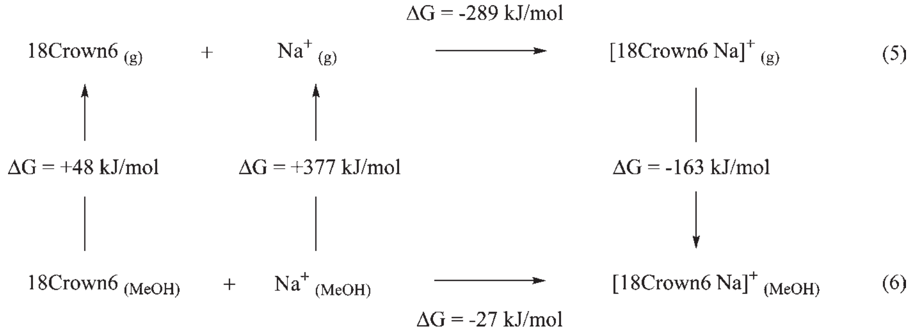

Figure 4. Born–Haber cycle for the complexation of sodium with 18-Crown-6 in methanol. See Tables 1, 2, and Supporting Information sections S2.1, and S2.2 for computational details.

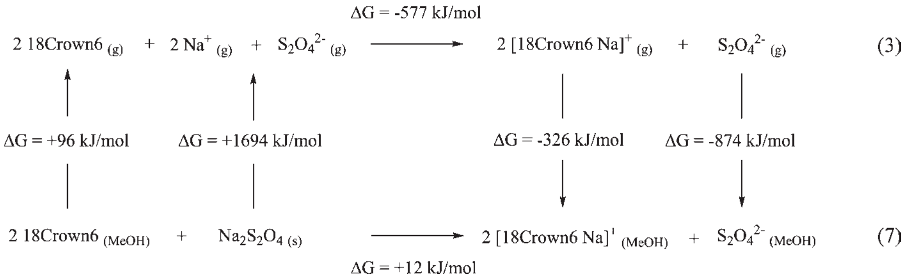

Figure 5. Born–Haber cycle for the complexation of sodium dithionite with 18-Crown-6 in the solid state to methanol solution. See Tables 1, 2, and Supporting Information sections S2.1, and S2.2 for computational details.

Table 1. Calculated Enthalpies and Free Energies (kJ mol^{-1}, 298 K) of Binding for Some Cationic Sodium and Lithium Crown Ether Complexes in the Gas Phase (Eq. 5) and MeOH Solution (Eq. 6)

complex	ΔH(gas)[a]	literature ΔH(gas)[b]	experim. ΔH(gas)	ΔG(gas)[a]	ΔG(MeOH) COSMO	experim. ΔG(MeOH)[51]
(12-Crown-4 Na)$^+$	−262	−271[36b]	−254 ± 13[39]	−216	−2	−9 ± 2
(15-Crown-5 Na)$^+$	−320	−320[34c]	−298 ± 18[40]	−278	−22	−19 ± 1
(18-Crown-6 Na)$^+$	−335	−336[37a]	−300 ± 19[40]	−289	−27	−25 ± 1
(12-Crown-4 Li)$^+$	−364	−389[36b]	−378 ± 51[41]	−318	−8	
(15-Crown-5 Li)$^+$	−417	−423[34c]		−377	−24	
(18-Crown-6 Li)$^+$	−413	−399[37a]		−366	−10	

[a] B3PW91/6-311+G(d,p). [b] MP2/6-31+G*.

phase energies for complex salt formation were calculated from the corresponding gas phase binding enthalpies by adding lattice enthalpy terms derived using a volume based thermodynamics (VBT) approach developed by Jenkins et al.[43] (See Supporting Information section 2.3 for details). Reference enthalpies of complex salt formation from their parent salts and crown ethers calculated for three known complex salts [18-Crown-6 Na]-[$GaCl_4$],[44] [15-Crown-5 Na]Br,[45] and [15-Crown-5 Na]$_2$-[$NiCl_4$][46] were positive for two of the salts [15-Crown-5 Na]Br (+70 ± 29 kJ mol^{-1}) and [15-Crown-5 Na]$_2$[$NiCl_4$]

