Supporting information

Experimental Part

All work was carried out excluding humidity and air in an atmosphere of dried and purified argon (Westfalen AG) using high-vacuum glass lines or a glove box (MBraun). Liquid ammonia (Westfalen AG) was dried and stored over sodium (VWR) in a special high-vacuum glass line. All reaction vessels for liquid ammonia handling were made out of borosilicate glass and were flame-dried before use. UF_4 was synthesized from $UO_2(NO_3)_2 \cdot 6\ H_2O$ (Merck, 99.9%) according to the literature.[1] Its purity was checked by powder X-Ray diffractometry and its IR spectrum. $TiCl_3$ (Sigma-Aldrich, 99.99%) was checked for its purity and could be used without further purification. Due to the thermal instability of the compounds, they decompose under loss of ammonia at temperatures above ca. −40 °C, the application of further analytic methods was hindered.

Synthesis of $[Ti(NH_3)_8]Cl_3 \cdot 6\ NH_3$

In a typical reaction, a vessel was charged with 161 mg (1 mmol) violet $TiCl_3$. After cooling to −78 °C, 10 mL dry NH_3(l) were distilled onto the solid upon which the violet color changed into grey. A clear, colorless solution was obtained and a grey residue remained undissolved (this may be the title compound in powderous form or, unlikely, $TiCl_3 \cdot 5$ or $6\ NH_3$, or all three). The reaction vessel was stored at −40 °C. Some of the solvent was carefully pumped off from time to time and after two weeks of crystallization time colorless crystals were obtained under the mother liquor. As the crystals decomposed upon warming above circa −40 °C, they were transferred into dry, cooled perfluoro-ether oil and selected under the microscope. Under these conditions the crystals appeared colorless to the eye, but faint blue colors may be easily overlooked under these circumstances. The conversion of $TiCl_3$ in NH_3 is quantitative, the yield of the title compound cannot be given due to its thermal instability.

Synthesis of $[UF(NH_3)_8]Cl_3 \cdot 3.5\ NH_3$

A reaction vessel was charged with 161 mg (1 mmol) $TiCl_3$ and 218 mg (0,69 mmol) UF_4. After cooling to −78 °C, 10 mL dry NH_3 were distilled onto the solids upon which the violet color of $TiCl_3$ changed into grey. A clear, pale green solution was obtained and a grey-greenish residue remained undissolved. The reaction vessel was stored at −40 °C. The solvent was carefully pumped off from time to time and after four weeks of crystallization time colorless crystals ($[Ti(NH_3)_8]Cl_3 \cdot 6\ NH_3$) were obtained besides the green cyrstals of $[UF(NH_3)_8]Cl_3 \cdot 3.5\ NH_3$ which decomposed upon further warming. The conversion of UF_4 seems to be quantitative as it could not be detected by powder X-ray diffraction after removal of the solvents. The yield of the title compound cannot be given due to its thermal instability.

Structure Solution and Refinement

Single crystals of the compounds were subjected to X-ray structure analysis at low temperatures by using an Oxford XCalibur3 diffractometer. Both structures were solved using Direct Methods implemented in Shelxs-

97,[2] and were refined against F^2 using Shelxl-97.[3] The atomic positions of the non-hydrogen atoms were obtained from difference-Fourier-syntheses, hydrogen atoms were either also obtained this way or were refined using a riding model. For the hydrogen atoms on ammonia molecules of crystallization of the uranium compound no positions could be determined so they were excluded from the refinement.

Table S1. Crystallographic details of the title compounds. Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein−Leopoldshafen (Germany), http://www.fiz-karlsruhe.de/icsd.html, on quoting the depository numbers CSD-429447 for the U-compound, CSD-429448 for the Ti-compound.

