axes that are perpendicular to the crystallographic 3-fold axis, bisecting the three C(4)–C(5) bonds and directed toward the central Ni(II) ion. The overall symmetry of the cation, therefore, is close to point group D_3. The Ni(II) ion is coordinated to the six nitrogen atoms in a pseudooctahedral arrangement with the average Ni–N bond distance of 2.10 Å. The twist angle between the equilateral triangle (N–N = 2.99 (1) Å) formed by the three N(3) atoms and the one (N–N = 3.00 (1) Å) by the three N(6) atoms is 59°. The Ni(II) ion is 0.004 Å from the best plane formed by the four nitrogen atoms of the octahedron, which are coplanar within ±0.15 Å.

All of the bond distances and angles around the Ni(II) ion are very similar to those of $[Ni(en)_3]^{2+}$.[11-13] The N(3)–C(4)–C(5)–N(6) torsion angle of 57 (1)° and the N(3)–N(6) distance of 2.79 (1) Å also agree well with 58° and 2.786 Å in the oxalate salt of $[Ni(en)_3]^{2+}$, respectively.[13] This indicates that addition of the two tris(methylene)amino groups does not exert significant influence on the coordination geometry around the Ni(II) ion. The average Co(II)–N distance of $[Co(\mathbf{1})]^{2+}$ was almost identical with that of $[Co(NH_3)_6]^{2+}$.[9] Therefore, the encapsulation of Ni(II) by **1** increases the stability of the complex without significant changes in the structural framework as well as ligand field strength compared with the case for $[Ni(en)_3]^{2+}$.

The two tris(methylene)amino groups reveal an interesting structural feature. The N(1) and N(8) atoms in the apexes of the caps are only 0.25 and 0.18 Å, respectively, apart from the best planes formed by three C(2) and three C(7) atoms. Furthermore, the C–N bond distances are 1.41 (2) and 1.44 (2) Å and the C–N–C bond angles are 117 (1) and 118 (1)° (Figure 1). These are indicative of near-sp^2 hybridization of the two tertiary amine nitrogens. The shift from normal sp^3 to near sp^2 is probably due to the long-range interaction of the cap nitrogen with the t_{2g} electrons of the Ni(II) ion. Similar sp^2 hybridization of the tertiary amine nitrogens capping the octahedron has been reported for $[M(trenpy)]^{2+}$ complexes.[14] In the trenpy complexes, the M–N interaction was greatly influenced by the number of t_{2g} electrons of the metal ions. The sp^2 hybridization of the nitrogen atoms of the amino caps was also observed in the Co(II) and Co(III) complexes of **1**.[9]

The large cations are packed in a cubic closest packing (ccp) mode, four nickel ions in the unit cell being near $(^1/_4, ^1/_4, ^1/_4)$, $(^1/_4, ^3/_4, ^3/_4)$, $(^3/_4, ^1/_4, ^3/_4)$, and $(^3/_4, ^3/_4, ^1/_4)$. Two smaller tetrahedral holes and one larger octahedral hole per cation are present in this ccp mode. In the present crystal structure, perchlorate **1** is in one of the tetrahedral holes and **2** in the octahedral hole. Perchlorate **2** might be disordered due to the larger hole size. The Ni–N(1) and Ni–N(8) distances are 2.96 (1) and 2.90 (1) Å, respectively. This asymmetry in distance may be partly attributed to the crystal packing forces, since N(1), N(8), and the two perchlorate Cl atoms are located on the body-diagonal 3-fold axis and the N(1)–Cl(1) distance is only 3.46 (1) Å while the N(8)–Cl(2) distance is 9.97 (1) Å. There is only one type of hydrogen bond in the structure (N(3)–H···O(2) = 3.10(1) Å).

The methylenediamine (N–C–N) linkage is easily fragmented unless both of the nitrogen atoms are tertiary.[15] The stability of the ligand in the present complex, however, implies that the N–C–N linkage containing a secondary amine can be stabilized by the coordination of the secondary nitrogen to a metal ion.

Acknowledgment. This work was supported in part by grants from the Korea Science and Engineering Foundation.

Registry No. $[Ni(\mathbf{1})](ClO_4)_2$, 88229-09-8; ethylenediamine, 107-15-3; formaldehyde, 50-00-0; ammonia, 7664-41-7.