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Table 2. Calculated Enthalpies and Free Energies (kJ mol^{-1}, 298 K) for Crown Complex Salt Formation in the Solid Phase (Eq. 4), and upon Dissolution to MeOH (Eq. 7)

salt	ΔH(solid)[a] (eq 4)	ΔG(solid/MeOH) (eq 7)
[12-Crown-4 Na]$_2$[S_2O_4]	+467 ± 57	+62
[15-Crown-5 Na]$_2$[S_2O_4]	+398 ± 49	+21
[18-Crown-6 Na]$_2$[S_2O_4]	+534 ± 46	+12
[12-Crown-4 Li]$_2$[S_2O_4]	+282 ± 58	−110
[15-Crown-5 Li]$_2$[S_2O_4]	+226 ± 50	−142
[18-Crown-6 Li]$_2$[S_2O_4]	+400 ± 47	−113
[18-Crown-6 Na]$_2$[CO_3]	+924 ± 77	+213
[15-Crown-5 Li]$_2$[CO_3]	+637 ± 87	+87
[18-Crown-6 Na][$GaCl_4$]	−62 ± 11	
[15-Crown-5 Na]Br	+70 ± 29	
[15-Crown-5 Na]$_2$[$NiCl_4$]	+141 ± 72	

[a] Per one mole of complex salt.

(141 ± 70 kJ mol^{-1}). Assuming that the formation reactions have been under thermodynamic control the VBT results appear to have a bias toward simple salts over the complex salts that is larger than the errors estimated from standard deviations of ionic volumes.[43a] However, in a recent comparative study the authors concluded the rms errors of the VBT predicted solid state heats of formation to be of the order of 120−150 kJ mol^{-1} depending on the salt type (e.g., 1:1, 1:2).[47] Therefore, it is not unreasonable to expect that the energy values obtained for the corresponding hypothetical complex salts to be about 200 kJ mol^{-1} more stable toward dissociation than predicted by the VBT approach. Even taking this into account the large positive value of ΔH (eq 4) of +534 kJ mol^{-1} unambiguously reflects the experimental result that the complex dissociates to its components in the solid state. Improved VBT lattice enthalpy models[48,49] are likely to give a better agreement between observations and predictions, but are unlikely to change the general conclusions.

The enthalpies of reaction for the formation of sodium or lithium crown ether dithionite salts are all predicted to be strongly endothermic in the solid state (see Table 2) with the most favorable formation {[15-Crown-5 Li]$_2$-[S_2O_4]} having enthalpy of over +200 kJ mol^{-1}. The predicted enthalpies of formation for all the considered complex dithionite salts are so endothermic that even if the systematic error observed for the known salts is accounted for the sodium or lithium crown ether salts of dithionite are unlikely to be stable in the solid state. The high predicted solid state enthalpies of formation (Table 2) together with the weaker binding of heavier alkali metals to crown ethers that has been illustrated by other authors,[34c,36b,37a] suggests that none of the alkali metal crown ether dithionite salts are likely to be stable toward a simple alkali metal dithionite salt in the solid state. Furthermore, given the relatively large volume of dithionite (0.113 nm^3) it seems improbable that alkali metal crown ether salts of the other simple oxy dianions (e.g., CO_3^{2-}, SO_4^{2-}) would be stable either. For example the solid state enthalpy for the formation of CO_3^{2-} salt of the strongest crown ether complex considered here (15-Crown-5 Li)$^+$ is far more endothermic than any of the dithionite complex salts (+637 ± 87 kJ mol^{-1}). The anions in the known examples of alkali metal crown ether complex salts of dianions are larger than the simple oxy dianions (e.g., $[Sb_2Se_{12}]^{2-}$ 0.442 nm^3 in [12-Crown-4 Li]$_2$[Sb_2Se_{12}][50] and $[NiCl_4]^{2-}$ 0.186 nm^3 in [15-Crown-5 Na]$_2$[$NiCl_4$][46]) substantially decreasing the energy of dissociation to crown and simple alkali metal salt.

