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# SUPPLEMENTARY MATERIAL

# Naked Fluoride Ion Sources: Synthesis, Characterization and Coupling Reaction of 1 - Methyl - hexamethylenetetramine Fluoride

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**Abstract**

Anhydrous 1-methyl-hexamethylenetetramine ( also referred to as N-methyl-urotropinium or methylhexaminium ) fluoride was prepared by either halogen exchange between the corresponding iodide and AgF or by a single step, one pot, self assembling synthesis from aqueous $CH_3NH_2$, HF, formaldehyde and $NH_3$. It was characterized by NMR and vibrational spectroscopy. Its hydrate undergoes at 70 °C a Sommelet-type ring opening and coupling reaction to form a potential cryptand system consisting of two bicyclic triazine groups which are connected through a methylene bridge and contain 8 ternary nitrogen atoms. The compound was characterized by multinuclear NMR and vibrational spectroscopy , and its structure was determined from single crystal X-ray diffraction data.

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Table S-1: STRUCTURE DETERMINATION SUMMARY

Crystal Data

| | |
|---|---|
| Empirical Formula | $C_{13}H_{28}N_8$ |
| Color; Habit | colorless, air-sensitive |
| Crystal Size (mm) | 0.2 x 0.2 x 0.2 |
| Crystal System | Monoclinic |
| Space Group | C2/c |
| Unit Cell Dimensions | a = 22.600(2) Å |
| | b = 7.579(2) Å |
| | c = 19.222(2) Å |
| | $\beta$ = 105.83(2)° |
| Volume | 3167.6(9) Å$^3$ |
| Z | 8 |
| Formula Weight | 296.4 |
| Density(calc.) | 1.243 g/cm$^3$ |
| Absorption Coefficient | 0.649 mm$^{-1}$ |
| F(000) | 1296 |

Table S-1 (continued): Data Collection

| | |
|---|---|
| Diffractometer Used | Siemens P4 |
| Radiation | CuKα (λ = 1.54178 Å) |
| Temperature (K) | 298 |
| Monochromator | Highly oriented graphite crystal |
| 2θ Range | 2.0 to 102.5° |
| Scan Type | ω |
| Scan Speed | Variable; 8.00 to 60.00°/min. in ω |
| Scan Range (ω) | 2.40° |
| Background Measurement | Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time |
| Standard Reflections | 3 measured every 100 reflections |
| Index Ranges | $-1 \leq h \leq 22$, $-1 \leq k \leq 7$ $-19 \leq \ell \leq 18$ |
| Reflections Collected | 2198 |
| Independent Reflections | 1672 ($R_{int}$ = 2.10%) |
| Observed Reflections | 1339 ($F > 4.0\sigma(F)$) |
| Absorption Correction | N/A |

Table S-1 (continued): Solution and Refinement

| | |
|---|---|
| System Used | Siemens SHELXTL IRIS |
| Solution | Direct Methods |
| Refinement Method | Full-Matrix Least-Squares |
| Quantity Minimized | $\sum w(F_o-F_c)^2$ |
| Absolute Structure | N/A |
| Extinction Correction | N/A |
| Hydrogen Atoms | Riding model, fixed isotropic U |
| Weighting Scheme | Unit weights |
| Number of Parameters Refined | 190 |
| Final R Indices (obs. data) | R = 3.61 %, wR = 3.91 % |
| R Indices (all data) | R = 4.70 %, wR = 7.04 % |
| Goodness-of-Fit | 1.53 |
| Largest and Mean $\Delta/\sigma$ | 0.914, 0.054 |
| Data-to-Parameter Ratio | 7.0:1 |
| Largest Difference Peak | 0.15 $e\text{Å}^{-3}$ |
| Largest Difference Hole | -0.15 $e\text{Å}^{-3}$ |

Table S-2. Anisotropic displacement coefficients ($Å^2 x 10^3$)