Supplementary Material Available: Anisotropic thermal parameters (Table II) and final values of $|F_o|$ and $|F_c|$ (Table III) (4 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
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A Centrosymmetric Hydrogen-Bonded Cyclic $(H_2O{\cdot}Br^-)_2$ System. Crystal Structure of 1-Methyl-1,3,5,7-tetraazaadamantan-1-ium Bromide Hydrate

Thomas C. W. Mak

Received June 15, 1983

A recent MNDO study[1] of 1,3,5,7-tetraazaadamantane (commonly known as hexamethylenetetramine), $(CH_2)_6N_4$ (**1**), and related cage molecules has shown that, when a lone pair of **1** is utilized in salt or adduct formation, the C–N$_{\text{quaternary}}$ bonds and adjacent C–N$_{\text{tertiary}}$ bonds become significantly lengthened and shortened, respectively, relative to the remaining six remote C–N bonds. This general trend is in accord with available structural data for $(CH_2)_6N_4{\cdot}BH_3$,[2] $(CH_2)_6N_4O$,[3] and several salts containing the $[(CH_2)_6N_4CH_3]^+$,[4,5] $[(CH_2)_6N_4CH_2C_6H_5]^+$,[6] $[(CH_2)_6N_4CH_2CH{=}CH_2]^+$,[7] and $[(CH_2)_6N_4H]^+$[8] cations. The title compound, $[(CH_2)_6N_4CH_3]Br{\cdot}H_2O$ (**2**), was isolated in the course of our synthetic and structural studies on various heterocyclic cage systems. The mode of hydrogen bonding involving the water molecule seemed intriguing and prompted us to undertake an X-ray crystallographic analysis.

Experimental Section

An equimolar quantity of methyl bromide was chilled to 0 °C and then added dropwise to a solution of **1** in ethanol/water. Slow evaporation of the resulting solution yielded hygroscopic crystals of **2** in the form of thick plates. A selected crystal (0.35 × 0.35 × 0.40 mm) was covered with petroleum jelly, lodged in a 0.5-mm-diameter Lindemann glass capillary, and sealed with epoxy resin. It was then centered on a Nicolet R3m four-circle diffractometer (graphite-monochromatized Mo K$_\alpha$ radiation, λ = 0.71069 Å), and determinations of the crystal class, orientation matrix, and accurate unit-cell parameters were performed according to established procedures.[9]

Crystal Data: $[(CH_2)_6N_4CH_3]Br{\cdot}H_2O$ (**2**), M_r = 253.15, monoclinic, space group $P2_1/c$, a = 6.840 (2) Å, b = 6.898 (2) Å, c = 22.597 (8) Å, β = 94.91 (3)°, V = 1062.3 (6) Å^3, D_{measd} = 1.584 g cm^{-3}, Z = 4, D_{calcd} = 1.583 g cm^{-3}, $F(000)$ = 519.86, μ(Mo K$_\alpha$) = 38.03 cm^{-1}.

Intensities ($h,k,\pm l$; 1577 unique data) were measured at 22 °C by using the ω–2θ variable-scan (2.02–8.37° min^{-1}) technique in the

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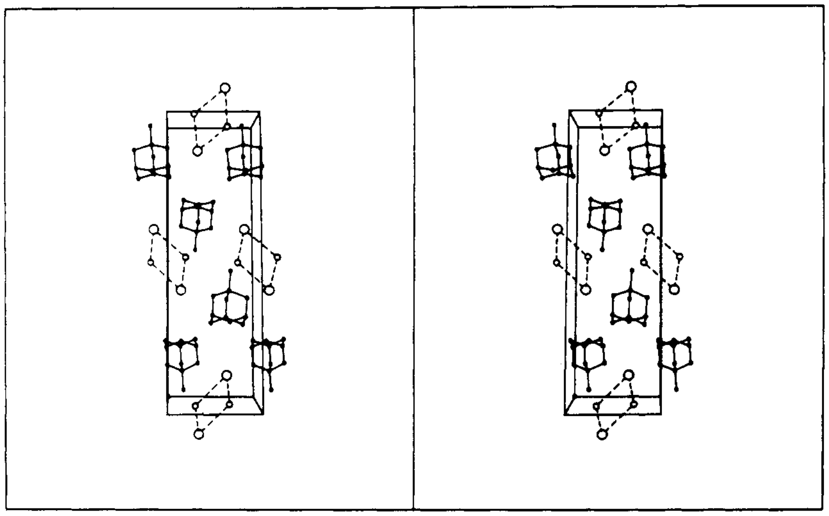

Figure 1. Packing of the $[(CH_2)_6N_4CH_3]^+$ and $(H_2O{\cdot}Br^-)_2$ species in the crystal structure of **2**. The O–H···Br hydrogen bonds are represented by broken lines. The unit-cell origin lies at the lower left corner, with *a* pointing toward the reader, *b* from left to right, and *c* upward.

