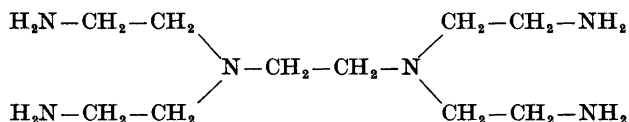# The Crystal Structure of N,N,N′,N′-Tetrakis(2-aminoethyl) ethylenediamine Pentahydrochloride

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The structure of N,N,N′,N′-tetrakis(2-aminoethyl)ethylenediamine pentahydrochloride has been determined by three-dimensional Patterson and Fourier methods. Least squares analysis of geometric parameters and of anisotropic temperature factors has been carried out. Hydrogen positions have not been refined. Atomic coordinates, thermal parameters and bond lengths are reported with their standard deviations.

The hexamine N,N,N′,N′-tetrakis(2-aminoethyl)ethylenediamine penta-hydrochloride, usually called penten, was prepared by Gauss, Moser and Schwarzenbach[1] in connection with investigations of metal complexes with polyamines.[2] The molecule has the constitution:

$$\begin{array}{c}
H_2N-CH_2-CH_2 \\\\ \qquad\qquad\qquad\quad N-CH_2-CH_2-N \\\\ H_2N-CH_2-CH_2
\end{array}\quad
\begin{array}{c}
CH_2-CH_2-NH_2 \\\\ \\\\ CH_2-CH_2-NH_2
\end{array}$$

It contains six basic nitrogen groups which may act as ligands in an octahedral complex with metal cations. Several hexadentate chelating agents are known, but because penten has a rather simple constitution and because it contains six similar groups which may coordinate to the same metal cation we found it worthwhile to determine the crystal structure of both penten and some of the metal complexes. This paper presents the results of a detailed structure analysis of the non-complexed penten molecule.

The hexamine itself is a colourless, oily liquid at room temperature. The pentahydrochloride is a white solid which can be recrystallized from a mixture of ethanol and hydrochloric acid as well developed needle shaped crystals. Recrystallization from ethanol without hydrochloric acid gives the tetra-hydrochloride.

In a previous note[3] some preliminary results for penten, 5HCl were reported.

EXPERIMENTAL

The crystals were kindly supplied by Professor G. Schwarzenbach, Zürich. Unit cell dimensions were determined from precession photographs recorded with $CuK\alpha$ radiations. For intensity measurements two crystals were used both with cross section about 0.08×0.1 mm. The crystals were rotated around [101] and [201], respectively. Integrated equiinclination Weissenberg photographs were taken using $CuK\alpha$ radiation and multiple film techniques. Integrated precession photographs were taken using $CuK\alpha$ radiation and multiple time exposure techniques. All intensities were measured photometrically. The Lorentz and polarisation corrections were made by digital computation. The two sets of Weissenberg reflexions overlap to some extent thus permitting a scaling between them. The reflexions from the precession photographs served as an extra check on the scaling and yielded also some reflexions which were not accessible from the Weissenberg photographs. 2450 independent reflexions were measured. No corrections for absorption and extinction were made. The linear absorption coefficient is 63.8 cm^{-1} for $CuK\alpha$ radiation.

STRUCTURE DETERMINATION

The crystals are monoclinic. The unit cell has the following dimensions:

$$a = 10.19 \text{ Å}, b = 23.18 \text{ Å}, c = 9.96 \text{ Å}, \beta = 120.0°.$$

The density estimated by the flotation method is 1.34 $g \cdot ml^{-1}$. The calculated density corresponding to four formula units in the unit cell is 1.35 $g \cdot ml^{-1}$. The following reflexions were found absent:

$$h0l \text{ for } l = 2n + 1, 0k0 \text{ for } k = 2n + 1.$$

Consequently the space group is $P2_1/c$ (No. 14, C_{2h}^5).

