irreversible. Rapid repetitive CV scans past the second wave showed that an unidentified product with a reversible couple at $E° = -1.15$ V was formed by the decomposition reaction of $(CO)_3Fe(C_2B_3H_5)^{2-}$.

Conclusions

The small cobalt and iron carboranes studied have $E°$ values that are shifted negative from those of the metallocenes and large metallocarboranes. One may conclude that there is an overall destabilization of low metal oxidation states for small metallocarboranes; concomitantly, these compounds allow easier access to higher formal metal oxidation states. Comparison of the differences in potential between successive redox processes gives further credence to an isoelectronic model for metallocenes and metallacarboranes.

Data on $(CO_3)Fe(C_2B_3H_5)$ show that $(CO)_3Fe$ derivatives of *closo*-carboranes can be reversibly reduced at rather accessible potentials.

Experimental Section

Compounds **1**–**5** were supplied by Dr. R. N. Grimes of the University of Virginia, and **6** was obtained from Dr. T. P. Fehlner of Notre Dame University. Spectrograde CH_3CN and CH_2Cl_2 were distilled under vacuum from calcium hydride. Tetrahydrofuran was distilled first from lithium aluminum hydride and then from sodium–benzophenone ketyl in vacuo just before use. The supporting electrolyte was 0.1 M Bu_4NPF_6, and the concentration of electroactive compound was between 1.5×10^{-4} and 6.0×10^{-4} M. Electrochemical equipment and procedures were as described elsewhere.[27] $(CO)_3Fe(C_2B_3H_5)$, which is air sensitive, was investigated within a Vacuum Atmospheres drybox. Electrode potentials are reported vs. the aqueous saturated calomel electrode.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grant No. CHE 80-04242) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We wish to thank Professors Grimes and Fehlner for providing the compounds to be studied and for enlightening conversations.

Registry No. **1**, 50860-25-8; **2**, 41660-23-5; **3**, 50932-66-6; **4**, 43061-99-0; **5**, 39980-35-7; **6**, 53363-10-3; **8**, 37100-20-2.

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Preparation and Analysis of Crystalline Alkalides

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The synthesis and analysis of crystalline salts which contain alkali-metal anions and alkali-metal cations, with the latter complexed by various cryptands or a crown ether, are described. Analysis included measurement of evolved hydrogen after decomposition with water, pH titration of OH^- and the cryptand, flame emission determination of alkali metals, and ^1H NMR spectra of the complexing agent. The analyses are in good agreement with the expected stoichiometry for $Cs^+C322{\cdot}Na^-$, $Cs^+18C6{\cdot}Na^-$, and $K^+C222{\cdot}Na^-$ in which C*mno* refers to the macrobicyclic cryptand [*m.n.o*] and 18C6 refers to the macrocyclic crown ether 18-crown-6. Analyses of $Rb^+C222{\cdot}Na^-$, $Li^+C211{\cdot}Na^-$, $Na^+C221{\cdot}Na^-$, $Rb^+C222{\cdot}Rb^-$, and $K^+18C6{\cdot}Na^-$ are in general accord with the proposed stoichiometry. However, in these cases some of the results are in poor agreement with the expectations, probably because of either partial decomposition of the complexant during the hydrogen evolution step or contamination of the crystals with excess metal. Crystals were also precipitated from solutions whose solution stoichiometry corresponded to $Cs^+C222{\cdot}Na^-$, $K^+C222{\cdot}K^-$, and $Cs^+C222{\cdot}Cs^-$. Nevertheless, for these crystals the analyses were poor and suggested decomposition prior to analysis and/or contamination by metal. A sample presumed to be $Cs^+C322{\cdot}Cs^-$ decomposed violently in vacuo at about −20 °C. Attempts to synthesize $Ba^{2+}C222{\cdot}(Na^-)_2$ failed to yield satisfactory analyses.

