

Barium Azacryptand Sodide, the First Alkalide with an Alkaline Earth Cation, Also Contains a Novel Dimer, $(\text{Na}_2)^{2-}$

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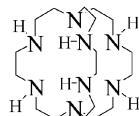
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Abstract: The first barium sodide, with stoichiometry $\text{Ba}^{2+}(\text{H}_5\text{Azacryptand}[2.2.2])\text{Na}^- \cdot 2\text{MeNH}_2$, was synthesized by the reaction of Ba, Na, and $\text{H}_6\text{Azacryptand}[2.2.2]$ in $\text{NH}_3\text{--MeNH}_2$ solution. It was characterized by X-ray crystallography, ^{23}Na MAS NMR, hydrogen evolution, DSC, optical spectroscopy, and magnetic susceptibility. This is the first sodide in which the sodium anions form $(\text{Na}_2)^{2-}$ dimers. Previous theoretical predictions were verified by a calculation of the potential energy curve for the dimer in the field of the surrounding charges, whose positions were determined from the crystal structure.

Introduction

We have made many attempts to synthesize “BaNaNa” with a complexed Ba^{2+} cation and two sodide anions. Here we report a sort of “half-success”, the first compound that contains Ba^{2+} cations and Na^- anions. During synthesis in ammonia–methylamine (MeNH_2) mixtures, however, reduction of one of the secondary amine protons of $\text{H}_6\text{Azacryptand}[2.2.2]$,¹ **1**, to form H_2 resulted in a compound with only one Na^- anion per Ba^{2+} cation. A second unusual feature of this sodide is that the Na^- anions exist in a loose dimer, $(\text{Na}_2)^{2-}$, as predicted theoretically for it and for K_2^{2-} in a previous paper.² This first barium sodide has the empirical formula, $\text{Ba}^{2+}(\text{H}_5\text{Azacryptand}[2.2.2])\text{Na}^- \cdot 2\text{MeNH}_2$ (abbreviated $\text{BaH}_5\text{Aza-222Na}$).



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Alkalides are crystalline salts that contain complexed cations, with charge balance provided by alkali metal anions.^{3–9} Correspondingly, electrides are salts that contain complexed metal cations, with trapped electrons to balance the charge.^{4,10–15} The

study of crystalline alkalides began in 1974 with the first synthesis and structure determination of $\text{Na}^+(\text{cryptand}[2.2.2])\text{Na}^-$.^{6,16} After more than a decade-long search, the first crystalline electride was synthesized and characterized in 1986.¹⁷

All but one of the 43 alkalides and electrides previously synthesized contained alkali metal cations complexed by crown ethers, cryptands, or their aza-analogues.⁹ Alkalides and electrides with crown ethers or cryptands usually decompose at temperatures above $\sim -30^\circ\text{C}$, with cleavage of the C–O bond and the release of ethylene.¹⁸ The corresponding fully methylated aza-complexes are more stable to irreversible decomposition, but aza-crown alkalides *decomplexed* at room temperature and above to yield the ligand and the free alkali metal.^{19,20} The complexant hexamethyl azacryptand[2.2.2] (abbreviated $\text{Me}_6\text{Aza222}$) was recently used to synthesize two alkalides, $\text{K}^+(\text{Me}_6\text{Aza222})\text{M}^-$, with $\text{M} = \text{K}$ and Na , which were stable in vacuo at ambient temperatures.²¹

Attempts to make barium-based alkalides and electrides started more than 20 years ago, but all were unsuccessful. Liquid ammonia is the only solvent that readily dissolves metallic barium without oxidation. While cryptands were stable in Ba--NH_3 solutions, removal of the solvent invariably led to decomposition, even at -78°C . Attempts to form the electride or sodide by using $\text{Me}_6\text{Aza222}$ and solutions of Ba (or Ba plus

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Na) in $\text{NH}_3\text{-MeNH}_2$ mixtures were unsuccessful. When $\text{H}_6\text{-Aza222}$ was used with Ba, but not Na in solution, the complexant decomposed. However, the reaction of metallic Ba and Na with this complexant in $\text{NH}_3\text{-MeNH}_2$ mixtures yielded hydrogen gas, a deprotonated negative complexant and the new barium sodide that is the subject of this paper.