bisecting mode for $2\theta < 50°$. Azimuthal scans of selected strong reflections were used to define a pseudoellipsoid for the application of absorption corrections.[10,11] The structure was solved by the heavy-atom method, and all non-hydrogen atoms were varied anisotropically. The methylene H atoms were generated geometrically and allowed to ride on their respective parent C atoms with fixed C–H bond distances (0.96 Å) and the same assigned isotropic temperature factor. A subsequent difference Fourier map contained maxima corresponding to H atoms of the methyl group and the water molecule. In the last stage of refinement, the methylene and methyl H atoms were treated with the riding model, the water H atoms held stationary, and all assigned fixed isotropic thermal parameters. Convergence for 1267 observed reflections ($|F_o| > 3\sigma|F_o|$) and 121 variables was reached at $R \equiv \sum\Delta/\sum|F_o| = 0.050$ and $R_w \equiv [\sum w\Delta^2/\sum w|F_o|^2]^{1/2} = 0.058$, where $\Delta = ||F_o| - |F_c||$ and $w = [\sigma^2(|F_o|) + 0.001|F_o|^2]^{-1}$. The final difference map showed diffraction ripples of +0.60 to −0.58 e $Å^{-3}$ in the neighborhood of the Br atom. All computations were performed on a Data Control Nova 3/12 minicomputer with the SHELXTL system of crystallographic programs.[12] Analytic expressions of neutral-atom scattering factors with anomalous dispersion corrections were employed.[13] Final positional parameters are given in Table I. Tables of hydrogen atomic coordinates, bond lengths and bond angles, anisotropic temperature factors, and structure factors are available as supplementary material.

Results and Discussion

The molecular packing in the crystal structure of **2** is illustrated in Figure 1. The most notable feature is that the water molecule forms "second-order" hydrogen bonds[14] with the "soft" Br^- ions in preference to expected "first-order" bonds[14] with the "hard" tertiary amino N atoms of the $[(CH_2)_6N_4CH_3]^+$ cation. The resulting cyclic $(H_2O{\cdot}Br^-)_2$ entity occupies a site of $\bar{1}$ symmetry (Figure 1); the O and Br atoms are necessarily coplanar, but the H atoms are not requried to lie exactly in this plane. Geometrical parameters: O···Br = 3.386 (5), O···Br* = 3.338 (5), $O{-}H_a$ = 0.958 (15), $O{-}H_b$ = 0.938 (15), $H_a{\cdots}Br$ = 2.463 (15), $H_b{\cdots}Br^*$ = 2.511 (15) Å; Br···O···Br* = 105.7 (4), $H_a{-}O{-}H_b$ = 126 (2)° (where the asterisk denotes the symmetry transformation $1 - x$, $1 - y$, $-z$). The H···Br separations are about 0.6 Å shorter than the sum of the relevant van der Waals radii and therefore fulfill Hamilton's criterion[15] for hydrogen-bond formation. The observed O···Br distances and $Br^-{\cdots}O{\cdots}Br^-$ angle agree closely with those reported for the $(H_2O{\cdot}Br^-)_\infty$ helical arrangement in codeine·HBr·$2H_2O$.[16]

Table I. Atomic Coordinates and Equivalent Isotropic Thermal Thermal Parameters[a]

	x	*y*	*z*	U_{eq},[b] $Å^2$
Br	0.61274 (10)	0.65070 (9)	0.10680 (3)	0.0596 (2)
O	0.7197 (7)	0.3015 (8)	0.0093 (2)	0.091 (2)
N(1)	0.1977 (7)	0.1656 (6)	0.1025 (2)	0.045 (1)
N(2)	0.3889 (6)	0.1422 (7)	0.1982 (2)	0.049 (2)
N(3)	0.0727 (6)	−0.0192 (7)	0.1824 (2)	0.047 (2)
N(4)	0.0870 (7)	0.3317 (6)	0.1884 (2)	0.048 (2)
C(1)	0.4040 (8)	0.1515 (8)	0.1357 (3)	0.049 (2)
C(2)	0.0818 (8)	−0.0106 (8)	0.1195 (3)	0.051 (2)
C(3)	0.0988 (8)	0.3486 (9)	0.1255 (3)	0.050 (2)
C(4)	0.2719 (9)	−0.0283 (8)	0.2124 (3)	0.055 (2)
C(5)	−0.0208 (8)	0.1564 (8)	0.2020 (3)	0.049 (2)
C(6)	0.2879 (8)	0.3151 (8)	0.2184 (3)	0.051 (2)
C(7)	0.2107 (10)	0.1804 (10)	0.0368 (3)	0.062 (2)

[a] Esd's given in parentheses. [b] Calculated as one-third of the trace of the orthogonalized U matrix.