Introduction

Since the preparation and characterization of the first crystalline salt of an alkali-metal anion (Na^-) in 1974,[1,2] we have observed the formation of a number of other alkalide salts which, by analogy, presumably consist of alkali-metal *cations* trapped inside of the macrobicyclic cryptand [2.2.2][3] with alkali-metal *anions* outside.[4–12] We report here the preparation and analysis of a number of such crystalline alkalides as well as others which utilized cryptands [2.1.1], [2.2.1], and [3.2.2].[3] We also report the first synthesis of two sodide salts which contain the crown ether 18-crown-6.[13]

The crystal structure of the parent compound, $Na^+C222{\cdot}Na^-$, may be approximately described[2] as closest-packed large cryptated cations with sodium anions in the octahedral holes. Within the hexagonal unit cell, the cations pack in ABC··· repeat layers. Thermodynamic arguments[6,8] show that the stabilization of Na^- is largely due to the stability of the cryptated sodium cation which is resistant to reduction by Na^-. Because crystals of $Na^+C222{\cdot}Na^-$ can be grown isothermally in tetrahydrofuran in the presence of cryptand [2.2.2]and

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0020-1669/82/1321-1966$01.25/0

excess solid sodium,[14] reaction 1 is thermodynamically favorable.

$$\mathrm{C222(s) + 2Na(s) \rightarrow Na^+C222{\cdot}Na^-(s)} \qquad (1)$$

Estimates have been made[6,8] of the stability of various other crystalline alkalides by means of thermodynamic cycles. Such calculations indicate that suitable salts of all of the alkalides (Li^- through Cs^-) should be stable with respect to the free cryptand and the metal. However, in some cases reaction 2

$$\mathrm{M^+Cry{\cdot}M^-(s) \rightarrow M^+Cry{\cdot}e^-(s) + M(s)} \qquad (2)$$

in which $M^+Cry{\cdot}e^-(s)$ is an electride[7,9,11,12,15] appears to be thermodynamically favorable. None of these calculations takes into account the ubiquitous *irreversible* decomposition of the complexing agent by M^- and/or e^- which is always thermodynamically possible but may be very slow under favorable circumstances. Our experience indicates that lithium tends to form electrides rather than lithide salts and that potassides, rubidides, and cesides have a much greater tendency to decompose irreversibly than sodides.

The synthesis of alkalide salts has been greatly aided by the ability to measure transmission spectra of thin solvent-free films produced by rapid solvent evaporation.[7-12] These spectra permit ready identification of particular alkalides and also indicate when trapped electrons are likely to be present. They also provide information about the stability of alkalides in the presence of various complexing agents. An example of the utility of film spectra is provided by the salt $K^+C222{\cdot}Na^-$. Equimolar solutions of sodium, potassium, and cryptand [2.2.2] in methylamine probably contain primarily K^+C222 and Na^-. This is favored over Na^+C222 and K^- both because of the greater stability of the K^+C222 complex[16] compared with that of the Na^+C222 complex and because Na^- is much more stable than K^-.[8] When such a solution is rapidly evaporated, the transmission spectrum of the resulting *solvent-free* film clearly shows the presence of Na^- with little or no K^-.[12] This indicates that the crystals described in this paper (which are obtained by replacing the methylamine in such a solution with isopropylamine, followed by cooling) are probably $K^+C222{\cdot}Na^-$ rather than $Na^+C222{\cdot}K^-$. Thin-film spectra also permit predictions to be made about stabilities in the presence of various complexing agents. Films of $K^+C222{\cdot}Na^-$ were unstable above −10 °C, suggesting that the corresponding crystals might also be thermally unstable. This has indeed been the case, and, because of instability, a number of attempts were required to obtain reasonably pure crystals of this salt. Corresponding behavior of both films and crystals was observed with $Rb^+C222{\cdot}Na^-$, $Cs^+C222{\cdot}Na^-$, and all alkalides other than sodides. By contrast, $Li^+C211{\cdot}Na^-$, $Cs^+18C6{\cdot}Na^-$, and $Cs^+C322{\cdot}Na^-$ formed films which were stable up to room temperature. Crystals of these three alkalides proved to be much more stable than the others described in this paper.

