N(2)	0.2244 (1)	0.3313 (2)	0.1019 (2)	2.81 (6)
N(3)	0.1127 (1)	0.5500 (2)	0.0538 (2)	2.52 (5)
N(4)	0.0931 (1)	0.6367 (2)	−0.0190 (2)	3.35 (6)
C(1)	0.1004 (1)	0.2700 (2)	0.2458 (2)	4.08 (9)
C(2)	0.0732 (1)	0.3313 (2)	0.1573 (2)	3.58 (8)
C(3)	0.1178 (1)	0.4311 (2)	0.0152 (2)	2.53 (6)
C(4)	0.1907 (1)	0.4036 (2)	0.0075 (2)	2.47 (6)
C(5)	0.1808 (1)	0.3112 (2)	0.1487 (2)	2.74 (7)
C(6)	0.0610 (1)	0.4078 (2)	−0.0875 (2)	3.32 (8)
C(7)	0.1349 (1)	0.5899 (2)	0.1567 (2)	3.31 (8)
C(8)	0.1283 (1)	0.7074 (2)	0.1503 (2)	4.23 (9)
C(9)	0.1029 (1)	0.7314 (2)	0.0420 (2)	4.13 (9)
C(10)	0.2315 (1)	0.5136 (2)	0.0082 (2)	3.22 (7)
C(11)	0.3031 (1)	0.4876 (2)	0.0202 (2)	2.99 (7)
C(12)	0.3481 (1)	0.4701 (2)	0.1221 (2)	4.02 (9)
C(13)	0.4138 (1)	0.4436 (3)	0.1354 (3)	5.1 (1)
C(14)	0.4351 (1)	0.4339 (3)	0.0468 (3)	5.0 (1)
C(15)	0.3914 (1)	0.4526 (2)	−0.0546 (3)	4.6 (1)
C(16)	0.3252 (1)	0.4793 (2)	−0.0679 (2)	3.77 (8)

Table 2. *Selected geometric parameters* (Å, °)

S—C(1)	1.759 (3)	S—C(5)	1.741 (2)
O—C(4)	1.400 (3)	N(1)—C(2)	1.386 (4)
N(1)—C(3)	1.447 (3)	N(1)—C(5)	1.368 (3)
N(2)—C(4)	1.473 (3)	N(2)—C(5)	1.283 (3)
N(3)—N(4)	1.353 (3)	N(3)—C(3)	1.480 (3)
N(3)—C(7)	1.357 (3)	N(4)—C(9)	1.331 (3)
C(1)—C(2)	1.322 (4)	C(3)—C(4)	1.613 (4)
C(3)—C(6)	1.515 (3)	C(4)—C(10)	1.536 (3)
C(7)—C(8)	1.365 (4)	C(8)—C(9)	1.373 (4)
C(10)—C(11)	1.507 (4)	C(11)—C(12)	1.384 (4)
C(11)—C(16)	1.379 (4)	C(12)—C(13)	1.383 (4)
C(13)—C(14)	1.376 (5)	C(14)—C(15)	1.371 (5)
C(15)—C(16)	1.394 (4)		
C(1)—S—C(5)	90.1 (1)	C(2)—N(1)—C(3)	134.1 (2)
C(2)—N(1)—C(5)	115.8 (2)	C(3)—N(1)—C(5)	109.2 (2)
C(4)—N(2)—C(5)	105.8 (2)	N(4)—N(3)—C(3)	119.1 (2)
N(4)—N(3)—C(7)	112.2 (2)	C(3)—N(3)—C(7)	127.9 (2)
N(3)—N(4)—C(9)	103.5 (2)	S—C(1)—C(2)	112.8 (2)
N(1)—C(2)—C(1)	112.0 (2)	N(1)—C(3)—N(3)	106.5 (2)
N(1)—C(3)—C(4)	99.6 (2)	N(1)—C(3)—C(6)	113.1 (2)
N(3)—C(3)—C(4)	112.3 (2)	N(3)—C(3)—C(6)	110.1 (2)
C(4)—C(3)—C(6)	114.6 (2)	O—C(4)—N(2)	110.8 (2)
O—C(4)—C(3)	106.9 (2)	O—C(4)—C(10)	110.2 (2)
N(2)—C(4)—C(3)	106.1 (2)	N(2)—C(4)—C(10)	110.0 (2)
C(3)—C(4)—C(10)	112.7 (2)	S—C(5)—N(1)	109.3 (2)
S—C(5)—N(2)	132.4 (2)	N(1)—C(5)—N(2)	118.2 (2)
N(3)—C(7)—C(8)	106.3 (2)	C(7)—C(8)—C(9)	105.2 (3)
N(4)—C(9)—C(8)	112.8 (3)	C(4)—C(10)—C(11)	112.5 (2)
C(10)—C(11)—C(12)	119.5 (2)	C(10)—C(11)—C(16)	121.8 (2)
C(12)—C(11)—C(16)	118.7 (2)	C(11)—C(12)—C(13)	120.7 (3)
C(12)—C(13)—C(14)	120.1 (3)	C(13)—C(14)—C(15)	119.9 (3)
C(14)—C(15)—C(16)	119.9 (3)	C(11)—C(16)—C(15)	120.6 (3)

Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods. H atoms were included as fixed contributors at positions found in difference syntheses and refined with an overall isotropic temperature factor which converged to 0.064 (2) Å^2. Refinement was by full-matrix least-squares techniques. Most of the calculations were performed at the Weizmann Institute of Science, Israel. Programs used were: *SHELXS*86 (Sheldrick, 1985), *SHELX*76 (Sheldrick, 1976) and *ORTEP* (Johnson, 1965).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: LI1084). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Molecular Co-Crystals of Carboxylic Acids. 18.† 1:1 Adduct of 1,3,5-Trinitrobenzene with 4-Aminobenzoic Acid

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Abstract

The structure of the title compound, $C_6H_3N_3O_6.C_7H_7NO_2$, one of three co-crystalline products formed in the reaction of 2,4,6-trinitrobenzoic acid with 4-aminobenzoic acid, comprises a 1:1 adduct of 1,3,5-trinitrobenzene (TNB) and 4-aminobenzoic acid (PABA), in which both molecules are involved in homomolecular hydrogen bonding. The PABA molecule forms an eight-membered cyclic dimer with another symmetry-generated acid molecule [O···O, 2.65 (1) Å]. The TNB molecule is also involved in possible C—H···O interactions. The layered structure and red col-

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† Part 17: Lynch, Smith, Byriel, Kennard, Whittaker & Hanna (1994).

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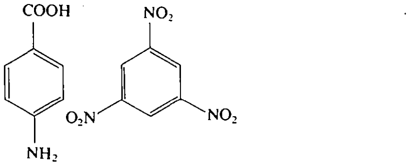
oration of the crystals indicate possible charge-transfer interactions.

Comment

4-Aminobenzoic acid (PABA) is one of the most versatile acids for co-crystal formation as it has the potential for extended linear hydrogen bonding through both carboxylic acid and amino groups. Such behaviour has been observed in the 1:1 structures of PABA with 3,5-dinitrobenzoic acid (DNBA) (Etter & Frankenbach, 1989), (2-carboxyphenoxy)acetic acid (Byriel, Lynch, Smith & Kennard, 1991) and the structure proposed for the 1:1 adduct with 4-chloro-3,5-dinitrobenzoic acid (Etter, Frankenbach & Bernstein, 1989). In these examples adduct preparation is also possible *via* solid-state reaction, simply by grinding the two acids together. Other structures that have utilized the unique interactive properties of PABA are the 1:1 co-crystals with 4-nitropyridine *N*-oxide (Lechat, 1984), 1,3-dimethyl-2-imidazolidinone (Ueda, Onishi & Nagu, 1986), 2,4,6-trinitrobenzoic acid (Lynch, Smith, Byriel & Kennard, 1992*a*), (2,4-dichlorophenoxy)acetic acid (Lynch, Smith, Byriel & Kennard, 1992*b*) and pyrazine-2,3-dicarboxylic acid (Lynch, Smith, Byriel, Kennard & Whittaker, 1994). A number of chemically characterized co-crystals of PABA whose X-ray structures have not been reported include those with 3,5-dinitrosalicylic acid (DNSA) (Issa, Hindaway, Issa & Nassar, 1980; Etter, Frankenbach & Adsmond, 1990), 4-methyl-3,5-dinitrobenzoic acid (Etter *et al.*, 1990), 3,5-dinitrobenzamide (Etter *et al.*, 1990), 4-nitrobenzoic acid (4-NBA) (Etter, 1991) and 1,3,5-trinitrobenzene (TNB) (Stecher, 1968). The structure of the 1,3,5-trinitrobenzene–4-aminobenzoic acid co-crystal, [(TNB)(PABA)] (1), is reported here.



