

Crystalline Salts of Na⁻ and K⁻ (Alkalides) that Are Stable at Room Temperature

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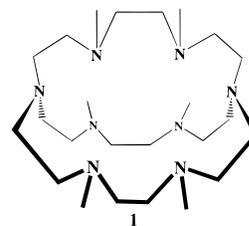
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Studies of alkalides and electrides have been complicated by thermal instability that makes it necessary to maintain most samples at $-20\text{ }^{\circ}\text{C}$ or colder at all times.^{1,2} The instability results from reductive cleavage of the C–O bond in the crown ether or cryptand complexant used to encapsulate the alkali cation, the counterion to M⁻ or e⁻.³ Alkalides are powerful two-electron reducing agents,⁴ but the routine use of these compounds in synthesis has been limited by their thermal instability. Electrides have a number of unusual electronic properties⁵ that might be exploited if they were more stable. We report here the synthesis and some properties of a sodide and a potasside that are stable at ambient temperatures.

Several salts of Na⁻ that used permethylated aza-analogues of crown ethers such as hexamethyl hexacyclen⁶ and the cryptand-like complexant, TMPAND,^{7,8} were stable at room temperature against *decomposition*, but the former *decomplexed* slowly and the latter contained methylamine, which enhanced the decomposition rate of crystals. Although most samples of the sodide, Na⁺(cryptand[2.2.2])Na⁻,^{9,10} decompose at room temperature, we recently found that very high-quality crystals are stable for weeks at ambient temperatures. All other known alkalides and electrides decompose rapidly at room temperature.

Our attempts to synthesize thermally stable alkalides and electrides focus on aza-cage complexants, in which the alkali cation is encapsulated in an appropriate-sized cavity to partially compensate for the weaker M⁺–N interaction compared with that of M⁺–O. No N–H groups can be present that could react with M⁻ or e⁻ to form molecular hydrogen. To provide facile entry of cations into the cage we synthesized the fully methylated aza-analogue, **1**, of cryptand [2.2.2] (abbreviated aza222)¹¹ via the Schiff-base condensation of tren with glyoxal in the presence of Na⁺ or K⁺ followed by reduction with NaBH₄.¹² Conversion to the free base was followed by Eschweiler–Clarke methylation as carried out for this complexant by Lehn.¹³ Vacuum sublimation produced white crystals whose structure was determined by X-ray diffraction. Details are given in the Supporting Information.



Space-filling models suggested that aza222 should encapsulate K⁺ to yield a nearly spherical complexed cation of diameter $\sim 10\text{ \AA}$. NaK and K dissolve slowly in methylamine (MeNH₂) solutions of **1**, in contrast to the rapid dissolution observed with crown ethers and cryptands. Addition of pentane resulted in decomplexation and the formation of metal particles. Thus, the ability of aza222 to complex K⁺ in MeNH₂ is only marginal. Neither Na nor Cs could be dissolved with the aid of this complexant.

Crystals of K⁺(aza222)Na⁻ and K⁺(aza222)K⁻ were grown by cooling saturated solutions in MeNH₂–Et₂O mixtures from -40 to $-70\text{ }^{\circ}\text{C}$ over a period of 30 h. After washing with Et₂O they were transferred into Pyrex tubes attached to the K-cell that were then flame-sealed. One of the tubes contained an optical cell for measurement of single-crystal reflectance. The crystals form as cubes with sharp edges and corners. The sodide crystals have shiny gold-bronze faces while the potasside is a darker red-bronze. It was a surprise to find that the crystals maintained their integrity in vacuo at ambient temperatures. Small crystals of K⁺(aza222)Na⁻ left on the lab bench in a K-cell for over three months were unchanged in appearance. The potasside has similar long-term stability. Submillimeter crystals of both alkalides react slowly (10–20 min) with laboratory air to form white crystals without a noticeable change in crystal habit. When dry oxygen is used in a glovebag the process takes many hours.

DSC studies of both K⁺(aza222)K⁻ and Na⁺(aza222)Na⁻ showed sharp endotherms at $50\text{ }^{\circ}\text{C}$ (independent of ramp rate) and broad exotherms over the range $80\text{--}150\text{ }^{\circ}\text{C}$ as shown in Figure 1. Visual observation in melting point tubes indicated slow release of metal by decomplexation above about $60\text{ }^{\circ}\text{C}$ without melting of the complexant. Thus, the similar endotherms for the K⁻ and Na⁻ salts result from decomplexation without melting. The exothermic process is presumably the reaction between the complexant and the alkali metal.