	$[Ti(NH_3)_8]Cl_3 \cdot 6\ NH_3$	$[U(NH_3)_8F]Cl_3 \cdot 3.5\ NH_3$
Sum formula	$TiCl_3N_{14}H_{40}$	$H_{34.5}FCl_3N_{11.5}U$
Color and habitus	colorless needles	green plates
Formula mass / g · mol^{-1}	392.73	559.27
Crystal system	monoclinic	monoclinic
Space group	$P2/c$	$C2/c$
a / Å	9.1065(3)	22.0165(3)
b / Å	9.4014(4)	14.7706(2)
c / Å	12.3552(5)	12.3866(2)
β / °	92.544(3)	107.69(1)
V / Å^3	1056.73(4)	3837.57(10)
Z	2	8
T / K	123(2)	123(2)
$\rho_{calc.}$ / g · cm^{-3}	1.23	1.94
λ / Å (Mo-K$_\alpha$)	0.71073	0.71073
μ(Mo-K$_\alpha$) / mm^{-1}	0.79	8.89
R_{int}	0.087	0.037
$R(F)$ ($I \geq 2\sigma(I)$, all data)	0.029, 0.053	0.020, 0.034
w$R(F^2)$ ($I \geq 2\sigma(I)$, all data)	0.053, 0.056	0.044, 0.047
S (all data)	0.86	0.98
Data, parameters, restraints	3231, 167, 0	11015, 203, 5
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e · Å^{-3}	0.46, −0.27	1.77, −1.27

Computational details

The $[Ti(NH_3)_8]^{3+}$ and $[Ti(H_2O)_6]^{3+}$ cations were investigated using quantum chemical methods. The structures of the cations were first fully optimized without any symmetry constraints using PBE0 hybrid density functional method.[4] All atoms were described with a Gaussian-type, all-electron triple-valence-zeta basis set (def2-TZVPP).[5,6] To counter the high charge of the studied cations, we applied the COSMO solvation model with electrostatically ideal solvent ($\varepsilon = \infty$).[7] The optimized $[Ti(NH_3)_8]^{3+}$- and $[Ti(H_2O)_6]^{3+}$-cations were close to S_8 and S_6 point group symmetries, respectively. The excited states were investigated with the Second-Order Approximate Coupled-

Cluster method (CC2), which is an approximation of the Coupled Cluster Singles and Doubles (CCSD) method.[8–10] The COSMO solvation model was applied also in the excited state calculations. All DFT and CC2 calculations were carried out using the TURBOMOLE program package (version 6.6).[11]

[Ti(NH$_3$)$_8$]Cl$_3 \cdot$ 6 NH$_3$

Table S2. Selected atomic distances and angles of the compound [Ti(NH$_3$)$_8$]Cl$_3 \cdot$ 6 NH$_3$.

	distance / Å		angle / °
Ti(1)—N(1)	2.3115(12)	N(1)#1—Ti(1)—N(1)	80.85(7)
Ti(1)—N(1)#1	2.3115(12)	N(2)—Ti(1)—N(1)	73.32(5)
Ti(1)—N(2)	2.3063(12)	N(3)—Ti(1)—N(1)	71.75(5)
Ti(1)—N(3)	2.2902(12)	N(4)—Ti(1)—N(1)	114.15(5)
Ti(1)—N(4)	2.2752(13)		

Hydrogen bonding in [Ti(NH$_3$)$_8$]Cl$_3 \cdot$ 6 NH$_3$

The Cl(1)-anion is coordinated by six ammine ligands of two different [Ti(NH$_3$)$_8$]$^{3+}$-cations and by three ammonia molecules of crystallization (Fig. S Abbildung). The Cl(2)-anion is an acceptor of six N−H···Cl-hydrogen bonds from two different [Ti(NH$_3$)$_8$]$^{3+}$-cations and from two ammonia molecules of crystallization (Fig. S Abbildung). These hydrogen bonds lead to a complex three-dimensional network interconnecting the [Ti(NH$_3$)$_8$]$^{3+}$-cations.
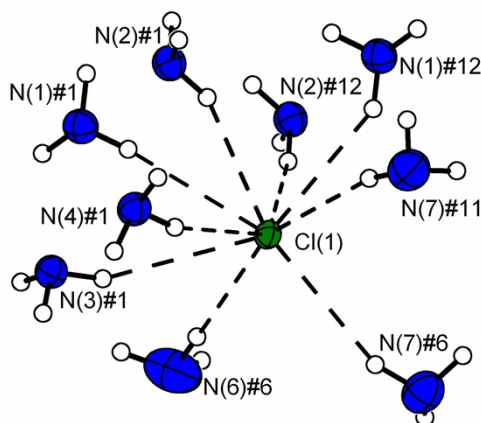
Fig. S1. The coordination sphere of the Cl(1)-anion of $[Ti(NH_3)_8]Cl_3 \cdot 6 NH_3$. The N−H⋯Cl-hydrogen bonds are drawn with dashed lines. Displacement ellipsoids are shown at the 70 % probability level at 123 K, H-atoms isotropic with arbitrary radii. Symmetry transformations for the generation of equivalent atoms: #1 −x, y, −z+1/2; #6 −x, −y, −z+1; #11 x, −y, z+1/2; #12 x, −y+1, z+1/2.
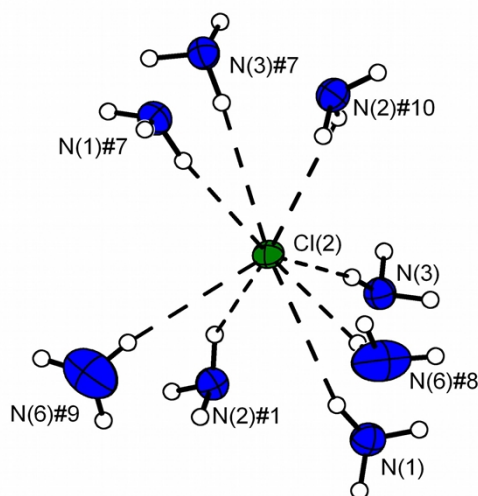