Experimental Section

A. Solution Preparation and Precipitation. The most difficult problem encountered in the synthesis of alkalides is solution decomposition. Solutions of alkali metals in amine and ether solvents are thermodynamically unstable with respect to reduction of the solvent. However, kinetically stable metal solutions can be prepared if solvents, metals, and complexing agents are appropriately treated to remove all easily reducible impurities. The use of rigorously clean glassware and high-vacuum techniques is equally important for the preparation of stable solutions. The required techniques have been previously described in detail.[11]

The borosilicate and/or fused silica glassware used in this study was cleaned as previously described[11] by first filling with an $HF-HNO_3$ detergent solution followed by thorough rinsing with doubly distilled water. It was then filled with aqua regia, allowed to stand overnight, and again thoroughly rinsed before oven drying.

Solvent purification and storage as well as the preparation of known amounts of Na, K, Rb, and Cs in calibrated glass tubing has been previously described.[11] Lithium (Alfa-Ventron, 99.9%) and barium (Metals Mart 99.2%) were weighed on a microbalance in an inert-atmosphere box and sealed into glass tubes. All metals were introduced into evacuated synthesis vessels through side arms fitted with a flexible connection made of Teflon heat-shrinkable tubing (Pope Scientific).

Cryptands (2.2.2), (2.2.1), and (2.1.1) (PCR, Inc.) were distilled before use under vacuum (~10^{-5} torr manifold pressure) at temperatures of 110, 100, and 65 °C, respectively. Cryptand (3.2.2), synthesized and purified as described by Lehn et al.,[17] was vacuum distilled at 150 °C before use. The crown ether, 18C6, was recrystallized from acetonitrile, vacuum-dried, and distilled under vacuum at ~60 °C. Because of the unknown toxicity of crown ethers and cryptands, they were handled in a fume hood and care was taken to avoid skin contact.

Weighed amounts of the appropriate complexing agent were introduced into the preparation vessel just before evacuation. When the pressure reached 10^{-5} torr or less, the metal tube was broken, moved into the preparation vessel side arm, and a flame seal-off was made in the glass side arm to remove the heat-shrinkable tubing. The metal (Na, K, Rb, and Cs) was then distilled under vacuum through the side arm and into the metal chamber of the synthesis vessel. Lithium and barium metals cannot be distilled in borosilicate or fused silica glassware and were therefore dissolved in ammonia or methylamine (Li) directly in the side arm. Solvents were introduced by distillation through an evacuated connector between solvent storage bottles and the preparation vessel.

Metal solutions were usually made by first dissolving the complexing agent and then the metal(s) with agitation at reduced temperatures. In some cases the metal and complexant were dissolved simultaneously. Alkalide crystals were precipitated from solution by cooling to −78 °C or below. In certain cases cooling alone was not effective; therefore, a cosolvent was added to cause precipitation. After precipitation, the solvent was poured away and the crystals were rinsed with diethyl ether and dried. The crystals were then distributed into glass tubes which were removed by making a vacuum sealoff. To avoid decomposition it was necessary to keep the solution and the precipitate cold at all times.

When possible, one should dissolve the metal and complexing agent directly in a solvent from which crystals can be easily precipitated. For example, appropriate amounts of sodium and C222 dissolve readily at 0 °C in ethylamine to form a saturated solution which will precipitate $Na^+C222{\cdot}Na^-$ crystals when cooled to −78 °C. The preparation of most other alkalide salt solutions is experimentally more difficult. Often solutions are less stable than those which contain Na^+C222 and Na^- so that during synthesis the dissolution of metal and complexant must be carried out at lower temperatures to avoid irreversible decomposition. At reduced temperatures the rate of dissolution often becomes prohibitively slow. These temperatures might also decrease the rate at which the dissolved metal cation is complexed. Observations made in this laboratory[18] indicate that for the case of $Li^+/C211$ in methylamine, the solutions must be stirred for several hours in order to obtain reproducible film spectra. Because solution decomposition competes with metal dissolution and complexation, syntheses which require large amounts of time can result in partial if not complete decomposition.