A wealth of experimental data,[17] complemented by theoretical studies,[18] is available for hydrogen-bonded systems with intramolecular monomeric, linear and cyclic dimeric, and linear polymeric structures (e.g. ortho-substituted phenols, HF_2^-, $(RCOOH)_2$, DNA base pairs, $(HF)_\infty$, etc.). In contrast to this, only a few cyclic polymeric species, such as the methanol tetramer[19] and the HF hexamer,[20] have been adequately characterized. The present centrosymmetric $(H_2O{\cdot}Br^-)_2$ system has no known analogue and could conceivably be the forerunner of a variety of similar cyclic hydrogen-bonded complexes. It may be noted that model systems such as $(H_2O)_4$ (S_4 symmetry with all O atoms coplanar)[21] and $(H_2O)_3{\cdot}OH^-$ (OH^- as double-proton acceptor)[22] have been shown to be stable by semiempirical molecular orbital calculations.

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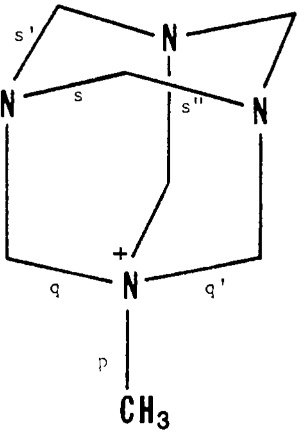

Figure 2. Averaged dimensions of the 1-methyl-1,3,5,7-tetraazaadamantan-1-ium cation, $[(CH_2)_6N_4CH_3]^+$: p, 1.500 (7) Å; q, 1.535 (4) Å; r, 1.430 (5) Å; s, 1.469 (3) Å; pq, 111.3 (3)°; qq', 107.8 (3)°; qr, 110.0 (3)°; rs, 109.8 (3)°; ss', 107.8 (3)°; ss'', 111.7 (3)°.

The cage-type $[(CH_2)_6N_4CH_3]^+$ cation, which forms a salt containing an I_8^{2-} anion in an "outstretched letter Z" configuration,[4] undoubtedly plays a similar dominant role in stabilizing the $(H_2O{\cdot}Br^-)_2$ species of opposite charge. This may be considered an extension of the principle of large ions stabilizing large counterions in the solid state.[23] The averaged dimensions of the organic cation (Figure 2) are in good agreement with corresponding values found in $[(CH_2)_6N_4CH_3]_2I_8$[4] and $[(CH_2)_6N_4CH_3]I_3$,[5] and the variation of C–N bond lengths follows the general pattern effected by quaternization of one N atom of the hexamethylenetetramine skeleton.[1]

Acknowledgment. The author acknowledges the useful comments on the results reported in this paper by Professors Jerry Donohue and George A. Sim.

Registry No. 2, 88343-76-4.

Supplementary Material Available: Tables of hydrogen atomic coordinates (Table II), bond lengths and bond angles (Table III), anisotropic thermal parameters (Table IV), and structure factors (Table V) (11 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
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Nucleophilicity of Thiolato Sulfur When Coordinated to Ruthenium(II). Kinetics of the Alkylation of (8-Mercaptoquinolinato)bis(2,2'-bipyridine)ruthenium(II) by Iodomethane[1]

Michael J. Root and Edward Deutsch*

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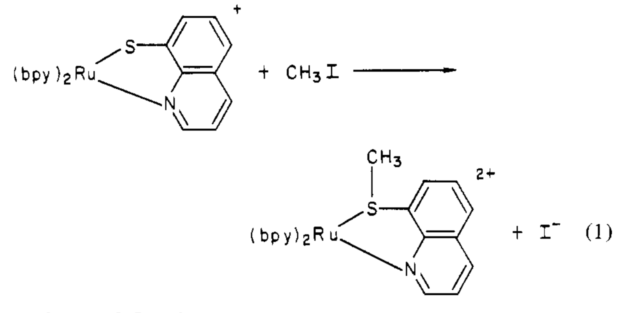
Perhaps the most important aspect of the reactivity of a coordinated thiol is its nucleophilicity.[2,3] The nucleophilicity of thiolate ligands coordinated to cobalt(III) and chromium(III), as measured by CH_3I methylation, is considerable, being approximately the same as that of other two-coordinate sulfur species such as noncoordinated thiols and noncoordinated thioethers.[3] In order to assess more fully the influence of the central metal ion in determining the nucleophilicity of coordinated thiolate, we have investigated the CH_3I methylation of $[(bpy)_2Ru(SC_9H_6H_6N)]^+$ (bpy = 2,2'-bipyridine; $^-SC_9H_6N$ = 8-mercaptoquinolinate), eq 1, and compared these results to those obtained for analogous Co(III),[3] Cr(III),[3] and Ni(II)[4] thiolate complexes.