Fig.S 2. The coordination sphere of the Cl(2)-anion of $[Ti(NH_3)_8]Cl_3 \cdot 6 NH_3$. The N−H⋯Cl-hydrogen bonds are drawn with dashed lines. Displacement ellipsoids are shown at the 70 % probability level at 123 K, H-atoms isotropic with arbitrary radii. Symmetry transformations for the generation of equivalent atoms: #1 −x, y, −z+1/2; #7 −x−1, y, −z+1/2; #8 −x−1, y+1, −z+1/2; #9 x, y+1, z; #10 x−1, y, z.

To asses the hydrogen bonding further, its percentual shortening compared to the sum of the van-der-Waals-radii and the deviation from 180° may be calculated as indicators of hydrogen bond strength. Here, the H⋯Cl-distances are observed between 15 % (deviation of 9°) and 5 % shortening (deviation of 21°), with H⋯A-distances of 2.604(7) to 2.969(18) Å (Table S2). As the shortening is only minute, the hydrogen bonds

may be seen as weak ones. The N−H⋯N-hydrogen bonds show a H⋯N-distance of 2.191(19) to 2.49(2) Å, which yields shortenings of 20 % (deviation of 9°) to 9 % (deviation of 15°). Further details of the hydrogen bonding in $[Ti(NH_3)_8]Cl_3 \cdot 6\,NH_3$ are given in Table S2.

Table S3. Hydrogen bonds of $[Ti(NH_3)_8]Cl_3 \cdot 6\,NH_3$ and the percentual shortening compared to the sum of the respective van-der-Waals-radii and the deviation of the *DHA*-angle from 180° (*D* = Donor and *A* = acceptor). Symmetry transformations for the generation of equivalent atoms: #1 −*x*, *y*, −*z*+1/2; #2 *x*, −*y*+1, *z*−1/2; #3 *x*+1, *y*, *z*; #4 *x*, −*y*, *z*−1/2; #5 *x*, *y*−1, *z*; #6 −*x*, −*y*, −*z*+1; #7 −*x*−1, y, −*z*+1/2.

Atoms	*D*−H / Å	H⋯*A* / Å	*D*⋯*A* / Å	*DHA* / °	Deviation from 180° / °	Shortening /%
N(1)—H(1A)⋯Cl(1)#2	0.875(18)	2.606(17)	3.3724(14)	146.7(13)	33	13.13
N(1)—H(1B)⋯Cl(1)#1	0.822(17)	2.682(18)	3.4611(15)	158.7(15)	21	10.60
N(1)—H(1C)⋯Cl(2)	0.899(18)	2.842(18)	3.6938(14)	158.6(15)	21	5.27
N(2)—H(2C)⋯Cl(1)#2	0.902(18)	2.618(18)	3.4760(14)	159.1(14)	2	12.73
N(2)—H(2B)⋯Cl(2)#3	0.84(2)	2.82(2)	3.4854(14)	138.0(15)	42	6.00
N(2)—H(2A)⋯Cl(1)#1	0.832(18)	2.619(19)	3.3949(14)	155.6(15)	24	12.70
N(3)—H(3A)⋯Cl(2)	0.852(16)	2.549(17)	3.3922(14)	170.7(13)	9	15.03
N(3)—H(3B)⋯N(7)	0.896(18)	2.239(18)	3.1273(19)	170.9(14)	9	18.58
N(3)—H(3C)⋯Cl(1)#1	0.856(17)	2.689(17)	3.4836(14)	155.0(13)	25	10.37