Elemental C, H, N analyses agree with the formulas given, showing that solvent is not present in the crystals. As shown in Figure 2, both reflectance spectra from single crystals and the absorbance of thin films confirm the presence of K⁻ and Na⁻ as expected. The thin films were obtained by rapid solvent evaporation¹⁴ (both MeNH₂ and Me₂O were used) from solutions of the crystalline alkalide. In addition, a thin film of the potasside, whose spectrum is shown in Figure 2, was made by high vacuum co-deposition¹⁵ of K and aza222 onto a sapphire substrate. The ²³Na MAS NMR spectrum of crushed crystals of the sodide gave the expected peak of Na⁻ at -61 ppm relative to Na⁺(aq).¹⁶ We were unable to obtain the ³⁹K NMR spectrum of either the sodide or the potasside, probably because of quadrupole broadening. Although alkalides are diamagnetic, defect electrons show a “Curie-tail” in which the magnetic susceptibility is proportional to $1/T$. SQUID measurements of K⁺(aza222)Na⁻ and K⁺(aza222)K⁻ yielded defect electron concentrations of <0.1 and $1.2\text{ mol } \%$, respectively. The EPR spectrum of single crystals

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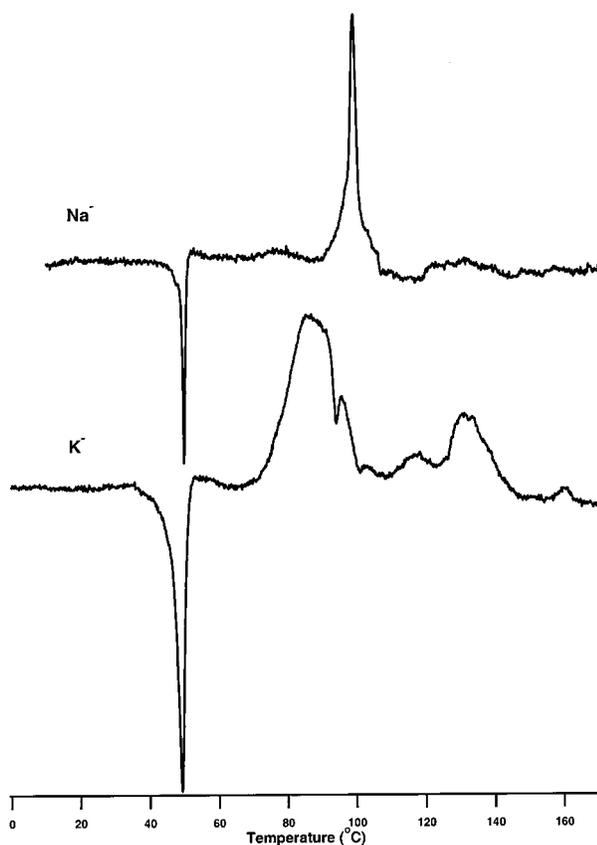


Figure 1. Differential scanning calorimeter traces for $\text{K}^+(\text{aza222})\text{Na}^-$ and $\text{K}^+(\text{aza222})\text{K}^-$.

of the former consisted of a single, orientation-independent Lorentzian line with $\Delta H_{\text{pp}} = 3.61$ G at 4 K and 1.66 G at 290 K, with $g = 2.0021$, as expected for defect electrons. By contrast, the potasside, with its higher electron content, showed an exchange-narrowed singlet at 300 K with $\Delta H_{\text{pp}} = 0.043$ G and $g = 2.00212$. However, below 30 K the EPR spectrum of single crystals was orientation-dependent and contained at least two Lorentzian lines (at 4 K, $\Delta H_{\text{pp}} = 2.92$ and ~ 0.4 G).

The excellent crystal morphology suggested that structure determination by X-ray diffraction should be straightforward. This turned out *not* to be the case, however! For the K^- salt, 772 unique reflections were observed, of which 296 had $F^2 > 4\sigma(F^2)$. For the Na^- salt the corresponding numbers were 411 and 225. All reflections indexed precisely for a face-centered cubic structure with $a = 15.2365(18)$ Å at 100 K for the sodide and 15.4424(18) Å at 173 K for the potasside. Since the symmetry of aza222 is not commensurate with a true fcc structure, the crystals are only pseudo-cubic. Direct methods failed to yield a structure. Attempts to refine the structure with a reasonable model of disorder were unsuccessful. This model placed the 3-fold axis of the known ligand structure (with included K^+) on the diagonals of the cube. The iodide salt $\text{K}^+(\text{aza222})\text{I}^- \cdot \text{CH}_3\text{CH}_2\text{OH}$ crystallizes in an orthorhombic habit (space group $Pbca$, see Supporting Information).