The use of solvents such as methylamine and ammonia which readily dissolve the metals, followed by replacement with another solvent, can also cause problems. These solvents support high concentrations of solvated electrons which appear to react with the complexing agent more rapidly than do alkali-metal anions. This can be especially troublesome during solvent replacement. Complete removal of ammonia or methylamine followed by introduction of a new solvent can lead to decomposition. Gradual replacement by successive condensations of the less volatile solvent and removal of the more volatile solvent by partial distillation is better but can be very time consuming

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Table I. Conditions Used for Alkalide Crystallization[a]

compd	dissoln conditions	crystn conditions	comments[b]
$Cs^+C322\cdot Na^-$	0.37 mmol/9 mL of EA, −20 °C/6 h	3 mL of EA + 7 mL of DEE + 2 mL of *n*-P, −78 °C/24 h, supersaturates easily	dendritic crystals, stable up to ~+20 °C
$Cs^+C322\cdot Cs^-$	0.13 mmol/4 mL of EA, −30 °C/2 h	2 mL of EA + 3 mL of DEE + 2 mL of *n*-P, −78 °C/24 h	dec violently at ~−20 °C
$[Ba^{2+}C222\cdot(Na^-)_2]$?	0.3 mmol/12 mL of NH_3, −40 °C/6 h	3 mL of NH_3 + 9 mL of MA, −78 °C/24 h	12 attempts under various conditions gave only dull bronze films mixed with white decn product
$Na^+C221\cdot Na^-$	0.51 mmol/7 mL of EA, −10 °C/20 h	2 mL of EA + 3 mL of DEE + *n*-P (trace), −78 °C/24 h, supersaturates easily	needle-shaped crystals, stable up to ~0 °C; color changed reversibly from dark bronze at −78 °C to bright metallic green at −15 °C; solvent content ~0.9 mole %
$K^+C222\cdot Na^-$	0.8 mmol/3 mL of NH_3, −45 °C/1 h	8 mL of *i*-PA/−92 °C/2 h, −78 °C/24 h	120° angles evident, stable up to ~−35 °C
$Cs^+C222\cdot Na^-$	0.4 mmol/5 mL of NH_3, −35 °C/1 h	6 mL of *i*-PA/−90 °C/1 h, −78 °C/24 h	mixture of dark bronze and gold crystals, dec at ~−25 °C
$Rb^+C222\cdot Na^-$	0.6 mmol/5 mL of NH_3, −40 °C/1 h	7 mL of *i*-PA/−92 °C/3 h, −78 °C/24 h	compact agglomerated crystals, 120° angles evident, stable up to ~−30 °C
$Rb^+C222\cdot Rb^-$	1.0 mmol/15 mL of NH_3, −35 °C/1 h	15 mL of *i*-PA, −90 °C/4 h	long flat crystals, 120° angles evident, dec at ~−20 °C, solvent content <0.1 mole %
$Cs^+C222\cdot Cs^-$	0.25 mmol/3 mL of NH_3, −33 °C/1 h	4 mL of *i*-PA/−90 °C/4 h	dec at ~−20 °C
$K^+C222\cdot K^-$	0.36 mmol/4 mL of NH_3, −33 °C/1 h	4 mL of *i*-PA/−90 °C/2 h, −78 °C/24 h	dendritic crystals, dec at ~−25 °C
$Li^+C211\cdot Na^-$	1.3 mmol/8 mL of MA, −35 °C/3 h	9 mL of *i*-PA + MA (trace), −78 °C/24 h	flat, mixture of square and rectangular crystals, very reflective, stable at room temperature for at least 30 min, solvent content <0.1 mole %
$Cs^+18C6\cdot Na^-$	0.81 mmol/10 mL of MA, −30 °C/2 h	10 mL of *i*-PA, −78 °C/24 h	reflective crystals, stable at room temperature for days, solvent content <0.1 mole %
$K^+18C6\cdot Na^-$	0.31 mmol/8 mL of MA, −20 °C/30 min	4 mL of *i*-PA + 2 mL of DEE, −78 °C/24 h	dendritic rods, stable up to ~+10 °C, solvent content ~16 mole %

[a] Abbreviations: EA, ethylamine; *i*-PA, isopropylamine; DEE, diethyl ether; *n*-P, *n*-pentane; MA, methylamine; dec, decomposed. [b] All crystals had reflective metallic appearance ranging from dark bronze to bright gold in color; flat faces tended to show various colors depending on illumination conditions.

with consequent increases in decomposition. Finally, the use of solvent-replacement techniques can lead to the precipitation of metal with the result that the alkalide crystals are contaminated with the free metal and/or "electride". For example, early attempts to synthesize $Li^+C211\cdot Na^-$ used NH_3 to hasten the dissolution of Li and Na metals. After evaporation of the ammonia, isopropylamine was added to promote the formation of Na^-. The $Li^+C211\cdot Na^-$ crystals obtained by cooling the isopropylamine solution were consistently contaminated with Na metal. So that this problem could be solved, methylamine was used instead of ammonia to dissolve the metals and the cryptands. Since the dominant negative species in methylamine solutions is Na^-, gradual replacement of methylamine by isopropylamine simply decreased the solubility of $Li^+C211\cdot Na^-$ without appreciable precipitation of sodium metal.