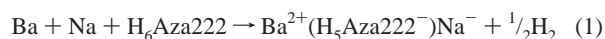
Experimental Section

Materials and Equipment. Oil-free Na and Ba metal ingots were purchased from Aldrich and Alfa Aesar, respectively. They were stored, and weighed amounts were cut as needed, in a He-filled glovebox. Compressed MeNH_2 and dimethyl ether (Me_2O) (Matheson) were purified by condensation onto Na-K alloy or Na-K-benzophenone, respectively.

Diethyl ether (Et_2O) was stirred with CaH_2 and then distilled into a glass vessel that contained Na-K. $\text{H}_6\text{Aza222}$ was made from $\text{N}(\text{CH}_2\text{-CH}_2\text{NH}_2)_3$ (tren) and 40% glyoxal (Aldrich) by modification of a method described elsewhere²² and purified by sublimation under vacuum. The vacuum-line methods used for alkali synthesis and the special "K-cells" have been described elsewhere.^{21,23-25}

The crystal structure was determined with a Bruker CCD diffractometer equipped with a low-temperature accessory. ^1H NMR spectra were recorded with a Varian VXR 300 spectrometer, elemental analysis was performed on a Thermo Jarrel Ash Polyscan 61E inductively coupled plasma atomic emission spectrometer (ICP-AES), and optical spectra were obtained with a Guided Wave model 260 spectrophotometer. Magnetic susceptibility data were obtained with a Quantum Design MPMS2 SQUID magnetometer. DSC measurements used sealed aluminum pans in a Shimadzu model DSC-50 calorimeter. Solid state ^{23}Na MAS NMR spectra were obtained with a Varian VXR 400S spectrometer.

Synthesis and Analysis Procedures. The syntheses were performed with "K-cells", to which metal and complexant were added in a glovebox prior to connection with a vacuum line. Purified solvents were introduced via the vapor phase and were dried just before use by condensation onto Na-K, followed by freeze-pump-thaw cycles. In a typical experiment (used to monitor H_2 evolution), 150 mg of Ba, 50 mg of Na, and 360 mg of $\text{H}_6\text{Aza222}$ were placed into one side of a cell in the He-filled glovebox. After evacuation to 1×10^{-5} Torr, about 10 mL of NH_3 was condensed onto the solids, which dissolved the Ba and Na to form a two-phase liquid mixture, together with incompletely dissolved solid $\text{H}_6\text{Aza222}$. About 20 mL of MeNH_2 was then condensed onto the mixture. The apparently homogeneous dark blue liquid phase that formed was stable at -78°C and did not react with the coexisting bronze phase. The good stability up to this point was shown by the fact that only a small amount of hydrogen had evolved after 12 h (1.5% of the theoretical value based on the amounts of Ba and Na present). At this stage, the solvents were slowly removed by evaporation through a glass frit. When only a small amount of solvent was left, hydrogen was rapidly evolved. The overall reaction that occurred was reductive deprotonation of the $\text{H}_6\text{Aza222}$ and incorporation of Ba^{2+} according to



After the solvent was removed by evacuation at -78°C , the reaction product was dissolved in MeNH_2 and transferred from the synthesis side to the product side of the cell. The bronze-colored polycrystalline product left after the MeNH_2 had been removed by evacuation at -50

Table 1. Crystallographic Data for $\text{Ba}^{2+}(\text{H}_5\text{Aza222}^-)\text{Na}^- \cdot 2\text{MeNH}_2$

cell parameters:	$a = 17.746(4) \text{ \AA}$ $b = 10.375(2) \text{ \AA}$ $c = 34.116(7) \text{ \AA}$ $\beta = 91.29(3)^\circ$ $V = 6280(2) \text{ \AA}^3$
temperature	173(2) K
space group:	monoclinic, Cc
Z	4
number of unique refl.	9206
number of parameters.	512
R for refl. with $I > 2\sigma$	0.0723
R for all refl.	0.1136

to -78°C was transferred to storage vials in a N_2 -filled glovebag. Sample temperatures were kept below -60°C at all times to minimize thermal decomposition.