Experimental Section

Materials. All materials were reagent grade unless otherwise noted. Triply distilled, charcoal-filtered water, spectral grade DMF (*N*,*N*-dimethylformamide), and methanol were used for kinetic experiments. Spectrophotometric and electrochemical measurements were conducted in spectral grade acetonitrile. Lithium perchlorate was recrystallized from water and dried at 110 °C for 24 h. Tetraethylammonium perchlorate (TEAP) was recrystallized twice from water and dried at 110 °C for 24 h. Iodomethane was distilled and stored over copper wire at −10 °C in the dark. $Ru(bpy)_2Cl_2{\cdot}H_2O$ was prepared by a published procedure.[5] The ligand 8-mercaptoquinoline was obtained from Sigma as the hydrochloride salt.

(8-Mercaptoquinolinato-*N*,*S*)bis(2,2'-bipyridine)ruthenium(II) Salts, $[(bpy)_2Ru(SC_9H_6N)]X$ (X = PF_6, BF_4). To 75 mL of dearerated 50/50 CH_3OH/H_2O containing 3.1 mL of 1 M KOH was added 0.297 g of $HSC_9H_6N{\cdot}HCl$ (1.5 mmol), and the resultant mixture was allowed to stir for ca. 15 min. At this time, 0.522 g of $(bpy)_2RuCl_2{\cdot}H_2O$ (1.0 mmol) was added, and the reaction mixture was refluxed for 2 h. The solution volume was reduced by one-third and the solution cooled to room temperature. Addition of excess solid NH_4PF_6 precipitated the desired complex. Purification was effected by column chromatography on alumina using $CH_3CN/C_6H_5CH_3$ eluents.[5] Reprecipitation from acetone/diethyl ether yielded a black powder that was dried in vacuo. Yield = 81% (based on Ru). Anal. Calcd for $RuC_{29}H_{22}N_5SPF_6$: N, 9.75; S, 4.46; P, 4.31. Found: N, 9.42; S. 4.48; P, 3.90. Visible–UV (CH_3CN) λ_{max}, nm (ϵ, M^{-1} cm^{-1}: 501 (9700), 457 sh (9200), 420 sh (7300), 371 sh (7200), 345 (7800), 331 sh (7600), 293 (45 000), 277 sh (31 000), 249 (32 000), 206 sh (31 000). Cyclic voltammetry (0.1 M TEAP in CH_3CN, glassy carbon vs. SSCE) $E_{1/2}$, V: 0.30, −1.49, −1.74.

$[(bpy)_2Ru\text{-}(SC_9H_6N)]BF_4$ was prepared and purified as above but was precipitated with $NaBF_4$. Anal. Calcd for $RuC_{29}H_{22}N_5SBF_4$: Ru, 15.30; N, 10.61; S, 4.85; B, 1.64. Found: Ru, 15.80; N, 11.38; S, 4.84; B, 1.78.

(Methyl 8-quinolinyl thioether-*N*,*S*)bis(2,2'-bipyridine)ruthenium(II) Hexafluorophosphate, $[(bpy)_2Ru(S(CH_3)C_9H_6N)](PF_6)_2$. This complex was prepared by CH_3I methylation of the parent thiolate complex.[6] $[(bpy)_2Ru(SC_9H_6N)]BF_4$ (0.110 g, 0.17 mmol) was dissolved in 10 mL of DMF producing a brown solution to which 1.04 mL of CH_3I (17 mmol) was added. The solution rapidly turned orange and was stirred for 15 min. At this time, 10 mL of H_2O contg. a large excess of NH_4PF_6 was added. To this solution was added 250 mL of diethyl ether, and the mixture was stirred for 30 min. The resulting yellow powder was collected and purified as above. Column chromatography (alumina, $CH_3CN/C_6H_5CH_3$ eluents[5]) showed that only one product was formed. Yield = 76% (based on Ru). Anal. Calcd for $RuC_{30}H_{25}N_5SP_2F_{12}$: N, 7.97; S, 3.65; P, 7.05. Found: N, 7.91; S, 3.86; P, 6.74. Visible–UV (CH_3CN) λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 422

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