B. Analysis. The air, water, light, and heat sensitivity of alkalides makes commercial analysis unreliable because of decomposition during shipping and handling. Therefore, an in-house analytical scheme was designed and used. This scheme is based on the reaction of these highly reducing compounds with water to form H_2 and OH^-. The amount of H_2 produced gives the total reducing power of the sample. Titration of the residue gives the amount of OH^- present and also, in the case of the cryptands, the amount of cryptand present since cryptands have two amine groups which can be titrated. The metal content was determined by using flame emission spectroscopy. Proton NMR was then used to check for possible cryptand decomposition. Integration of the complexant NMR signal relative to that of an internal reference compound was used to provide an additional measure of the amount of complexing agent present. When 18-crown-6 was used the ^1H NMR integration provided the only analysis for complexant.

The H_2 evolution apparatus used in this study was patterned after a similar device which has been previously described in detail.[19,20] Cold alkalide samples were placed in the apparatus and evacuated before reaction with water. Care was taken to keep the sample cold until the reaction with water was complete. This usually prevented thermal decomposition of the complexing agent during reaction with water. However, in some cases, especially when a few drops of water contacted the sample, considerable complexant decomposition occurred during this step resulting in discoloration of the sample. A calibrated pipet was used to measure the hydrogen volume and a mercury leveling bulb was used to measure its pressure.

The residue was dissolved in water and titrated with standard HCl solution. An Orion Model 701A pH meter was used to monitor the pH. With cryptands, the titration curve shows two equivalence points, the first for hydroxide ion and the second for cryptand. All titrations were done under nitrogen to avoid CO_2 absorption.

Flame emission samples were diluted to appropriate concentrations with distilled water and adjusted to pH 2–3. A Jarrell-Ash Model 82-500 spectrometer was used. A plot of the relative emission vs. concentration for standard metal samples yielded a curve from which the unknown metal concentrations were determined. Interferences from the cryptand and/or other alkali metals were negligible.

The residue after H_2 evolution was also analyzed for complexing agent by using quantitative ^1H NMR integration. The internal integration standard first used was *tert*-butyl alcohol. One aliquot of solution from the pH titration was evaporated to dryness and dissolved in 2.0 mL of D_2O which contained a known concentration of *tert*-butyl alcohol. The relative ^1H NMR integration of the *tert*-butyl alcohol and complexing agent were then used to calculate the amount of complexing agent present. Problems with gradual evaporation of *tert*-butyl alcohol caused us to switch to potassium hydrogen phthalate (KHP) as the internal ^1H NMR integration standard. Interference from H_2O caused more problems with cryptands than with crown ethers.

The intrinsic errors of analysis depend strongly on sample size. Typical samples were in the 0.01–0.1-mmol range. Estimated standard errors over this range are as follows: H_2 evolution, 5–1%; total base by titration, 2.0–1.0%; cryptand by titration, 5–2%; metals by flame emission, 3%; complexant by ^1H NMR, 10% for cryptands and 5% for crown ethers. The analysis of compounds which partially decompose during the hydrogen evolution step are subject to larger errors, particularly for this step and for the determination of the complexant by ^1H NMR.