(1)

The title compound comprises a 1:1 adduct of 1,3,5-trinitrobenzene (molecule *A*) and 4-aminobenzoic acid (molecule *B*), which are both involved in homomolecular hydrogen bonding. The PABA molecule forms an eight-membered cyclic dimer with another symmetry-generated PABA molecule [O(10*B*)···O(11*B*)($1-x$, y, $\frac{1}{2}-z$) 2.65 (1) Å; graph set $R_2^2(8)$] (Fig. 2). This compares with 2.641 and 2.612 Å for the two independent molecules in the parent acid (Lai & Marsh, 1967). The TNB molecule is also involved in possible C—H···O interactions [C(2*A*)···O(31*A*)($-x$, y, $\frac{1}{2}-z$) 3.39 (1), C(4*A*)···O(32*A*)($-x$, $-y$, $-z$) 3.28 (1), C(6*A*)···O(11*A*) ($\frac{1}{2}-x$, $\frac{1}{2}-y$, $-z$), 3.27 (1) Å]. In the two independent parent TNB molecules distances of *ca* 3.30 Å are also reported (Choi & Abel, 1972). Both the PABA and TNB molecules are essentially planar with the rings of each stacking in the **b** direction. The planes of the rings are parallel but with no significant ring overlap, although at two separate points the layers come within 3.4 Å (the van der Waals interactive distance) [O(32*A*)···C(2*B*) ($x-\frac{1}{2}$, $\frac{1}{2}-y$, $z-\frac{1}{2}$) 3.26 (1), C(5*A*)···O(10*B*)($\frac{1}{2}-x$, $\frac{1}{2}-y$, $-z$) 3.26 (1) Å]. This indicates some form of charge-transfer interaction which would account for the intense red colour of the crystals.

Atom-numbering schemes for the two independent molecules are shown in Fig. 1, while Fig. 2 shows the unit-cell packing arrangement (*PLUTO*; Motherwell & Clegg, 1978).

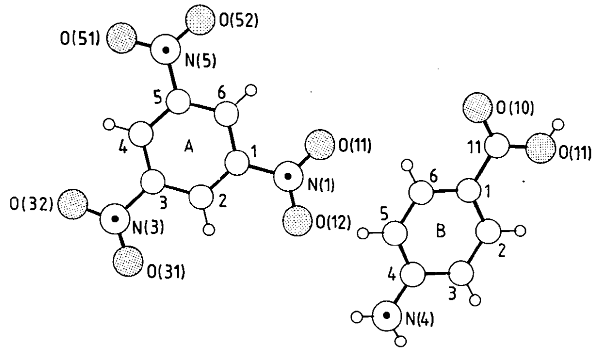


Fig. 1. The molecular conformation and atom-numbering scheme for the individual molecules in the adduct. (C atoms unless otherwise indicated.)

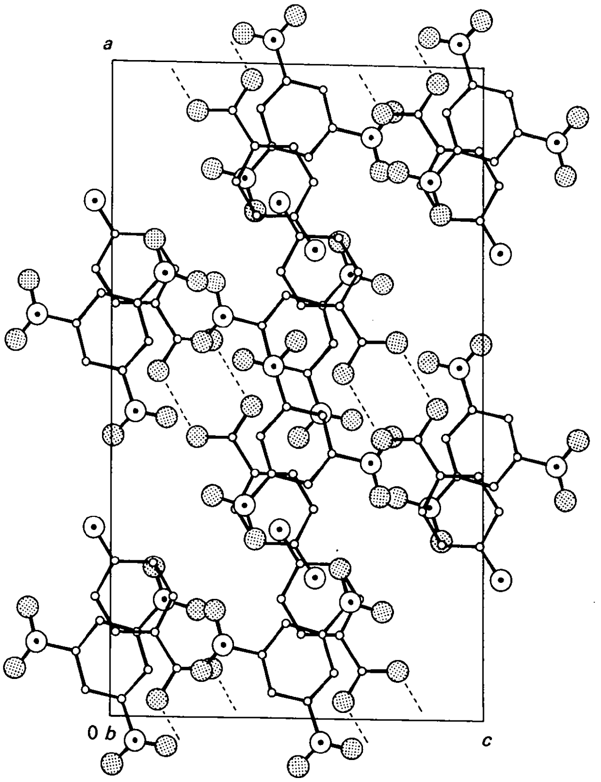


Fig. 2. Packing of the molecular adduct [(TNB)(PABA)] in the unit cell.