The lattice parameters of the Na^- and K^- salts are consistent with close-packing of the nearly spherical complexed cation (~ 10 Å diameter) and either Na^- (~ 5.4 Å) or K^- (~ 6.2 Å).¹⁷ The structure of complexed K^+ (from the iodide salt) and the observed lattice parameter of $\text{K}^+(\text{aza222})\text{Na}^-$ were used with the program CHEM 3D to construct the computer-generated fcc arrangement shown in Figure 3A. The simulated complex packing on one face of the cube is shown in Figure 3B. This simulation indicates that

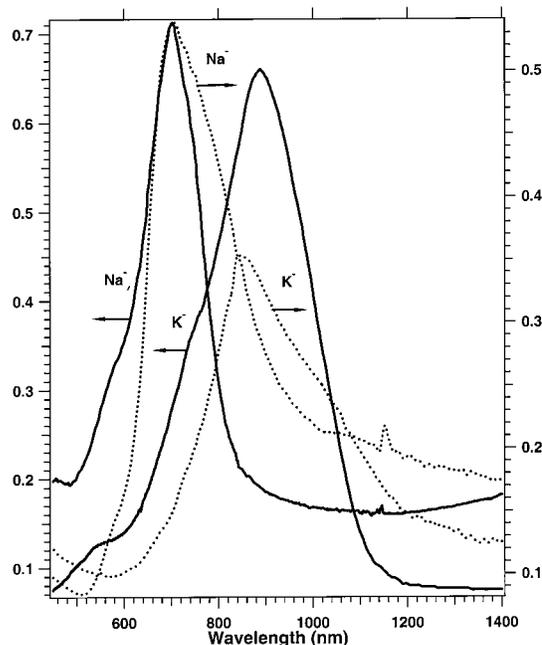


Figure 2. Absorbance (solid lines, left axis) of thin films and reflectance (dotted lines, right axis) of single crystals of $\text{K}^+(\text{aza222})\text{Na}^-$ and $\text{K}^+(\text{aza222})\text{K}^-$.

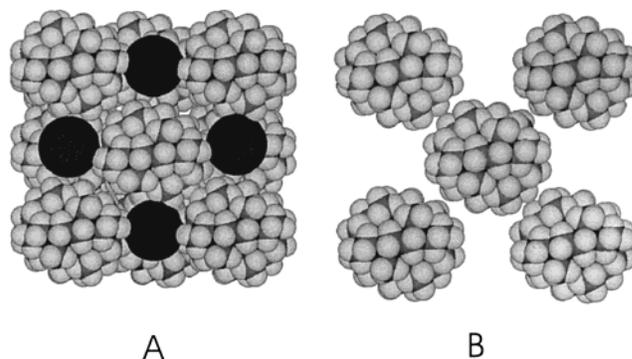


Figure 3. (A) Simulated pseudo fcc structure of $\text{K}^+(\text{aza222})\text{Na}^-$; (B) complexant packing on one face. Presumably the complexant orientation is disordered in the actual structure.

there is scarcely any contact between adjacent complexes. Since Na^- and K^- have spherical charge distributions, there is little incentive for preferred orientation of the pseudo-spherical complex so that packing in a disordered fcc structure might be favored, especially if the complex undergoes nearly free rotation at the temperature of crystallization.

A major goal of alkali-electride research is the synthesis of room-temperature stable *electrides*. Numerous attempts to synthesize $\text{K}^+(\text{aza222})\text{e}^-$ failed, presumably because K^+ is not complexed strongly enough by aza222. Work is currently in progress to synthesize better aza complexants for alkali cations that might permit the formation of thermally stable crystalline electrides.

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Supporting Information Available: Synthetic schemes for **1**, tables of crystal data, structure solutions and refinement, atomic coordinates, bond distances and angles, and general thermal parameters for **1** and for $\text{K}^+(\text{aza222})\text{I}^- \cdot \text{CH}_3\text{CH}_2\text{OH}$, and space-filling representations of aza222 and $\text{K}^+(\text{aza222})$ (PDF). X-ray crystallographic files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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