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| N(1) | 42(1) | 33(1) | 50(1) | 1(1) | 14(1) | 7(1) |
| N(2) | 46(1) | 43(1) | 43(1) | -5(1) | 16(1) | 8(1) |
| N(3) | 49(1) | 43(1) | 41(1) | -3(1) | 10(1) | -1(1) |
| N(4) | 45(1) | 35(1) | 36(1) | -4(1) | 16(1) | 1(1) |
| N(5) | 41(1) | 29(1) | 35(1) | 5(1) | 15(1) | 5(1) |
| N(6) | 50(1) | 38(1) | 33(1) | 0(1) | 15(1) | -2(1) |
| N(7) | 41(1) | 40(1) | 39(1) | 4(1) | 8(1) | 4(1) |
| N(8) | 43(1) | 32(1) | 47(1) | -6(1) | 13(1) | -5(1) |
| C(1) | 69(1) | 47(1) | 81(1) | 14(1) | 27(1) | 10(1) |
| C(2) | 56(1) | 37(1) | 51(1) | -7(1) | 15(1) | 9(1) |
| C(3) | 42(1) | 53(1) | 56(1) | -2(1) | 3(1) | 7(1) |
| C(4) | 64(1) | 55(1) | 39(1) | 2(1) | 21(1) | 7(1) |
| C(5) | 39(1) | 51(1) | 50(1) | -2(1) | 16(1) | 8(1) |
| C(6) | 54(1) | 32(1) | 51(1) | -6(1) | 23(1) | -3(1) |
| C(7) | 59(1) | 34(1) | 41(1) | 1(1) | 16(1) | 4(1) |
| C(8) | 53(1) | 35(1) | 40(1) | 2(1) | 20(1) | 0(1) |
| C(9) | 41(1) | 44(1) | 43(1) | 0(1) | 15(1) | 4(1) |
| C(10) | 53(1) | 54(1) | 34(1) | -6(1) | 2(1) | 4(1) |
| C(11) | 51(1) | 44(1) | 46(1) | 0(1) | 22(1) | 4(1) |
| C(12) | 53(1) | 33(1) | 51(1) | 6(1) | 15(1) | 3(1) |
| C(13) | 67(1) | 50(1) | 78(1) | -15(1) | 18(1) | -6(1) |

The anisotropic displacement factor exponent takes the form:

$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

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Table S-3. H-Atom coordinates ($x10^4$) and isotropic displacement coefficients ($Å^2 x10^3$)

| | x | y | z | U |
|---|---|---|---|---|
| H(1) | 754 | 9106 | 134 | 88 |
| H(2) | 437 | 8883 | -686 | 88 |
| H(3) | 174 | 7928 | -121 | 88 |
| H(4) | 75 | -1812 | 1536 | 80 |
| H(5) | 548 | -2893 | 1260 | 80 |
| H(6) | 589 | -2856 | 2079 | 88 |
| H(7) | 1390 | 8130 | -828 | 65 |
| H(8) | 1737 | 8043 | -13 | 65 |
| H(9) | 265 | 4982 | -632 | 64 |
| H(10) | 416 | 6082 | -1242 | 64 |
| H(11) | 1355 | 5510 | -1574 | 70 |
| H(12) | 1757 | 3891 | -1253 | 70 |
| H(13) | 2459 | 4064 | -59 | 59 |
| H(14) | 2352 | 5513 | 463 | 59 |
| H(15) | 915 | 2487 | -111 | 56 |
| H(16) | 1411 | 1846 | -473 | 56 |
| H(17) | 1849 | 4857 | 1234 | 62 |
| H(18) | 1164 | 4796 | 790 | 62 |
| H(19) | 1494 | 4211 | 2178 | 57 |
| H(20) | 822 | 3711 | 1775 | 57 |
| H(21) | 2057 | 875 | 1163 | 55 |
| H(22) | 2346 | 2265 | 1750 | 55 |
| H(23) | 2146 | 2055 | 2923 | 62 |
| H(24) | 1865 | 341 | 3138 | 62 |
| H(25) | 780 | -162 | 2718 | 60 |
| H(26) | 377 | 1046 | 2124 | 60 |
| H(27) | 1613 | -1766 | 1491 | 63 |
| H(28) | 1611 | -2083 | 2288 | 80 |

Table S-5. Bond lengths (Å) and bond angles (°) for ( II )

| | | | |
|---|---|---|---|
| N(1)-C(1) | 1.460(4) | N(1)-C(2) | 1.470(4) |
| N(1)-C(3) | 1.461(4) | N(2)-C(2) | 1.450(4) |
| N(2)-C(4) | 1.454(4) | N(2)-C(5) | 1.462(4) |
| N(3)-C(3) | 1.448(4) | N(3)-C(4) | 1.454(4) |
| N(3)-C(6) | 1.462(4) | N(4)-C(5) | 1.461(4) |
| N(4)-C(6) | 1.457(3) | N(4)-C(7) | 1.450(4) |
| N(5)-C(7) | 1.462(4) | N(5)-C(8) | 1.474(4) |
| N(5)-C(9) | 1.467(3) | N(6)-C(8) | 1.450(4) |
| N(6)-C(10) | 1.452(4) | N(6)-C(11) | 1.445(4) |
| N(7)-C(9) | 1.458(4) | N(7)-C(10) | 1.457(4) |
| N(7)-C(12) | 1.447(4) | N(8)-C(11) | 1.460(4) |
| N(8)-C(12) | 1.465(4) | N(8)-C(13) | 1.455(4) |