Experimental

The title compound was the second minor by-product of the reaction between 2,4,6-trinitrobenzoic acid and 4-aminobenzoic acid (Lynch *et al.*, 1992*a*). These crystals, which were separated manually from the other products, were different in both colour and morphology from those of the yellow major product [(TNBA)(PABA)(H_2O)] and the first minor product. The first minor product (red prismatic crystals) was found to be a 3:1:1 tricrystal of PABA with TNBA and TNB [$(PABA)_3$(TNBA)(TNB)] (Lynch, Smith, Byriel & Kennard, 1992*c*). The X-ray structure for the crystal modification reported here is the 1:1 molecular complex of 1,3,5-trinitrobenzene with 4-aminobenzoic acid [(TNB)(PABA)] which indicates decarboxylation of TNBA (Coffey, 1977). A sufficient quantity for chemical analysis could not be isolated.

Crystal data

$C_6H_3N_3O_6.C_7H_7NO_2$
$M_r = 350.2$
Monoclinic
$C2/c$
$a = 22.46$ (1) Å
$b = 10.051$ (1) Å
$c = 13.096$ (6) Å
$\beta = 90.65$ (3)°
$V = 2955$ (2) Å^3
$Z = 8$
$D_x = 1.574$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6$–14°
$\mu = 0.130$ mm^{-1}
$T = 297$ K
Ellipsoidal
0.36 × 0.28 × 0.14 mm
Red

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\omega$ scans
Absorption correction: empirical (*MolEN*; Fair, 1990)
$T_{\min} = 0.97$, $T_{\max} = 1.00$
4634 measured reflections
2601 independent reflections
653 observed reflections [$I > 2.5\sigma(I_o)$]

$R_{\rm int} = 0.0246$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 26$
$k = 0 \rightarrow 11$
$l = -15 \rightarrow 15$
3 standard reflections monitored every 250 reflections intensity variation: −4.6%

Refinement

Refinement on F
$R = 0.049$
$wR = 0.043$
$S = 2.05$
639 reflections
91 parameters
H-atom parameters not refined
$w = (\sigma^2F_o + 0.000085F_o^2)^{-1}$

$(\Delta/\sigma)_{\max} = 0.02$
$\Delta\rho_{\max} = 0.14$ e Å^{-3}
$\Delta\rho_{\min} = -0.15$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C(1*A*)	0.1287 (4)	0.2089 (8)	0.0692 (6)	0.094 (4)
N(1*A*)	0.1777 (3)	0.2332 (9)	0.1427 (6)	0.118 (4)
O(11*A*)	0.2281 (2)	0.2264 (9)	0.1139 (4)	0.174 (4)
O(12*A*)	0.1634 (2)	0.2592 (7)	0.2302 (4)	0.148 (3)
C(2*A*)	0.0708 (4)	0.2163 (9)	0.0996 (6)	0.105 (4)
C(3*A*)	0.0265 (4)	0.1872 (9)	0.0285 (8)	0.104 (5)
N(3*A*)	−0.0363 (4)	0.1917 (10)	0.0649 (7)	0.138 (5)
O(31*A*)	−0.0441 (3)	0.2435 (12)	0.1469 (5)	0.239 (6)
O(32*A*)	−0.0731 (2)	0.1521 (8)	0.0036 (6)	0.171 (4)
C(4*A*)	0.0392 (4)	0.1541 (9)	−0.0691 (7)	0.113 (4)
C(5*A*)	0.0976 (4)	0.1460 (8)	−0.0974 (7)	0.105 (4)
N(5*A*)	0.1112 (4)	0.1035 (10)	−0.2014 (6)	0.139 (4)
O(51*A*)	0.0698 (3)	0.0734 (8)	−0.2573 (5)	0.212 (4)
O(52*A*)	0.1631 (3)	0.0983 (3)	−0.2242 (4)	0.158 (3)
C(6*A*)	0.1431 (3)	0.1743 (8)	−0.0291 (7)	0.107 (4)
C(1*B*)	0.3722 (4)	0.0682 (8)	0.3833 (6)	0.101 (4)
C(11*B*)	0.4265 (3)	0.0693 (9)	0.3232 (7)	0.114 (4)
O(10*B*)	0.4261 (2)	0.0843 (7)	0.2293 (3)	0.142 (3)
O(11*B*)	0.4743 (2)	0.0554 (6)	0.3755 (3)	0.135 (2)
C(2*B*)	0.3715 (3)	0.0491 (8)	0.4880 (7)	0.108 (4)
C(3*B*)	0.3196 (5)	0.0528 (9)	0.5417 (5)	0.123 (4)
C(4*B*)	0.2658 (4)	0.0831 (9)	0.4927 (8)	0.125 (5)
N(4*B*)	0.2145 (3)	0.0835 (8)	0.5465 (5)	0.162 (4)
C(5*B*)	0.2668 (4)	0.0975 (10)	0.3887 (7)	0.143 (5)
C(6*B*)	0.3181 (4)	0.0935 (9)	0.3361 (5)	0.123 (4)