Results and Discussion

Table I lists the systems which have been studied and for which crystalline precipitates have been observed. This table gives the solvents used, crystallization conditions, crystal shapes

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Table II. Analysis of Crystalline Alkalides[a]

		% dev from predicted stoichiometry				
compd	sample size,[b] mol × 10^4	H_2 evolved	cryptand by titration	M by flame emission	N by flame emission	cryptand or crown by ^1H NMR
$Cs^+C322\cdot Na^-$	1.05	0	0	0	+3	+1
$Rb^+C222\cdot Na^-$	0.715	0	0	0	+5	−16
	0.983	+3	−7	−1	+11	−8
$Na^+C221\cdot Na^-$	1.33	−3	+1	+1		−11
	1.29	−51[c]	−2	+14		+10
$K^+C222\cdot Na^-$	0.887	−3	+2	+4	+2	+9
	2.00	−6	0	+2	+7	+5
$Cs^+18C6\cdot Na^-$	0.471	*b*	(−5)[d]	0	+3	+1[e]
$Rb^+C222\cdot Rb^-$	0.060	+3	+1	−1		+23
	0.053	−1	−6	+16		−11
	0.518	−81[c]	−3	+3		−30
$Li^+C211\cdot Na^-$	0.159	+16	−5	+7	+1	−1
	2.67	−8	+1	+9	+8	+4
$K^+18C6\cdot Na^-$	0.856	*b*	(−4)[d]	+3	+13	+9[e]
$K^+C222\cdot K^-$	0.597	−3	−14	+17		−19
	0.338	−54[c]	−23	+13		−33
$Cs^+C222\cdot Cs^-$	0.137	+5	*f*	+29		+23
	0.077	+20		+15		+29
$Cs^+C222\cdot Na^-$	0.365	−10	*f*	+30	−31	−2
	0.188	−12		+30	−18	+15

[a] On the basis of the reaction $M^+C\cdot N^- + 2H_2O \rightarrow H_2 + M^+ + N^+ + C + 2OH^-$, where M^+ is an alkali-metal cation, N^- is an alkali-metal anion, and C is a cryptand or crown ether; for all samples analyzed there was no visual evidence of decomposition prior to analysis. [b] Sample size calculated as total base/4 for cryptates and as H_2 evolved for the crown ether compounds. [c] Dark color of residue indicated substantial cryptand decomposition during H_2 evolution. [d] OH^- by titration. [e] Crown ether determined by ^1H NMR with a separate sample. [f] The lack of a definite first break in the titration curve prevented the determination of cryptand by this method.

and colors (for those crystals which could be examined by optical microscopy), and comments about stability. The parent compound, $Na^+C222\cdot Na^-$, which has a hexagonal unit cell,[2] tends to crystallize in plates in which 120° angles are clearly evident.[21] Table II gives the results of the analyses in approximate increasing order of the deviations from the expected stoichiometry. We emphasize that only samples which were obviously crystalline and free of apparent decomposition were analyzed. Sample masses could not be determined for most systems because of the need to keep the samples cold. Therefore, for the cryptate salts the analytical results are referred to the total base present as determined by a pH titration. The total amount of base can be accurately determined and is insensitive to decomposition so that its determination should be the most reliable measure of the total amount of sample.

For the salts $Cs^+18C6\cdot Na^-$ and $K^+18C6\cdot Na^-$, the amount of hydrogen evolved was used rather than the total base present. The crown ether seems to be resistant to decomposition during the hydrogen evolution step so that this method of analysis is more reliable than with cryptands. In addition, the titration of hydroxide ion when 18-crown-6 is present is plagued by instability of the pH meter, especially in the vicinity of the end point. This was verified by titration of a mixture of alkali-metal hydroxide and 18-crown-6.

Table II gives the percent deviation from the expected stoichiometry for each analysis method. The compounds are listed in approximate order of increasing deviations. Analyses of $Cs^+C322\cdot Na^-$, $Cs^+18C6\cdot Na^-$, and $K^+C222\cdot Na^-$ agree with the presumed stoichiometry to within the estimated errors. One of the samples of $Rb^+C222\cdot Na^-$ gave satisfactory analysis results except for the determination of cryptand by NMR. The other sample was low in cryptand and high in sodium, suggesting coprecipitation of the sodide salt and free sodium. The somewhat large deviations observed with $Li^+C211\cdot Na^-$ are puzzling since this salt appears to be stable even at room temperatures. While one sample of the relatively stable salt $Na^+C221\cdot Na^-$ gave satisfactory results, the other sample decomposed upon the addition of water to yield a very dark residue. The amount of hydrogen evolved was very low and the sodium content was high for this sample. Evidently excess sodium was present and the sample was sensitive to cryptand decomposition with water. Samples of $Rb^+C222\cdot Rb^-$ were very difficult to prepare because of their tendency to decompose. The three samples analyzed gave poor results for the ^1H NMR integration, for the determination of rubidium in one sample, and for hydrogen in another sample which showed extensive decomposition of the cryptand during the hydrogen evolution step. The samples of $K^+18C6\cdot Na^-$ were reasonably stable but gave only marginally acceptable analyses. One of them was apparently contaminated with excess sodium and another contained appreciable amounts of solvent.

