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"Inverse Sodium Hydride": A Crystalline Salt that Contains H^+ and Na^-

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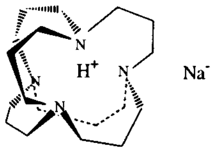
The charge distribution in sodium hydride is Na^+H^-. We report here the synthesis and properties of a crystalline salt that contains the reverse, $\mathbf{H^+}$ and $\mathbf{Na^-}$. The key is irreversible encapsulation of H^+ in 3^6adamanzane (Adz). This species is so kinetically resistant to deprotonation that it survives in the presence of strong bases and even alkali metal solutions in ammonia and amines. Such robust behavior permitted isolation of the crystalline salt $AdzH^+Na^-$ (**1**).



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All previous alkalides and electrides made in our laboratory contain complexed alkali metal cations, with alkali metal anions or electrons to balance the charge.[1,2] The main problem in working with these compounds is their instability at room temperature and their high chemical reactivity. Crown ethers and cryptands are cleaved at the C−O bonds. Analogous complexants with only C−N linkages and no amine hydrogens are considerably more stable and can even form room-temperature stable alkalides.[3] Such compounds frequently undergo *decomplexation* rather than *decomposition* when the temperature is increased.[4,5]

If all the nitrogen lone pairs in polyaza cages without amine hydrogens were pointed inward toward the metal cation, the complexes would enjoy both thermodynamic and kinetic stability. Such ligands would also be more stable toward highly basic and reducing reagents that are known to cleave the C−O bonds in cryptands and crown ethers. On the basis of findings in model studies, an ideal candidate was Li^+ encapsulated in 3^6adamanzane. However, all our attempts to synthesize this complex yielded only the internally protonated species, $AdzH^+$.

$AdzH^+Br^-$ was made by the published procedure[6,7] and allowed to stand with Li and Na in liquid NH_3 and methylamine ($MeNH_2$) at −78 °C. Under these conditions $AdzH^+Br^-$ was insoluble and unreactive toward the alkali metals. It was unclear whether $AdzH^+$ cations did not react with solvated electrons and Na^- anions because of their intrinsic stability or because of the low solubility of the corresponding salt.

We were unable to find an adamanzane salt that was soluble in those solvents that also dissolve alkali metals. The compounds $AdzH^+X^-$, (X = Cl, I, CH_3OSO_3, $C_{12}H_{25}OSO_3$, CH_3COO, and NH_2CH_2COO), prepared from $AdzH^+Br^-$ by ion exchange, exhibited very low solubility in liquid amines and were not decomposed by alkali metals dissolved in these solvents, provided the temperature was below 0 °C. The ^1H NMR spectra of solutions of the reaction products in D_2O revealed that $AdzH^+$ cations survived intact with no exchange of the encapsulated proton by D^+. This is in contrast to the behavior of internally protonated cryptand [1.1.1], which is destroyed by metal−ammonia solutions.[8]

A new method for the synthesis of alkalides and electrides that uses sacrificial anions[9] suggested that adamanzane cations might be brought into solution by reacting $AdzH^+X^-$ salts (in which X^- is a redox-active anion) with sodium in an amine solvent. Indeed, nitrate, isethionate, and glycolate salts of $AdzH^+$ reacted with Na in liquid NH_3 to yield $AdzH^+Na^-$ in solution when a cosolvent was added. The driving forces were reduction of NO_3^- ion with Na metal, accompanied by precipitation of insoluble inorganic compounds, or reductive deprotonation of isethionate or glycolate anions, followed by precipitation of $NaOCH_2CH_2SO_3Na$ or $NaOCH_2CO_2Na$, respectively.

Protonated adamazane glycolate reacted with Na in the most reproducible way and gave the highest yield of the sodide. The overall reaction is:

$$AdzH^+HOCH_2COO^- + 3Na \rightarrow AdzH^+Na^- + NaOCH_2CO_2Na\downarrow + {}^1/_2H_2\uparrow$$

In a typical experiment, a ∼100 mg sample of powdered $AdzH^+HOCH_2CO_2^-$, prepared from the corresponding bromide by anion exchange on a Dowex 1 resin, was put into the reactant side of a two-compartment "H-cell"[10,11] in a helium-filled glovebox. A piece of Na metal (∼30 mg) was placed in a small depression near the coarse glass frit that separated the compartments. After evacuation to $\sim 10^{-5}$ Torr, ammonia was condensed onto the glycolate salt and ultrasonicated for 20 min at −78 °C to break the crystals. Then the ammonia was frozen with liquid nitrogen, and the cell was tilted so that the piece of Na dropped onto the frozen ammonia. The reaction mixture was warmed to −78 °C and ultrasonicated at that temperature for 20 min. The resulting suspension was brought to liquid nitrogen temperatures and the hydrogen that had been evolved during the reaction was pumped out. Dimethyl ether (Me_2O) was then condensed onto the mixture, and all solvents were pumped out at −78 °C. When fresh Me_2O was condensed onto the reaction mixture, only $AdzH^+Na^-$ dissolved. The dark-blue solution was filtered through the glass frit into the second compartment, and the solvent vapor was transferred back into the synthesis part with a temperature gradient (−78/−196 °C). A new portion of $AdzH^+Na^-$ was dissolved in this way, and the process was repeated until the dimethyl ether no longer turned blue when condensed onto the reaction mixture. The use of $MeNH_2-Me_2O$ mixtures increased the solubility of $AdzH^+Na^-$, but this resulted in the transfer of some sodium metal along with the $AdzH^+Na^-$.