The three-dimensional Patterson function of the structure was calculated. It was not possible to determine the positions of all the chlorine atoms from this Patterson function. The Harker section $(2x, \frac{1}{2}, \frac{1}{2}+2z)$ and Harker line $(0, \frac{1}{2}+2y, \frac{1}{2})$ of the sharpened Patterson function were calculated using $\exp(12 \cdot \sin^2\theta/\lambda^2) \cdot F^2$ as coefficients. It was now possible to determine the five chlorine positions from the sharpened sections. On the basis of the coordinates of the chlorine atoms the structure factors were calculated using a temperature factor of 3.0 $Å^2$. The conventional R-value was 0.41. From this calculation the signs of about 1600 structure factors were determined. These were used in a three-dimensional Fourier synthesis which gave the positions of the remaining six nitrogen and ten carbon atoms. A structure factor calculation on the basis of the coordinates of all the atoms and using an overall isotropic temperature factor of 3.0 $Å^2$ gave an R-value of 0.22. All Fourier and structure factor calculations were made on the Danish computer GIER using programs written by Lauesen [4] and Danielsen.[5]

The atomic parameters were first refined by a least-squares method employing the diagonal approximation. The program was written by Danielsen [6] for the computer GIER. The parameters refined were the atomic coordinates and the individual isotropic temperature factors. Only observed reflexions were included in the calculations. The strong reflexions 020, 141, 221, and 242 were apparently heavily affected by extinction and were not included in the least-squares refinement. Atomic scattering factors were calculated using an approximation suggested by Bassi:[7]

$$f_n = Z_n - s^2/(a_n + b_n\ s + c_n\ s^2 + d_n\ s^3 + e_n\ s^4), \text{ where } s = \sin\theta/\lambda.$$

The coefficients were calculated using tabulated f_n values from *Intern. Tables*, Vol. III, p. 202—207. The numerical values are given in Table 1. After eight cycles of refinement the R-value was 0.12.

Table 1. Coefficients employed in structure factor calculations.

	Cl	N	C
Z	17.00	7.00	6.00
a	5.300624×10^{-3}	1.094839×10^{-2}	9.566876×10^{-3}
b	3.104569×10^{-3}	6.028510×10^{-3}	6.580848×10^{-3}
c	2.022904×10^{-2}	8.458399×10^{-2}	9.869528×10^{-2}
d	1.906431×10^{-1}	1.587858×10^{-1}	2.463541×10^{-1}
e	-1.599024×10^{-1}	-8.817067×10^{-2}	-1.662073×10^{-1}

Further refinement was achieved on an IBM 7090 computer using a full-matrix least-squares program written by Gantzel, Sparks, Long and True-blood.[8] The parameters refined were atomic coordinates and individual aniso-tropic temperature factors. At this stage the twenty hydrogen atoms at the carbon atoms were included in the calculations, but neither their atomic position parameters nor their isotropic temperature factors were varied. The hydrogen atom parameters were computed from the positions of the carbon atoms, assuming regular tetrahedral bond angles and a C—H distance of 1.0 Å. The coordinates are given in Table 2. An overall isotropic temperature factor of 5.0 Å² was used for the hydrogen atoms. The refinement process was continued

Table 2. Calculated hydrogen positions in fractions of cell edges.

Atom	x/a	y/b	z/c
$H_1(a)$	0.4142	0.7086	0.2494
$H_1(b)$	0.2400	0.7016	0.1089
$H_2(a)$	0.3367	0.6930	0.4346
$H_2(b)$	0.2423	0.7468	0.3226
$H_3(a)$	0.4936	0.6245	0.1286
$H_3(b)$	0.3206	0.6389	-0.0057
$H_4(a)$	0.4222	0.5261	0.1186
$H_4(b)$	0.4103	0.5489	-0.0418
$H_5(a)$	0.4791	0.5575	0.3440
$H_5(b)$	0.4053	0.5951	0.4279
$H_6(a)$	0.5830	0.6682	0.4925
$H_6(b)$	0.6399	0.6424	0.3782
$H_7(a)$	0.1068	0.7218	0.4518
$H_7(b)$	-0.0293	0.6747	0.3705
$H_8(a)$	0.2785	0.6483	0.5844
$H_8(b)$	0.1422	0.6491	0.6248
$H_9(a)$	0.0191	0.7075	0.0653
$H_9(b)$	-0.0618	0.7294	0.1618
$H_{10}(a)$	-0.1485	0.6284	0.1439
$H_{10}(b)$	-0.1019	0.6202	0.0107

until the shifts obtained in both the positional and thermal parameters were considerably less than the corresponding standard deviations. The final R-value was 0.105.