The last three entries in Table II are for samples which were nominally $K^+C222\cdot K^-$, $Cs^+C222\cdot Cs^-$, and $Cs^+C222\cdot Na^-$, based upon the compositions of the solutions from which they were crystallized. All were difficult to handle and subject to thermal decomposition and decomposition of the cryptand upon addition of water. Evidently, excess metal was also present in the potasside and ceside samples. Flame photometric analysis of $Cs^+C222\cdot Na^-$ indicated an excess of cesium and deficiency of sodium. The sample consisted of a mixture of two types of crystals which suggests the presence of both ceside and sodide.

So that the presence of solvent in the crystals could be checked, the analysis of five compounds given in Table II included determination of the pH of the water which was distilled from the sample after the hydrogen evolution step. In three of the five cases the pH was within experimental error of the pH of the water used. In a sample of $Na^+C221\cdot Na^-$ the pH was slightly high and indicated that up to 0.9 mol % of amine could have been present in the initital sample. One sample of $K^+18C6\cdot Na^-$ contained ≈16 mol % of amine. Since the sample had been evacuated to $\sim 1 \times 10^{-5}$ torr for 1 h before sealoff, it is likely that solvent had been incorporated in the crystals.

A sample of $Cs^+C322\cdot Cs^-$ was isolated as apparently uniform bronze crystals. However, they decomposed violently

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(21) For a photograph of crystals of $Na^+C222\cdot Na^-$, see ref 5.

in the vacuum system upon warming to −20 °C. An indication of the difficulties involved in these syntheses is that 54 separate attempts were required to produce the data presented here.

Numerous attempts to prepare $Ba^{2+}C222\cdot(Na^-)_2$ over a time span of 6 years by three different investigators in our laboratory have failed to yield conclusive results. While bronze precipitates can be formed, the analyses are poor, decomposition products are obviously present, and crystals of $Na^+C222\cdot Na^-$ are present in the precipitate.

It is clear that the easiest crystals to prepare and the most stable are sodides. This is probably because of the stability of Na^- to dissociation into Na^+ and trapped electrons. While no experimental data are available for the thermodynamics of this dissociation in solids, estimates of the equilibrium constants for eq 3 in ethylenediamine[8] are revealing. We

$$M^- \rightleftharpoons M^+ + 2e^-_{solv} \qquad (3)$$

expect Na^+ to be stabilized more than K^+, Rb^+, or Cs^+ in this solvent. In spite of this, the dissociation constant, K_3, for Na^- is about 5, 4, and 6 orders of magnitude *smaller* than for K^-, Rb^-, and Cs^-, respectively. The much lower stability of electrides than alkalides suggests that the formation of trapped electrons by dissociation of M^- would greatly decrease the stability of the solid alkalide salt. For this reason also, coprecipitation of alkalides and electrides would lead to lower stability. Finally, both electrides and sodides appear to be more stable when 18-crown-6 is used as the complexing agent instead of a cryptand. For example, crystals of $Cs^+18C6\cdot Na^-$ did not change in appearance when allowed to remain at room temperature for 1 week, whereas crystals of $Cs^+C222\cdot Na^-$ decomposed rapidly above −20 °C.