N(4)—H(4A)···Cl(1)#1	0.850(17)	2.703(17)	3.4867(14)	153.9(14)	26	9.90
N(4)—H(4C)···N(5)#1	0.892(18)	2.191(19)	3.075(2)	170.8(15)	9	20.33
N(4)—H(4B)···Cl(1)#4	0.839(18)	2.969(18)	3.5676(13)	130.1(13)	50	1.03
N(6)—H(6B)···Cl(2)#5	0.79(2)	2.84(2)	3.620(2)	169.5(18)	11	5.33
N(6)—H(6A)···Cl(1)#6	0.91(2)	2.58(2)	3.4916(19)	175.9(18)	4	14.00
N(7)—H(7C)···Cl(1)#4	0.84(2)	2.76(2)	3.5846(17)	166.1(18)	14	8.00
N(7)—H(7B)···N(6)#7	0.84(2)	2.49(2)	3.310(2)	165.3(17)	15	9.45
N(7)—H(7A)···Cl(1)#6	0.856(19)	2.67(2)	3.4733(16)	155.9(16)	24	11.00

$[UF(NH_3)_8]Cl_3 \cdot 3.5\ NH_3$

Table S4. Selected atomic distances and angles of $[UF(NH_3)_8]Cl_3 \cdot 3.5\ NH_3$.

	Distance / Å		Angle / °
U(1)—F(1)	2.1174(11)	F(1)—U(1)—N(1)	77.54(5)
U(1)—N(1)	2.5599(17)	F(1)—U(1)—N(2)	76.93(5)
U(1)—N(2)	2.5670(17)	F(1)—U(1)—N(3)	135.96(5)
U(1)—N(3)	2.6302(16)	F(1)—U(1)—N(5)	139.17(5)
U(1)—N(4)	2.6106(16)	N(1)—U(1)—N(3)	68.47(5)

U(1)—N(5)	2.6094(17)	N(2)—U(1)—N(3)	69.01(5)
U(1)—N(6)	2.5966(19)	N(1)—U(1)—N(6)	138.37(6)
U(1)—N(7)	2.5590(16)	N(5)—U(1)—N(4)	73.56(5)
U(1)—N(8)	2.5875(17)		
U(1)···Cl(1)	5.0986(5)		
U(1)···Cl(2)	4.7222(5)		
U(1)···Cl(3)	5.1416(5)		

Hydrogen bonding in [UF(NH$_3$)$_8$]Cl$_3$ · 3.5 NH$_3$

The fluorine atom may be an acceptor of three bifurcated hydrogen bonds, all of them come from three ammine ligands of a single [UF(NH$_3$)$_8$]$^{3+}$-cation. The chlorine atom Cl(1) is coordinated by six N−H···Cl-hydrogen bonds from three [UF(NH$_3$)$_8$]$^{3+}$-cations (Fig. S Abbildung) and the chlorine atoms Cl(2) and Cl(3) are coordinated by seven N−H···Cl-hydrogen bonds from also three [UF(NH$_3$)$_8$]$^{3+}$-cations (Figs. S Abbildung, S Abbildung). These N−H···Cl-, N−H···F-, and N−H···N-hydrogen bonds lead to a complex three-dimensional network.
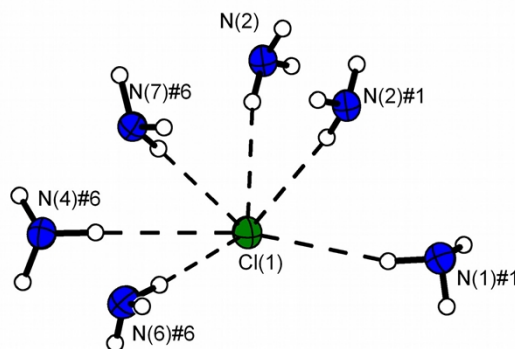