Table 2. *Bond lengths* (Å) *and angles* (°)

N(1*A*)—C(1*A*)	1.47 (1)	C(2*A*)—C(1*A*)	1.37 (1)
C(6*A*)—C(1*A*)	1.38 (1)	O(11*A*)—N(1*A*)	1.20 (1)
O(12*A*)—N(1*A*)	1.22 (1)	C(3*A*)—C(2*A*)	1.39 (1)
N(3*A*)—C(3*A*)	1.49 (1)	C(4*A*)—C(3*A*)	1.35 (1)
O(31*A*)—N(3*A*)	1.21 (1)	O(32*A*)—N(3*A*)	1.21 (1)
C(5*A*)—C(4*A*)	1.37 (1)	N(5*A*)—C(5*A*)	1.46 (1)
C(6*A*)—C(5*A*)	1.38 (1)	O(51*A*)—N(5*A*)	1.21 (1)
O(52*A*)—N(5*A*)	1.21 (1)	C(11*B*)—C(1*B*)	1.46 (1)
C(2*B*)—C(1*B*)	1.38 (1)	C(6*B*)—C(1*B*)	1.38 (1)
O(10*B*)—C(11*B*)	1.24 (1)	O(11*B*)—C(11*B*)	1.28 (1)
C(3*B*)—C(2*B*)	1.37 (1)	C(4*B*)—C(3*B*)	1.40 (1)
N(4*B*)—C(4*B*)	1.36 (1)	C(5*B*)—C(4*B*)	1.37 (1)
C(6*B*)—C(5*B*)	1.35 (1)		
C(2*A*)—C(1*A*)—N(1*A*)	120.4 (7)	C(6*A*)—C(1*A*)—N(1*A*)	118.1 (7)
C(6*A*)—C(1*A*)—C(2*A*)	121.4 (7)	O(11*A*)—N(1*A*)—C(1*A*)	119.0 (7)
O(12*A*)—N(1*A*)—C(1*A*)	116.5 (7)	O(12*A*)—N(1*A*)—O(11*A*)	124.5 (7)
C(3*A*)—C(2*A*)—C(1*A*)	118.1 (8)	N(3*A*)—C(3*A*)—C(2*A*)	116.9 (9)
C(4*A*)—C(3*A*)—C(2*A*)	121.9 (8)	C(4*A*)—C(3*A*)—N(3*A*)	121.2 (8)
O(31*A*)—N(3*A*)—C(3*A*)	116.3 (9)	O(32*A*)—N(3*A*)—C(3*A*)	114.7 (8)
O(32*A*)—N(3*A*)—O(31*A*)	128.7 (9)	C(5*A*)—C(4*A*)—C(3*A*)	118.9 (8)
N(5*A*)—C(5*A*)—C(4*A*)	118.7 (8)	C(6*A*)—C(5*A*)—C(4*A*)	121.1 (8)
C(6*A*)—C(5*A*)—N(5*A*)	120.2 (8)	O(51*A*)—N(5*A*)—C(5*A*)	118.0 (8)
O(52*A*)—N(5*A*)—C(5*A*)	117.0 (8)	O(52*A*)—N(5*A*)—O(51*A*)	125.0 (8)
C(5*A*)—C(6*A*)—C(1*A*)	118.6 (7)	C(2*B*)—C(1*B*)—C(11*B*)	123.7 (7)
C(6*B*)—C(1*B*)—C(11*B*)	119.6 (7)	C(6*B*)—C(1*B*)—C(2*B*)	116.7 (7)
O(10*B*)—C(11*B*)—C(1*B*)	122.7 (7)	O(11*B*)—C(11*B*)—C(1*B*)	114.4 (7)
O(11*B*)—C(11*B*)—O(10*B*)	122.9 (7)	C(3*B*)—C(2*B*)—C(1*B*)	121.6 (7)
C(4*B*)—C(3*B*)—C(2*B*)	120.5 (7)	N(4*B*)—C(4*B*)—C(3*B*)	119.9 (8)
C(5*B*)—C(4*B*)—C(3*B*)	117.2 (8)	C(5*B*)—C(4*B*)—N(4*B*)	122.5 (8)
C(6*B*)—C(5*B*)—C(4*B*)	121.8 (8)	C(5*B*)—C(6*B*)—C(1*B*)	122.0 (7)