An analysis problem which is particularly troublesome with the more reactive alkalides, especially with salts of K^-, Rb^-, and Cs^- occurred during the hydrogen evolution step. Reaction with water which was condensed from the vapor onto the salt caused some decomposition of the cryptand without hydrogen evolution. When this occurred, the residue was straw colored and the subsequent ^1H NMR analysis showed that (unidentified) decomposition products of the cryptand were formed. This is believed to be the cause of low analyses for H_2 in many cases. For example, a sample of $Rb^+C222\cdot Rb^-$ (5×10^{-5} mol) which contained only shiny, bronze crystals before reaction with water, formed a dark residue upon reaction with water at about −20 °C. Only 19% of the expected H_2 was formed, and, while the pH titrations and flame analyses were satisfactory, the ^1H NMR spectrum showed substantial amounts of cryptand decomposition products. These products were not identified, but the complex ^1H NMR spectra show that the cryptand was altered. The autocatalytic nature of alkalide decomposition reactions suggests that free radical formation probably occurs which could lead to oligomerization of the cryptand. Attempts to decrease the extent of decomposition during the hydrogen evolution step by maintaining lower temperatures were not successful probably because ice formation occurred rather than direct reaction of water with the crystalline alkalide. Especially to be avoided is the addition of small amounts of *liquid* water to the crystalline sample since this results in excessive decomposition of the complexant.

This work shows that, except for salts of Li^-, it is possible to prepare crystalline salts of all alkali-metal anions. However, so far only certain salts containing Na^- are stable at room temperatures for extended periods of time. The most stable of these are $Na^+C222\cdot Na^-$, $Li^+C211\cdot Na^-$, $Cs^+18C6\cdot Na^-$, and $Cs^+C322\cdot Na^-$. It is especially encouraging that a stable salt of Na^- can be synthesized by using the relatively inexpensive crown ether 18-crown-6 since this should permit the preparation of bulk samples at moderate cost. The determination of the crystal structure of $Cs^+18C6\cdot Na^-$ is in progress.

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Registry No. $Cs^+C322\cdot Na^-$, 32611-46-4; $Rb^+C222\cdot Na^-$, 32611-96-4; $Na^+C221\cdot Na^-$, 80737-30-0; $K^+C222\cdot Na^-$, 66446-73-9; $Cs^+18C6\cdot Na^-$, 80737-31-1; $Rb^+C222\cdot Rb^-$, 57450-09-6; $Li^+C211\cdot Na^-$, 80737-32-2; $K^+18C6\cdot Na^-$, 80737-33-3; $K^+C222\cdot K^-$, 80737-34-4; $Cs^+C222\cdot Cs^-$, 57450-10-9; $Cs^+C222\cdot Na^-$, 80720-90-7.

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Attempted Syntheses of Low-Oxidation-State Organometallic Derivatives of Aluminum, Gallium, and Indium. A New Synthesis of $Al(CH_2SiMe_3)_3$

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The synthesis of $KAl(CH_2SiMe_3)_2$ by a reductive-elmination reaction between $Al(CH_2SiMe_3)_3$ and KH has been attempted, but a pure product could not be isolated. The reactants combine at 70 °C to form $KAl(CH_2SiMe_3)_3H$, a white pyrophoric solid, which has been fully characterized. A molecular weight study indicates the presence of a mixture of monomeric and dimeric species in benzene solution. The pyrolysis of $KAl(CH_2SiMe_3)_3H$ at 205 °C produces $Si(CH_3)_4$ but also CH_4. The formation of $Si(CH_3)_4$ suggests that $KAl(CH_2SiMe_3)_2$ might have been formed, but the presence of CH_4 indicates that a decomposition reaction occurs either prior to or after the formation of $KAl(CH_2SiMe_3)_2$. The reactions of mixtures of KH–$Al(CH_3)_3$, KH–$Ga(CH_3)_3$, NaH–$Ga(CH_3)_3$, KH–$In(CH_3)_3$, and NaH–$In(CH_3)_3$ have also been investigated in order to determine the role of the organic substituent in the attempted reductive-elimination reactions. In all cases the formation of CH_4 during pyrolysis of $KAl(CH_3)H$, $KGa(CH_3)_3H$, and the other reaction mixtures is consistent with the occurrence of reduction, but no pure compounds could be isolated. A new synthetic route to $Al(CH_2SiMe_3)_3$ from $AlBr_3$ and $LiCH_2SiMe_3$ in refluxing hexane is also described.

Introduction

An interesting new area of research activity centers on the chemistry of the organometallic derivatives of main-group metals in their low oxidation states. In group 3 chemistry the list of low-oxidation-state compounds that are thermally stable at room temperature is very limited but includes KGa-