Fig. S3. The coordination sphere of the Cl(1)-atom in [UF(NH$_3$)$_8$]Cl$_3$ · 3.5 NH$_3$. Displacement ellipsoids are shown at the 70 % probability level at 123 K, H-atoms isotropic with arbitrary radii. Symmetry transformations for the generation of equivalent atoms: #1 −x+1/2, −y+1/2, −z+1; #6 x, −y, z+1/2.
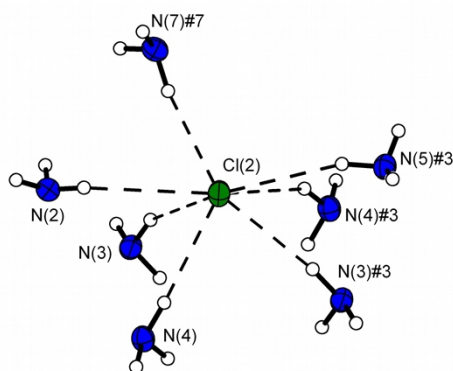
Fig. S4. The coordination sphere of the Cl(2)-atom in [UF(NH$_3$)$_8$]Cl$_3$ · 3.5 NH$_3$. Displacement ellipsoids are shown at the 70 % probability level at 123 K, H-atoms isotropic with arbitrary radii. Symmetry transformations for the generation of equivalent atoms: #3 −x+1/2, −y+1/2, −z; #7 −x+1/2, y+1/2, −z+1/2.

Fig. S5. The coordination sphere of the Cl(3)-atom in [UF(NH$_3$)$_8$]Cl$_3$ · 3.5 NH$_3$. Displacement ellipsoids are shown at the 70 % probability level at 123 K, H-atoms isotropic with arbitrary radii. Symmetry transformations for the generation of equivalent atoms: #1 −x, y, −z+1; #6 x, −y, −z+1/2.
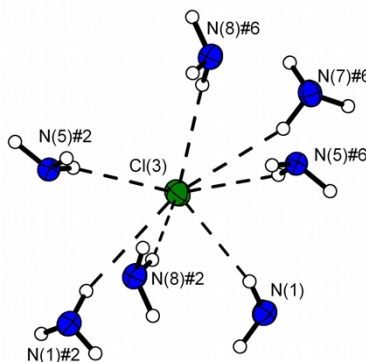
In the assessment of the hydrogen bonds, the nitrogen atoms N(3), N(4), N(7) and N(8) are excluded as their hydrogen atoms were localized and refined using a riding model. Also, the hydrogen bonds to the ammonia molecules of crystallization will not be discussed, as their hydrogen atoms could not be localized. For the other N−H···Cl-hydrogen bonds a maximum shortening of 17 % (deviation: 17°) is observed for N(1)—H(1A)···Cl(3), whereas for all others the mean shortening is only 12 % (deviation: 18°).

Table S5. Hydrogen bonds of [UF(NH$_3$)$_8$]Cl$_3$ · 3.5 NH$_3$ and the deviation of the *DHA*-angle from 180 ° and its percentual shortening. Symmetry transformations for the generation of equivalent atoms: #1 −x+1/2, −y+1/2, −z+1; #2 −x, y, −z+1/2; #3 −x+1/2, −y+1/2, −z; #4 x, −y, z−1/2.

Atoms	D−H	H⋯A	D⋯A	DHA	Deviation	Shortening
	/ Å	/ Å	/ Å	/ °	from 180° / °	/ %
N(1)—H(1A)⋯Cl(3)	0.83(2)	2.48(2)	3.2798(18)	163(2)	17.33	17
N(1)—H(1B)⋯Cl(1)#1	0.88(3)	2.58(3)	3.4286(19)	161(2)	14.00	19
N(1)—H(1C)⋯C(l3)#2	0.85(2)	2.73(2)	3.4782(19)	147(2)	9.00	33
N(2)—H(2B)⋯Cl(1)#1	0.79(2)	2.64(2)	3.4247(19)	173(3)	12.00	7
N(2)—H(2A)⋯Cl(1)	0.86(2)	2.56(2)	3.4117(19)	169(2)	14.67	11
N(2)—H(2C)⋯Cl(2)	0.79(3)	2.79(3)	3.5547(19)	164(2)	7.00	16
N(5)—H(5C)⋯Cl(2)#3	0.89(3)	2.60(3)	3.4460(18)	160(2)	13.33	20
N(5)—H(5A)⋯Cl(3)#2	0.83(2)	2.59(2)	3.3595(18)	156(3)	13.67	24
N(5)—H(5B)⋯Cl(3)#4	0.80(3)	2.82(3)	3.571(2)	159(2)	6.00	21
N(6)—H(6A)⋯N(9)#1	0.78(3)	2.28(3)	3.052(3)	172(3)	17.09	8
N(6)—H(6C)⋯Cl(1)#4	0.80(3)	2.61(3)	3.391(2)	165(3)	13.00	15