The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985) and refined by full-matrix least squares (*SHELX*76; Sheldrick, 1976) with anisotropic displacement parameters for all non-H atoms.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and torsion angles have been deposited with the IUCr (Reference: AS1101). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Hydroxide Inclusion Complex of a Methylene-Bridged Tetrapyrimidinium Macrocycle

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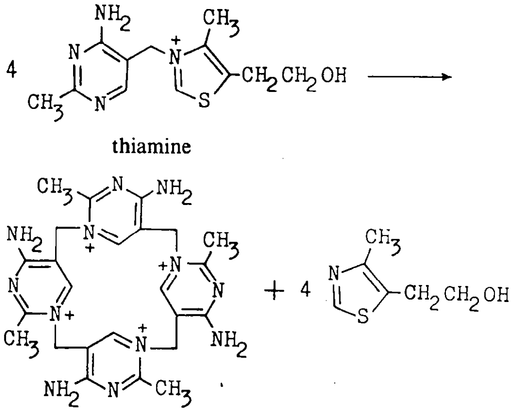
Abstract

In the structure of 4,10,16,22-tetraamino-6,12,18,24-tetramethyl-5,11,17,23-tetraaza-1,7,13,19-tetraazoniapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(26),9,11,13(27),15,17,19(28),21,23-dodecaene dichloride dihydroxide octahydrate, $C_{24}H_{32}N_{12}^{4+}.2OH^-.2Cl^-.8H_2O$, the tetracationic macrocycle consists of four substituted pyrimidinium rings connected by four methylene bridges. The cation captures two hydroxide anions, one on either side of the plane through the macrocycle, *via* pyrimidinium ring–OH^- electrostatic interactions and C—H···O hydrogen bonds, while two chloride anions are located outside the macrocycle. The orientation of the OH^- ions is affected by hydrogen bonds between OH^- and a chloride ion and OH^- and a water molecule.

Comment

Macrocyclic molecules as anion receptors have received much attention because of their selective complexation with a variety of chemically and biologically important anions (Lehn, 1988). Polyammonium macrocycles have been studied extensively in order to find species capable of binding anions (Graf & Lehn, 1976; Dietrich, Hosseini, Lehn & Sessions, 1981). However, stable anion complexes of macrocyclic ligands remain less common than their metal-ion complexes. Recently, a new class of cyclic polypyrimidinium cations has been reported (Cramer & Carrie, 1990; Cramer, Fermin, Kuwabara, Kirkup, Selman, Aoki, Adeyemo & Yamazaki, 1991; Hu, 1993). These were produced by the oligomerization of thiamine resulting from thiazole displacement by the pyrimidine ring. The two isolated polypyrimidinium cations are the cyclic tetramer 16-pyrimidinium crown-4 (1) and the hexamer 24-pyrimidinium crown-6 (Cramer & Carrie, 1990; Cramer *et al.*, 1991). The cyclic cations hold Cl^-, NO_3^- or HgI_4^{2-} anions, depending upon their cavity size, using a combination of weak non-covalent interactions. We report here the crystal structure of a hydroxide inclusion complex of (1), [16-pyrimidinium crown-4].2OH.2Cl.8H$_2$O.



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