CRYSTAL DATA

Crystal system: monoclinic.
Unit cell from precession photographs using $CuK\alpha$ radiation ($\lambda = 1.542$ Å):

$$a = 10.19 \text{ Å}, b = 23.18 \text{ Å}, c = 9.96 \text{ Å}, \beta = 120.0°.$$

Space group from extinctions: $P2_1/c$ (No. 14, C_{2h}^5).
Calculated density (four formula units in the unit cell): 1.35 g·ml⁻¹.
Observed density: 1.34 g·ml⁻¹.
Absorption coefficient for $CuK\alpha$ radiation: 63.8 cm⁻¹.
Residual factor $R = \sum ||F_o| - k|F_c||/\sum|F_o|$. Final R-value: 0.105.
The final atomic coordinates and their standard deviations are listed in Table 3. The thermal parameters and their standard deviations are listed in Table 4.

Interatomic and intermolecular distances were calculated using a program written by Danielsen and Nyborg.[9]

Table 5 gives interatomic distances and bond angles with their standard deviations and in Table 6 are listed some van der Waals' distances with their standard deviations.

The calculated and observed structure factors are not printed. The author will gladly send copies of the table of these values to other crystallographers on request.

Table 3. Final atomic coordinates in fractions of cell edges and their estimated standard deviations. The standard deviations are multiplied by 10^5.

Atom	x/a	$\sigma x/a$	y/b	$\sigma y/b$	z/c	$\sigma z/c$
Cl_1	0.21481	24	0.04268	8	0.18051	23
Cl_2	0.13672	23	0.52083	8	0.21252	22
Cl_3	0.36922	27	0.23735	9	0.32927	26
Cl_4	0.02076	25	0.84882	9	0.30452	25
Cl_5	0.48270	26	0.42540	9	0.25632	26
N_1	0.34378	71	0.62362	23	0.21004	70
N_2	0.11352	72	0.67441	24	0.28381	70
N_3	0.20256	79	0.53325	26	−0.06141	75
N_4	0.71295	78	0.59375	29	0.57835	76
N_5	0.13393	87	0.57995	28	0.49356	85
N_6	−0.27950	80	0.67639	29	−0.05223	79
C_1	0.31642	94	0.68770	30	0.21555	99
C_2	0.25736	87	0.70405	31	0.32458	92
C_3	0.38542	88	0.61282	32	0.08526	87
C_4	0.36424	95	0.55218	33	0.02720	91
C_5	0.45517	88	0.59765	30	0.36264	88
C_6	0.60435	85	0.63157	29	0.45142	82
C_7	0.08118	108	0.68094	33	0.41123	99
C_8	0.16675	111	0.64083	36	0.54063	101
C_9	−0.01502	94	0.69560	32	0.13934	93
C_{10}	−0.13483	91	0.64887	32	0.06342	100

Table 4. Thermal parameters. The estimated standard deviations (in parentheses) are multiplied by 10^5. The temperature factor for an atom is of the form $\exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})\}$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl_1	0.01096 (34)	0.00167 (3)	0.00958 (31)	0.00020 (16)	0.01155 (61)	0.00094 (15)
Cl_2	0.01027 (34)	0.00164 (3)	0.00911 (31)	-0.00167 (16)	0.01074 (61)	-0.00118 (15)
Cl_3	0.01420 (41)	0.00176 (4)	0.01298 (38)	0.00212 (19)	0.01681 (74)	0.00158 (18)
Cl_4	0.00872 (34)	0.00178 (4)	0.00915 (34)	0.00013 (17)	0.00458 (64)	-0.00009 (17)
Cl_5	0.01076 (37)	0.00203 (4)	0.01104 (35)	-0.00104 (18)	0.01040 (68)	0.00084 (18)
N_1	0.00857 (103)	0.00130 (10)	0.00762 (94)	-0.00120 (49)	0.00916 (188)	-0.00029 (47)
N_2	0.00828 (105)	0.00148 (10)	0.00751 (99)	0.00030 (53)	0.00776 (193)	-0.00050 (52)
N_3	0.01209 (120)	0.00172 (12)	0.00919 (109)	0.00110 (57)	0.01216 (213)	0.00083 (53)
N_4	0.00791 (109)	0.00198 (13)	0.00650 (105)	0.00036 (60)	0.00105 (201)	0.00114 (58)
N_5	0.01512 (128)	0.00169 (13)	0.01225 (115)	0.00041 (63)	0.01642 (222)	0.00001 (59)
N_6	0.00996 (119)	0.00195 (13)	0.00913 (111)	0.00061 (63)	0.00608 (214)	0.00019 (61)
C_1	0.01132 (135)	0.00135 (13)	0.01322 (138)	-0.00031 (63)	0.01463 (254)	0.00040 (63)
C_2	0.00733 (120)	0.00160 (13)	0.01026 (131)	-0.00125 (63)	0.00785 (238)	-0.00229 (65)
C_3	0.00874 (127)	0.00177 (14)	0.00829 (119)	-0.00183 (62)	0.01047 (233)	-0.00070 (60)
C_4	0.01063 (134)	0.00187 (15)	0.00757 (117)	-0.00026 (69)	0.00963 (235)	-0.00042 (63)
C_5	0.00738 (123)	0.00142 (13)	0.00732 (123)	-0.00076 (61)	0.00327 (234)	0.00009 (59)
C_6	0.00561 (120)	0.00148 (13)	0.00559 (114)	0.00048 (59)	0.00164 (224)	-0.00108 (60)
C_7	0.01744 (170)	0.00153 (14)	0.01235 (136)	0.00068 (75)	0.02011 (286)	-0.00058 (67)
C_8	0.01548 (172)	0.00216 (18)	0.00982 (142)	0.00026 (86)	0.01337 (293)	0.00141 (77)
C_9	0.00958 (140)	0.00159 (14)	0.00835 (131)	0.00032 (68)	0.00631 (256)	-0.00103 (66)
C_{10}	0.00713 (136)	0.00149 (13)	0.01159 (143)	0.00040 (63)	0.00612 (260)	-0.00046 (67)