| | | | |
|---|---|---|---|
| C(1)-N(1)-C(2) | 110.0(2) | C(1)-N(1)-C(3) | 110.5(2) |
| C(2)-N(1)-C(3) | 110.7(2) | C(2)-N(2)-C(4) | 108.3(2) |
| C(2)-N(2)-C(5) | 115.0(2) | C(4)-N(2)-C(5) | 107.5(2) |
| C(3)-N(3)-C(4) | 107.8(2) | C(3)-N(3)-C(6) | 115.3(2) |
| C(4)-N(3)-C(6) | 108.2(2) | C(5)-N(4)-C(6) | 112.9(2) |
| C(5)-N(4)-C(7) | 117.8(2) | C(6)-N(4)-C(7) | 116.0(2) |
| C(7)-N(5)-C(8) | 106.8(2) | C(7)-N(5)-C(9) | 111.6(2) |
| C(8)-N(5)-C(9) | 111.6(2) | C(8)-N(6)-C(10) | 108.3(2) |
| C(8)-N(6)-C(11) | 115.0(2) | C(10)-N(6)-C(11) | 108.5(2) |
| C(9)-N(7)-C(10) | 108.0(2) | C(9)-N(7)-C(12) | 114.9(2) |
| C(10)-N(7)-C(12) | 108.3(2) | C(11)-N(8)-C(12) | 111.7(2) |
| C(11)-N(8)-C(13) | 109.9(3) | C(12)-N(8)-C(13) | 110.3(2) |
| N(1)-C(2)-N(2) | 114.2(2) | N(1)-C(3)-N(3) | 114.2(2) |
| N(2)-C(4)-N(3) | 111.3(2) | N(2)-C(5)-N(4) | 117.2(2) |
| N(3)-C(6)-N(4) | 117.0(2) | N(4)-C(7)-N(5) | 111.3(2) |
| N(5)-C(8)-N(6) | 115.0(2) | N(5)-C(9)-N(7) | 114.5(2) |
| N(6)-C(10)-N(7) | 110.9(2) | N(6)-C(11)-N(8) | 113.8(3) |
| N(7)-C(12)-N(8) | 114.5(2) | | |

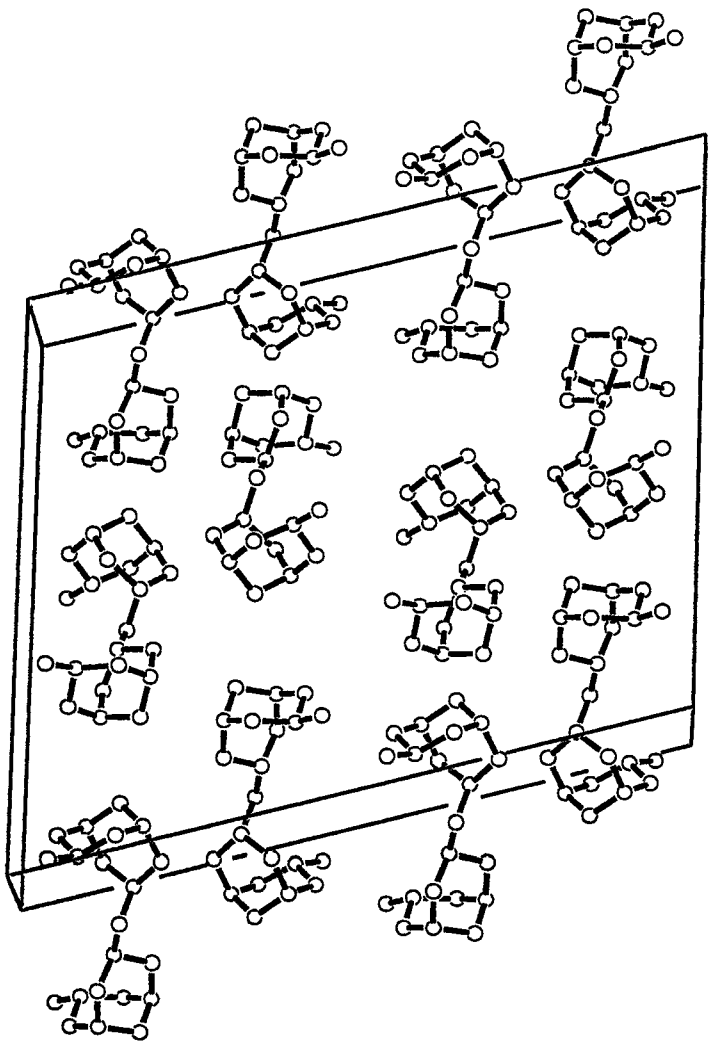


**Figure S-1. Packing diagram for ( II ) viewed along the *b* axis.**