Transfer of solutions in MeNH_2 through the coarse frit of the K-cell was accompanied by the transfer of some free sodium. Its presence in the polycrystalline samples was detected by ^{23}Na MAS NMR and by DSC. It was first thought that Na might be formed during decomposition, but samples transferred with dimethyl ether (Me_2O) showed only traces of sodium metal by DSC. This solvent could not be used without MeNH_2 to prepare bulk samples because the solubility of the sodide is so low that only very small samples could be prepared. Because the properties of the polycrystalline samples were all in accord with those expected from the crystal structure, the presence of some sodium metal was not considered detrimental.

After reaction of the sodide with methanol and collection of the evolved H_2 , a weighed amount of potassium hydrogen phthalate was added to the flask, and the sample was dissolved in 5% $\text{DCl-D}_2\text{O}$ solution. Quantitative ^1H NMR spectra were used to determine the amount of $\text{H}_6\text{Aza222}$, and ICP-AES was used for Na^+ and Ba^{2+} . The amount of MeNH_2 was not determined because of its volatility. A sample of the polycrystalline product gave $\text{H}_6\text{Aza222}:\text{Ba}:\text{Na}:\text{H}_2$ mole ratios of 1.00:1.03:1.09:0.99, in accord with the composition obtained from the crystal structure.

To grow crystals of the sodide large enough for structure determination, the product was dissolved in $\text{MeNH}_2\text{-Et}_2\text{O}$ mixtures, and the more volatile MeNH_2 was preferentially removed under vacuum over a two-week period at -78°C . The remaining solvent (primarily Et_2O) was poured back into the synthesis side, leaving a mixture of bronze crystals and a small amount of dark-blue solid. The crystals were covered with cold hexane in a glovebag and examined with a microscope. Selected crystals were transferred to a cooled holder for X-ray structure determination.

Optical spectra were obtained by dissolving a polycrystalline sample in MeNH_2 in a precooled optical cell to form a liquid film on the surface of the cell. Rapid evaporation of the solvent into a separate liquid N_2 -cooled compartment formed a solvent-free film whose spectrum was recorded at -60°C . The magnetic susceptibility of polycrystalline samples was measured as a function of temperature in a thin-walled quartz tube in the SQUID magnetometer. For DSC measurements, samples were sealed in precooled aluminum cups and scanned from -60 to $+150^\circ\text{C}$, after which their mass was determined. Samples were loaded into precooled zirconia sample spinners for ^{23}Na MAS NMR measurements at -60°C .

Results and Discussion

Crystal Structure. Crystals grown from $\text{MeNH}_2\text{-Et}_2\text{O}$ mixtures have the overall stoichiometry $\text{Ba}^{2+}(\text{H}_5\text{Aza222}^-)\text{Na}^- \cdot 2\text{MeNH}_2$. The crystal system is monoclinic with space group Cc (No. 9). The cell parameters are listed in Table 1, and a diagram of the local structure is shown in Figure 1. Full crystal structure data are given in the Supporting Information.

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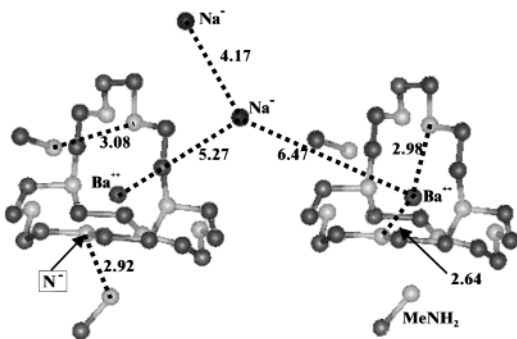


Figure 1. Local structure and selected distances (in Å) in $\text{Ba}^{2+}(\text{H}_5\text{Aza222}^-)\text{Na}^- \cdot 2\text{MeNH}_2$.

This compound has some remarkable structural features that deserve special consideration. The Ba^{2+} cation is surrounded by eight nitrogen atoms of the Aza222 cage. Seven of the eight distances to the amine nitrogen atoms range from 2.87 to 3.02 Å with an average value of 2.98 Å, which is normal for the donor–acceptor Ba^{2+} –N bond. The remaining distance to a secondary amine nitrogen is 2.64 Å, which indicates deprotonation of this nitrogen and the formation of a short bond between the Ba^{2+} cation and this amide anion. The formation of an amide is further indicated by the value of 359° as the sum of the C–N–C and two C–N–Ba angles for this nitrogen atom. This shows that the three bonds to the amide nitrogen are essentially coplanar. By contrast, the sum of the corresponding angles for the other secondary amine nitrogens ranges from 327 to 340° , characteristic of nearly tetrahedral geometries.