Optimized cartesian coordinates of the studied systems in atomic units (DFT-PBE0/def2-TZVPP)

[Ti(NH$_3$)$_8$]$^{3+}$

```
  0.00002056904710    -0.00000627977006     0.00007426128260     ti
  3.35130425862700    -1.41352021994364     2.37853759536351     n
  5.00798017689957    -0.49143837423385     2.07580298467417     h
  3.01593860289326    -1.22149946419828     4.26015892196271     h
  3.76542285375074    -3.27265135641035     2.13760660834160     h
  1.41348720238153     3.35120918603331     2.37927316404701     n
  3.27257431495097     3.76592432743634     2.13871255564315     h
  0.49107770687641     5.00772735342892     2.07656432850135     h
  1.22143734709679     3.01560793889208     4.26085728373500     h
 -1.41314855015817    -3.35120214268558     2.37917018226642     n
 -0.49088547686286    -5.00794041630807     2.07712672345180     h
 -3.27227563721585    -3.76584764295918     2.13886980718753     h
 -1.22117190545462    -3.01531464846648     4.26072579765514     h
 -3.35161183153154     1.41365408798875     2.37896490719336     n
 -3.01579285164609     1.22154368641312     4.26499700105818     h
 -3.76593955491117     3.27283358771259     2.13848122549923     h
 -5.00834673663407     0.49148250416251     2.07666822208857     h
  3.35153465496908     1.41397449232109    -2.37846480384108     n
  5.00794746765987     0.49147659326310    -2.07551371497047     h
  3.01623703029008     1.22167411095222    -4.26007746705155     h
  3.76633922838595     3.27306317376870    -2.13805531397072     h
  1.41392731094082    -3.35146163953800    -2.37920463301903     n
  3.27296825023437    -3.76688553519424    -2.13917407485513     h
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 0.49108717518720      -5.00770782568116      -2.07627541234363      h
 1.22157908257778      -3.01590584829318      -4.26077654643989      h
-1.41362314959632       3.35143978765775      -2.37907823897077      n
-0.49092472355806       5.00790226447181      -2.07681096043689      h
-3.27270247147563       3.76679980338158      -2.13930210310340      h
-1.22136873186155       3.01562892387465      -4.26062658689569      h
-3.35183955257173      -1.41410983518264      -2.37891085763866      n
-3.01604933026164      -1.22169618296572      -4.26042963206282      h
-3.76687779683751      -3.27324638759676      -2.13898141914312      h
-5.00830493219167      -0.49150802233122      -2.07640980520850      h
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[Ti(H$_2$O)$_6$]$^{3+}$

```
-0.00001007492612       0.00106082762511       0.00061721821978      ti
 0.14479986452889      -3.16051911165522      -2.17974265035464      o
 2.81147883963679      -1.45337828219923       2.17972816239610      o
-2.66230421966160      -1.70465160232380       2.18691278559174      o
-2.80991923145664       1.45229313332810      -2.18142367429508      o
 2.66993328064615       1.70066646648473      -2.18024655220360      o
-0.14157670254214       3.16250111615047       2.18024994016657      o
 4.03446581607121      -2.70452012687186       1.65425051632335      h
 4.34837105019847       2.17769155539364      -1.63922928364903      h
 0.88155965168083      -3.27848228217622      -3.84688033579731      h
-3.27741976964122       0.87193458745266      -3.84900113467206      h
-2.38428624638769      -2.40157530421430       3.85216063676703      h
 0.28304077723013       4.85659715460082       1.64431101464696      h
 3.29396324431038      -0.87295838101358       3.84305626405509      h
 2.40660088691655       2.40684484519866      -3.84411377982544      h
-0.32564953003652      -4.84852453240394      -1.66342538922315      h
-4.04266768352704       2.69754875371222      -1.66467040713003      h
-4.34535045820794      -2.18462168083045       1.66297487623348      h
-0.88502949483252       3.28209286374226       3.84447179275036      h
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