Table 5. Interatomic distances and bond angles with their standard deviations.

Bond lengths in Å

N_1-C_1	1.517	0.009
N_1-C_3	1.521	0.013
N_1-C_5	1.495	0.008
N_2-C_2	1.480	0.011
N_2-C_7	1.470	0.015
N_2-C_9	1.464	0.008
N_3-C_4	1.494	0.011
N_4-C_6	1.481	0.009
N_5-C_8	1.472	0.011
N_6-C_{10}	1.486	0.009
C_1-C_2	1.529	0.016
C_3-C_4	1.494	0.011
C_5-C_6	1.538	0.010
C_7-C_8	1.470	0.011
C_9-C_{10}	1.521	0.011

Bond angles in degrees

$C_1-N_1-C_3$	108.8	0.7
$C_1-N_1-C_5$	114.7	0.6
$C_3-N_1-C_5$	112.6	0.7
$C_2-N_2-C_7$	109.5	0.6
$C_2-N_2-C_9$	113.0	0.7
$C_7-N_2-C_9$	109.7	0.7
$N_1-C_1-C_2$	114.4	0.8
$N_2-C_2-C_1$	112.2	0.6
$N_1-C_3-C_4$	115.2	0.8
$N_3-C_4-C_3$	114.1	0.7
$N_1-C_5-C_6$	114.1	0.6
$N_4-C_6-C_5$	106.9	0.6
$N_2-C_7-C_8$	113.6	0.9
$N_5-C_8-C_7$	112.7	0.6
$N_2-C_9-C_{10}$	110.6	0.6
$N_6-C_{10}-C_9$	108.6	0.6

Table 6. Van der Waals' distances with their standard deviations.

Bond	Relative positions of second atom*			Bond lengths in Å	
Cl_1-N_3	$x,$	$0.5-y,$	$0.5+z$	3.169	0.008
Cl_1-N_4	$1.0-x,$	$-0.5+y,$	$0.5-z$	3.239	0.009
Cl_1-N_5	$-x,$	$-0.5+y,$	$0.5-z$	3.197	0.008
Cl_1-N_5	$x,$	$0.5-y,$	$-0.5+z$	3.270	0.007
Cl_2-N_1	$x,$	$y,$	z	3.191	0.007
Cl_2-N_3	$x,$	$y,$	z	3.132	0.009
Cl_2-N_3	$-x,$	$1.0-y,$	$-z$	3.254	0.007
Cl_2-N_4	$1.0-x,$	$1.0-y,$	$1.0-z$	3.248	0.007
Cl_2-N_5	$x,$	$y,$	z	3.129	0.009
Cl_3-N_6	$-x,$	$1.0-y,$	$-z$	3.150	0.008
Cl_3-N_6	$-x,$	$-0.5+y,$	$0.5-z$	3.130	0.010
Cl_4-N_3	$x,$	$1.5-y,$	$0.5+z$	3.196	0.006
Cl_4-N_4	$-1.0+x,$	$1.5-y,$	$-0.5+z$	3.101	0.006
Cl_5-N_4	$1.0-x,$	$1.0-y,$	$1.0-z$	3.188	0.010
Cl_5-N_6	$-x,$	$1.0-y,$	$-z$	3.127	0.007
Cl_1-C_6	$1.0-x,$	$-0.5+y,$	$0.5-z$	3.434	0.010
Cl_2-C_5	$x,$	$y,$	z	3.329	0.008
Cl_4-C_3	$x,$	$1.5-y,$	$0.5+z$	3.468	0.007
Cl_5-C_8	$1.0-x,$	$1.0-y,$	$1.0-z$	3.462	0.009
Cl_1-Cl_2	$-x,$	$-0.5+y,$	$0.5-z$	4.247	0.004
Cl_1-Cl_5	$1.0-x,$	$-0.5+y,$	$0.5-z$	3.918	0.003
Cl_2-Cl_4	$-x,$	$-0.5+y,$	$0.5-z$	4.270	0.003
Cl_2-Cl_5	$x,$	$y,$	z	3.997	0.003
Cl_3-Cl_4	$-x,$	$-0.5+y,$	$0.5-z$	4.353	0.003