Neither the CH_3 protons nor the NH_2 protons of MeNH_2 could be resolved. However, identification of the amine end of one of the molecules was confirmed by the short distance (2.92 Å) to the amide nitrogen of the complexant. This indicates the formation of a $\text{N}\cdots\text{H}\cdots\text{N}$ hydrogen bond. The nitrogen atom of the second MeNH_2 molecule is 3.08 Å from one of the secondary amine nitrogens, which indicates the probable formation of a $\text{N}\cdots\text{H}\cdots\text{N}$ hydrogen bond via the secondary amine hydrogen of the complexant. The formation of these two hydrogen bonds between MeNH_2 and the $\text{Ba}^{2+}(\text{H}_5\text{Aza222}^-)$ species may stabilize the compound against further deprotonation of the complexant or the MeNH_2 molecules.

Dimerization of Na^- . Although dimers of K^- and Rb^- and chains of Rb^- and Cs^- have been observed,²⁶ all previous sodides contained individual Na^- ions. The stabilization of K_2^{2-} in the presence of positive charges in a linear array was confirmed theoretically,² and stabilization of Na_2^{2-} was also predicted.²⁷ The crystal structure of $\text{BaH}_5\text{Aza222Na}$ clearly shows the presence of dimers of Na^- . The internuclear distance of 4.17 Å is 1.3 Å shorter than the average diameter (5.5 Å) of Na^- .²⁶ A view of the dimer and complexant orientation is shown in Figure 2, in which the van der Waals sizes of the Na^- and Ba^{2+} ions are displayed along with a ball-and-stick representation of the complexant. Further agglomeration of Na^- ions does not occur. Two next-nearest-neighbor Na^- ions are located 9.3 Å from each Na^- ion in the dimer.

As shown in Figure 1, each Na^- ion is situated between two complexed Ba^{2+} cations at distances of 5.27 and 6.47 Å,

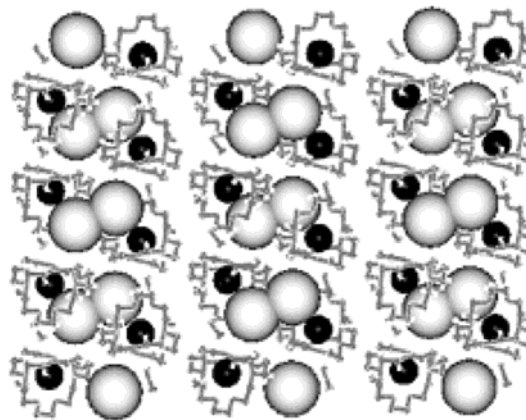


Figure 2. View of the structure of $\text{Ba}^{2+}(\text{H}_5\text{Aza222}^-)\text{Na}^- \cdot 2\text{MeNH}_2$ down the b axis. The ionic sizes of Ba^{2+} (black) and Na^- (grey) are drawn to scale. This view shows the contraction of the Na^- to Na^- distance as a result of dimer formation.

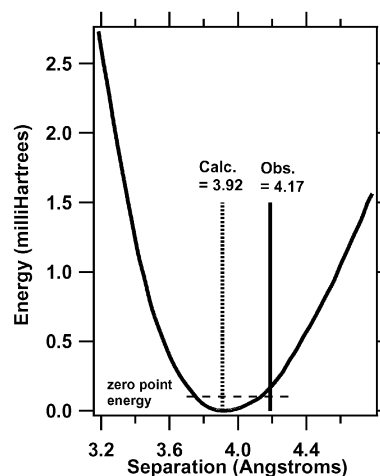


Figure 3. Calculated potential energy curve for Na_2^{2-} dimers as a function of separation distance at the CISD level. The calculated vibration frequency is only 47 cm^{-1} .

respectively. The presence of four amine nitrogen atoms at distances of 4.39, 4.40, 4.49 (MeNH₂ nitrogen), and 4.50 Å from each Na^- ion suggests that the formation of $\text{N}\cdots\text{H}\cdots\text{Na}^-$ interactions may be important.