3.5. Role of 18-Crown-6 in Solution of $Na_2S_2O_4$ into Methanol. The free energies of formation for sodium crown ether complexes in MeOH have been determined with various experimental methods, and values judged to be most reliable have been evaluated in a recent review.[51] We have estimated the free energies of complex formation in MeOH using the COSMO solvation model (see Table 1). The COSMO results are in good agreement with the experimentally determined reaction energies for sodium crown ether complexes (For comparison, results with the IEFPCM solvation model are presented in the Supporting Information, Table S2.3). The calculated free energies of complexation for (12-Crown-4 Li)$^+$ and (15-Crown-5 Li)$^+$ suggest similar or stronger complexation in MeOH than the corresponding sodium complexes in contrast to the experimental formation constants that have been reported in the literature [cf. lg K 1.32 ± 0.01 (12-Crown-4 Li)$^+$, 1.5 ± 0.2 (12-Crown-4 Na)$^+$, 1.24 ± 0.05 (15-Crown-5 Li)$^+$, 3.32 ± 0.12 (15-Crown-5 Na)$^+$][51] indicating the limitations of the calculations in reproducing all the experimental observations. No formation constant for (18-Crown-6 Li)$^+$ has been reported in the literature but the less favorable calculated complexation energy compared to (15-Crown-5 Li)$^+$ is in line with the size mismatch between the small lithium cation and the relatively large 18-Crown-6 ring.

The experimental observations suggested that the solution of $Na_2S_2O_4$ into MeOH is aided by 18-Crown-6 via complex formation. The solution of $Na_2S_2O_4$ into MeOH can be thought to form solvated Na^+ and $S_2O_4^{2-}$ ions according to reaction 8 (Scheme 1). The free energy calculated for reaction 8 (at 298 K) was +65 kJ mol^{-1}. Simultaneous complexation of Na^+ ions with 18-Crown-6 starting from solid 18-Crown-6 would result in reaction 1. However, to minimize the unnecessary errors related to the calculations, it is more convenient to estimate the effect of 18-Crown-6 to the solution of $Na_2S_2O_4$ from a reaction 7 where 18-Crown-6 is already dissolved in MeOH. The free energy of reaction determined for 7 is +12 kJ mol^{-1} suggesting that 18-Crown-6 complexation does indeed improve the energetics of solution of $Na_2S_2O_4$ into MeOH although the solution process is still predicted to be endoergic. The energetics of solution of $Na_2S_2O_4$ into MeOH are improved to a lesser extent by complexation with the smaller crown ethers 12-Crown-4 and 15-Crown-5 than with the 18-Crown-6, albeit the effect of 12-Crown-4 to the solution of $Na_2S_2O_4$ is minimal. In contrast to $Na_2S_2O_4$ the calculations suggest that the hitherto unknown $Li_2S_2O_4$ would be readily soluble in MeOH (ΔG = −94 kJ mol^{-1}).

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Scheme 1

$$Na_2S_2O_{4\,(s)} \longrightarrow 2\,Na^+_{\,(MeOH)} + S_2O_4^{2-}{}_{(MeOH)} \qquad (8)$$

$$Na_2S_2O_{4\,(s)} \longrightarrow Na^+_{\,(MeOH)} + NaS_2O_4^-{}_{(MeOH)} \qquad (9)$$

$$2\ 18Crown6_{\,(MeOH)} + Na_2S_2O_{4\,(s)} \longrightarrow [18Crown6\ Na]^+_{\,(MeOH)} + NaS_2O_4^-{}_{(MeOH)} \qquad (10)$$