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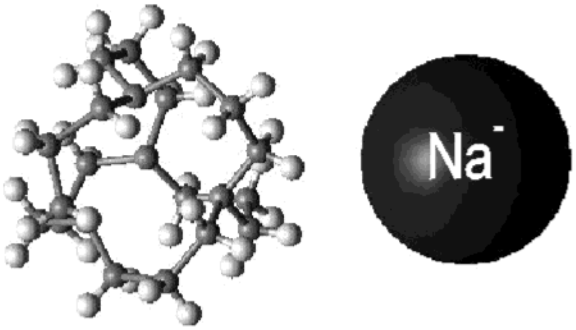

Figure 1. 3^6Adamanzane (from the glycolate structure) compared with the sodium anion.

When single crystals were desired, another solvent (Et_2O or Me_3N) was condensed onto the product solution, and the more volatile solvent vapor was slowly removed by evacuation at −78 °C through two additional frits. In many experiments $AdzH^+Na^-$ crystallized as shiny golden-colored needlelike crystals. However, only one preparation yielded a crystal that diffracted just well enough to permit determination of the unit cell size and geometry, but not the structure. $AdzH^+Na^-$ crystallized in a tetragonal system with $a = b = 8.936$ Å, $c = 31.66$ Å. The factors that resulted in poor-quality diffraction may include disorder because of the near-spherical nature of the complexant (Figure 1), twinning, or residual motion. Crystals of $AdzH^+HOCH_2CO_2^-$, obtained by condensing $MeNH_2$ onto an ethanol solution of the glycolate salt, diffracted well, and the structure was solved (see Supporting Information).

Analysis was initiated by condensing methanol onto the polycrystalline sample of $AdzH^+Na^-$ at −196 °C, followed by warming to −78 °C. This temperature is high enough to melt methanol and to enable the production of H_2 by reaction with Na^-, but not high enough to *thermally* decompose $AdzH^+Na^-$. The amount of evolved hydrogen was determined with a hydrogen-collection apparatus[12,13] with the excess methanol captured in a liquid N_2-cooled trap. The residue was combined with a weighed amount of potassium hydrogen phthalate (KHP). This mixture of reaction products and KHP was then dissolved in D_2O, and the amount of $AdzH^+$ in the sample was determined by quantitative ^1H NMR spectra. In all cases the signal of the encapsulated proton was observed with no exchange with D^+ cations from the D_2O. The concentration of Na^+ was measured by ICP-AES. Quantitative analysis is made difficult by the inadvertent transfer of some sodium metal during synthesis and occasional pre-decomposition before H_2 collection. The $AdzH^+$-to-Na^+-to-H_2 ratios of four polycrystalline samples made with three different sacrificial anions were: (a) 1.0:1.4:1.4, (b) 1.0:0.99:1.1, (c) 1.0:1.1:0.79 and (d) 1.0:0.91:1.04. In view of the difficulties of analysis, the formula $AdzH^+Na^-$ proposed for **1** is reasonable.

The ^{23}Na solid-state MAS NMR spectra of samples of **1** showed the characteristic peak of Na^- at −61 ppm [relative to Na^+(aq)]. A small additional peak occurred at 1120 ppm, showing that the samples also contained small amounts of sodium metal.

The optical transmission spectrum (Figure 2) of dark-blue thin films, obtained by rapid evaporation of a methylamine solution of **1**, showed the absorption peak at 810 nm that is characteristic of the sodide anion. No peak or shoulder of trapped electrons was observed in the near-IR region.

The DSC pattern of a powdered sample of **1** showed that exothermic decomposition started at −25 °C and reached a peak at +3 °C with $\Delta H = -215$ kJ mol^{-1}. When the decomposition was performed in the cell in which **1** was made, the course of its decomposition depended upon size of the crystals. When a dark polycrystalline film was warmed, it gradually lost color at −30 to 0 °C, to form a colorless oily liquid. Larger golden crystals of **1** gradually lost their shine and tended to rupture violently in vacuo to form a sodium mirror on the glass. **(WARNING: POSSIBLE EXPLOSION HAZARD!)** Attempts to prepare the electride by using lithium instead of sodium resulted in irreversible decomposition when the solvent was removed.

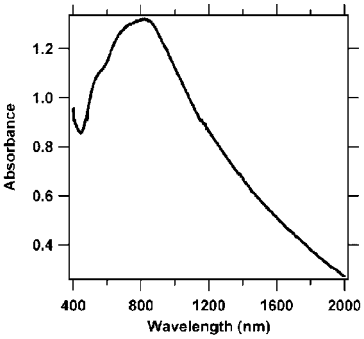

Figure 2. Optical absorption spectrum of a thin film of $AdzH^+Na^-$ produced by rapid evaporation of methylamine from solution.

In summary, we have synthesized the first hydrogen sodide, in which the proton is stabilized by complexation with four nitrogen atoms of an adamanzane cage. This allows it to survive in the presence of Na^- anions in the solid state and in solution and also with solvated electrons in solution. The synthesis of this unusual alkalide was carried out by the reaction of the alkali metal with the salt that contained the desired cation and a sacrificial anion. We expect that this approach may permit the synthesis of new alkalides and electrides in which the cations are kinetically trapped by irreversible complexation within polyaza cages.

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Supporting Information Available: Crystallographic data of $AdzH^+HOCH_2CO_2^-$. This material is available free of charge via the Internet at http://pubs.acs.org.

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