Additional insights into the nature of the Na_2^{2-} dimer were obtained by ab initio calculations²⁸ of the internuclear separation at the CISD level by using a 6-311+G basis set on each Na in the dimer. The crystal environment around the central Na_2^{2-} dimer was simulated with point charges (+2 and –1) fixed at the experimental locations of the closest 6 Ba^{2+} , 6 N^- , and 4 Na^- ions. Within this overall neutral cluster, the calculated Na_2^{2-} potential energy curve (Figure 3) has a minimum at 3.92 Å. This distance is somewhat smaller than the experimental separation of 4.17 Å. Given the simplicity of the model, with

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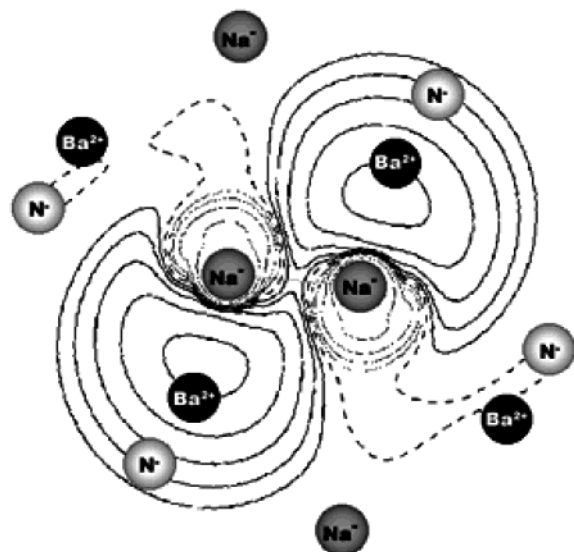


Figure 4. A view of the Na_2^{2-} dimer (in the plane through the two nearest Ba^{2+} ions) and the placement of surrounding charges used to calculate the electron density contours. The contours shown are differences between the total charge density and that of Na atoms at the same positions. The dashed line represents zero difference, solid lines represent positive values, and dotted lines refer to negative difference densities. The contour values (in electrons per cubic bohr) range (in powers of 2) from $\pm 6.25 \times 10^{-5}$ to $\pm 1.00 \times 10^{-3}$. Note that the Ba^{2+} ions toward which the contour lobes point are the closest ions to the respective Na^- ions.

no contribution from the aza-cage molecules except for the charges, the agreement is satisfactory. The calculation clearly shows that dimer formation is stabilized despite the negative charge on each of the Na^- ions. Figure 4 shows the difference between the calculated electron density of the dimer and that of two separated noninteracting Na atoms placed at the equilibrium positions. Clearly the additional electron density is polarized toward the nearest-neighbor Ba^{2+} ions. The calculated internuclear distance of 3.92 Å for Na_2^{2-} is somewhat larger than that of Na_2^- , 3.647 Å calculated at the 6-31++G level.²⁹

General Properties. The visible and near-IR optical spectrum of a thin film, shown in Figure 5, is typical of that observed for other sodides.³⁰ It consists of a large, broad peak centered at 648 nm with a shoulder at 480 nm and a “tail” into the IR. No absorption peak is present in the wavelength region 1200–1500 nm, which indicates that the concentration of trapped electrons is too small to be measured optically. This result was supported by magnetic susceptibility measurements on two samples, in which the absence of a “Curie tail” showed that the unpaired electron concentration was less than 0.1%.

The ^{23}Na MAS NMR spectrum showed a peak at -32 ppm relative to Na^+ (aq). This is considerably shifted from the value of -61 ppm characteristic of isolated Na^- in other sodides and in solutions.³¹ This suggests that the spherical symmetry of individual Na^- ions is perturbed by interaction with neighbors. Dimer formation would be expected to shift the NMR peak in the positive direction, as occurs³² with dimers and chains of Rb^- and with Cs^- chains.³³ All samples also showed a small