* This is the transformation relating each "second atom" to the corresponding atom in Table 3.

DISCUSSION

Fig. 1 shows a projection of a penten molecule along [010].

From Table 5 it is seen that the C—C distances are between 1.470 and 1.538 Å. The average of all C—C distances is 1.510 Å. The average of all N—C distances is 1.488 Å. However, the average of the bond distances N_1(tert)—C, N_2(tert)—C and N(prim)—C are 1.511, 1.471, and 1.483 Å, respectively.

Interatomic distances between 2.0 and 4.5 Å were calculated to analyse the packing of the molecules. Some of these distances are listed in Table 6. Fig. 2 shows a projection of four units along [010]. The distances between each primary nitrogen atom and the nearest Cl⁻ neighbours are between 3.10 and 3.27 Å. The distance between N_1(tert) and the nearest Cl⁻ neighbour (N_1(tert)—Cl_2) is 3.19 Å while the distance between N_2(tert) and the nearest Cl⁻ neighbour (N_2(tert)—Cl_2) is 3.66 Å. A difference Fourier map shows a small peak which may be a hydrogen atom about 1.2 Å from N_1(tert) and in the direction N_1(tert)—Cl_2. The calculated bond angles C_1—N_1(tert)—H, C_3—N_1(tert)—H, and C_5—N_1(tert)—H are about 97°, 112°, and 111°, respectively. Perhaps we can conclude that the crystal is to be described as built from penten H_5^{5+} ions and Cl⁻ ions with four primary nitrogens and only one tertiary nitrogen protonised.

The primary aim of this work is a comparison between coordinated and free penten molecules. Structure analysis of some cobalt complexes with penten are in progress.[3] From the present structure determination of penten, 5HCl it is obvious that the penten molecule must be considerably distorted by coordination to the metal ion.
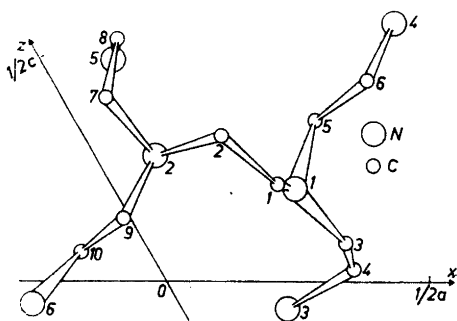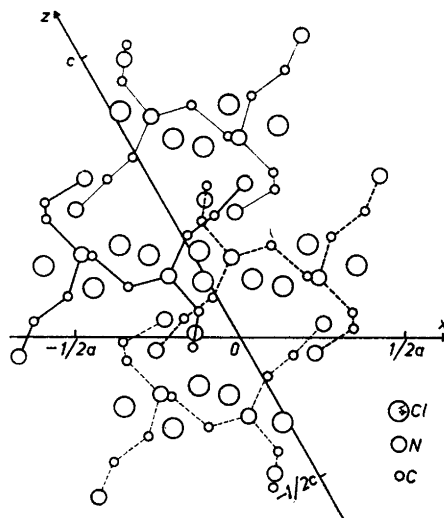

Fig. 1. Projection of a penten molecule along [010].

Fig. 2. Projection of four units along [010].

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