In addition to the full dissociation of $Na_2S_2O_4$ upon solution into MeOH (eq 8), $Na_2S_2O_4$ can be thought to form solvated sodium ions and $[Na-S_2O_4]^-$ ion pairs according to reaction 9. Similar ion pair formation has been predicted/observed in solutions of other salts of dianions.[52] We have estimated the energetics of ion pair formation for $MS_2O_4^-$ and MCO_3^- (where M = Na, Li) at the B3PW91/6-311G(2d) level of theory (See Supporting Information section S2.2 for discussion on the minimum structures). The calculated free energy for the $[Na-S_2O_4]^-$ ion pair formation in the gas phase is -982 kJ mol^{-1}, which is much higher than the complexation energy of Na^+ with 18-Crown-6. The free energy for reaction 9 was determined to be -27 kJ mol^{-1} which suggests that $Na_2S_2O_4$ would be thermodynamically allowed to dissolve into MeOH as ion pairs although no significant solution of $Na_2S_2O_{4\ (s)}$ into MeOH was experimentally observed. The addition of 18-Crown-6 to the reaction according to eq 10 improves the energetics further to -54 kJ mol^{-1}. Apart from the reactions considered here a complex equilibria of other reactions (e.g., $S_2O_4^{2-} \rightleftarrows 2\,SO_2^-$) is expected to be present in the MeOH solution improving the energetics of dissolution further.

For comparison with the dithionite salts the energetics of solution of Na_2CO_3 and Li_2CO_3 into MeOH are also considered, and calculations show them to be strongly endoergic by +267 kJ mol^{-1} and +135 kJ mol^{-1}, respectively. The simultaneous complexation of the metal cations with crown ethers is not enough to make the dissolution favorable (see Table 2) and even the energy gained from ion-pair formation is not likely enough to make the solution process favorable at least in the case of Na_2CO_3. The calculated free energies of solution are consistent with an experimental study by El-Dossoki[53] that showed Na_2CO_3 and Li_2CO_3 to be only sparingly soluble in MeOH even in the presence of 18-Crown-6.

4. Conclusion

The 18-Crown-6 sodium dithionite complex was prepared in methanol solution but dissociates into $Na_2S_2O_{4\ (s)}$ and 18-Crown-6$_{(s)}$ on removal of the solvent as shown by vibrational spectroscopy and X-ray powder diffraction, contrary to the previous claim that the solid acts as a complex in all respects.[15] Theoretical calculations support the instability of the complex in the solid state with a large positive free energy. In addition calculations indicate that the formation of stable crown ether (12-Crown-4, 15-Crown-5, or 18-Crown-6) complex salts of alkali metal dithionites or other simple oxy dianions (smaller than dithionite) is unlikely. Furthermore the calculations show that the dissolution of sodium dithionite alone in methanol is unfavorable and that adding 18-Crown-6 improves the energetics of dissolution. Also, the formation of sodium dithionite ion pairs improves the energetics even further, and the possibility for complex equilibria of other reactions in solution is likely to aid in the dissolution of sodium dithionite in methanol, thus accounting for our experimental observations. For a complex of sodium dithionite and complexing agent that is similar in size to 18-Crown-6 to be stable in the solid state we predict that the complexation energy in the gas phase would need to be in the range of -500 to -600 kJ mol^{-1}.

Acknowledgment. We thank NSERC of Canada Strategic Grants for financial support, Dr. Ven Reddy at the University of New Brunswick for assistance with the powder XRD, and Dr. Heikki Tuononen, University of Jyväskylä, Jyväskylä, Finland, for help with the COSMO calculations.

Supporting Information Available: Procedure for the preparation of $[18\text{-Crown-6 Na}]_2S_2O_4$ in methanol, procedure for the solubility of sodium dithionite in methanol, mass analysis for the 18-Crown-6 $Na_2S_2O_4$ reaction, comparison of calculated crown ether and crown ether metal complex structures with previous computational studies, equilibrium geometries and properties of the CO_3^{2-} (D_{3h}) and $S_2O_4^{2-}$ (C_{2h}) dianions and $CO_3M^-/S_2O_4M^-$ ion pairs (M = Li,Na), procedure for using the volume-base thermodynamics approach, table of volumes, lattice enthalpies, and solid state entropies of some known and hypothetical salts, table of gas phase entropies and solvation free energies in MeOH, figure of reaction vessel, FT-IR spectra of starting materials and products. This material is available free of charge via the Internet at http://pubs.acs.org.

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