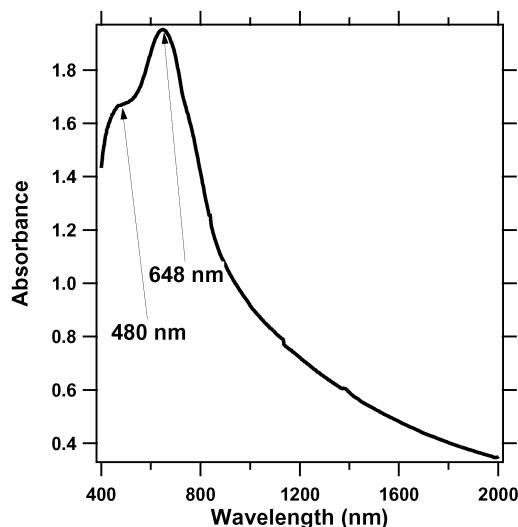


Figure 5. Optical absorption spectrum of a thin, solvent-free film of $\text{BaH}_5\text{Aza}_{222}\text{Na}$ at -60°C .

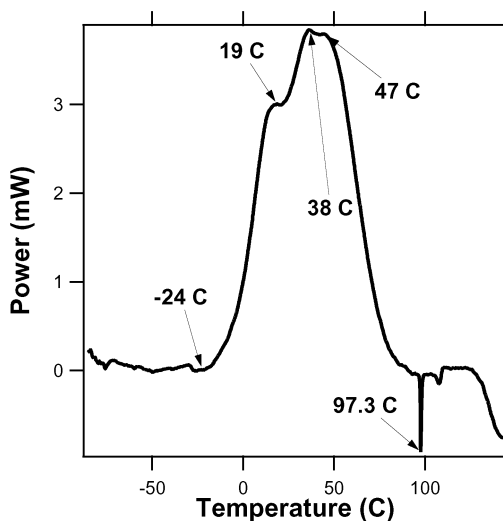


Figure 6. DSC trace of a 6 mg sample of $\text{BaH}_5\text{Aza}_{222}\text{Na}$.

peak at $+1120$ ppm, characteristic of contamination with Na metal as described above.

The DSC trace given in Figure 6 shows the onset of an exothermic decomposition peak at -24°C , with a peak at $+38^\circ\text{C}$ and a melting transition of Na at $+97^\circ\text{C}$. The enthalpy of decomposition was ~ -210 kJ per mol of $\text{BaH}_5\text{Aza}_{222}\text{Na}$. The enthalpy of melting of Na indicated the presence in this sample of about 0.25 mol of Na per mol of sample. A sample made by using Me_2O instead of MeNH_2 to transfer the compound through the frit of the K-cell had the same general DSC characteristics, but without the endothermic peak of sodium.

Conclusions

The synthesis of the first barium sodide provides another demonstration of the utility of polyaza-cages as ligands for the synthesis of alkalides and electrides. Such complexants were used to synthesize a stable potasside and a stable sodide,²¹ as well as a sodide in which an encapsulated proton served as the cation.³⁴ The title compound is the first alkaline earth-based

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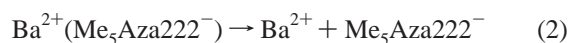
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alkalide and the second alkalide with a nonalkali cation. This complexation mode is promising for the synthesis of a number of such compounds. For example, it may be possible to synthesize a family of compounds $M^{2+}(H_5Aza222^-)X^-$, in which $M = Ca, Sr, Ba, Eu, Sm, Yb$, all of which are soluble in NH_3 , and $X = Na, K, Rb, Cs$. The variety of structures in such a series would be informative.

The synthesis of the first barium sodide also suggests that the thermal stability of alkalides and electrides may be increased by incorporation of divalent metal cations into negatively charged polyaza-cages that contain no ionizable protons. For example, it is likely that the usual decomposition routes would be prevented in a compound such as $Ba^{2+}(Me_5Aza222^-)Na^-$, which has no remaining ionizable protons. Decomplexation of such a compound, according to



would be unlikely, because the Ba^{2+} cation would probably be

trapped inside the cage both kinetically and thermodynamically. Similarly, complete decomposition to the amide, such as occurs with $Ba(NH_3)_6$, would probably not occur because of the absence of NH groups in the complex.

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Supporting Information Available: Crystallographic data of $Ba^{2+}(H_5Aza222^-)Na^- \cdot 2MeNH_2$ (PDF and TXT). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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