# Chains of fused rings in the hydrogen-bonded structure of *meso*-6,13-diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane–2,2′-biphenol (1/2)

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The title compound is a salt, $[C_{12}H_{32}N_6]^{2+}\cdot2[HOC_6H_4C_6H_4O]^-$. The centrosymmetric cation contains two intramolecular N—H···N hydrogen bonds with an N···N distance of 2.8290 (13) Å, and the pendent amino groups are in axial sites; the anion contains an intramolecular O—H···O hydrogen bond with an O···O distance of 2.4656 (11) Å. The ions are linked into continuous chains by means of four types of N—H···O hydrogen bonds with N···O distances ranging from 2.7238 (12) Å to 3.3091 (13) Å, associated with N—H···O angles in the range 148–160°.

## Comment

The simple macrocyclic tetraamine 1,4,8,11-tetraazacyclotetradecane [cyclam, $C_{10}H_{24}N_4$, (I)] forms a 1:2 salt-type adduct with 2,2′-biphenol in which all four of its axial N—H bonds participate in intermolecular hydrogen bonding, so that the supramolecular structure consists of chains of fused $R_2^2(10)$ and $R_6^4(12)$ rings (Ferguson *et al.*, 1999). In contrast, in the analogous adduct formed by *meso*-5,7,7,12,14,14-hexa-*C*-methyl-1,4,8,11-tetraazacyclotetradecane [tet-a, $C_{16}H_{36}N_4$, (II)], the steric congestion adjacent to the *gem*-dimethyl units means that only two of the axial N—H bonds are involved in the supramolecular structure, which thus consists of finite aggregates (Gregson *et al.*, 2000). We have now investigated the corresponding adduct formed with 2,2′-biphenol by a third related macrocycle, namely *meso*-6,13-diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane [diammac, $C_{12}H_{30}N_6$, (III)], based upon the same macrocyclic skeleton as (I) and (II), but bearing pendent hydrogen-bonding functionality. We report here the structural characterization of the resulting 1:2 adduct $C_{12}H_{30}N_6\cdot2C_{12}H_{10}O_2$, (IV).

The constitution of adduct (IV) is that of a salt, $[C_{12}H_{32}N_6]^{2+}\cdot2[HOC_6H_4C_6H_4O]^-$, in which the asymmetric unit consists of one phenolate anion and one half of a $[(diammac)H_2]^{2+}$ cation lying across a centre of inversion (Fig. 1). As commonly found in salts of both $[(cyclam)H_2]^{2+}$ and $[(tet-a)H_2]^{2+}$ cations (Ferguson *et al.*, 1998, 1999; Gregson *et al.*, 2000; Lough *et al.*, 2000), two protons are held by means of N—H···N hydrogen bonds within the $N_4$ cavity of the macrocycle in an $R_2^2(10)$ motif, leaving four axial N—H bonds, all of which are essentially normal to the mean plane of the centrosymmetric macrocycle.



(I)          (II)

(III)          (IV)
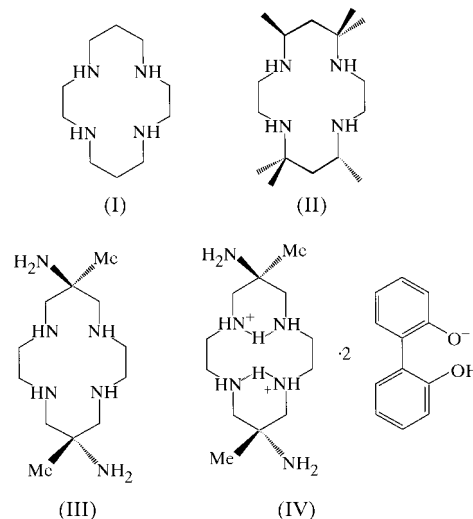
The cation in (IV) adopts the *trans*-III conformation (Barefield *et al.*, 1986; Adam *et al.*, 1994), with almost perfect staggering about the C—C and C—N bonds (Table 1), as typically found in salts of $[(cyclam)H_2]^{2+}$ and $[(tet-a)H_2]^{2+}$ cations. The methyl groups are equatorial and the amino groups, which remain unprotonated, are axial (Fig. 1 and Table 1). The configuration of the bonds at the exocyclic N6 atom is pyramidal, and the conformation about the N6—C6 bond is almost perfectly staggered, with the nitrogen lone pair synclinal to C61 (Fig. 1). There are thus four N—H bonds on each face of the macrocycle, all of which participate in inter-molecular N—H···O hydrogen bonds (Table 2).

There is a marked difference between the C—N bond lengths involving the protonated N1 atom and those involving the unprotonated N4 and N6 atoms; the values are typical of those observed in $[(cyclam)H_2]^{2+}$ cations where the internal H atoms are fully ordered (Ferguson *et al.*, 1998, 1999). It is notable that the C5—C6 and C6—C7 distances are significantly longer in (IV) than the corresponding distances in the analogous $[(cyclam)H_2]^{2+}$ salt, 1.515 (2) and 1.508 (3) Å; in the $[(diammac)H_2]^{2+}$ cation, C6 is a quaternary C atom and both steric and electronic effects may contribute to the bond-length difference. The phenolate anion, in which the two aryl rings are inclined at an angle of 41.0 (1)°, contains a very short intramolecular O—H···O hydrogen bond forming an $S(7)$ motif; as normally observed for bis-phenolate mono-anions, the C—O⁻ bond is significantly shorter than the C—O(H) bond (Table 1).

In the supramolecular structure, each cation acts as an eightfold donor in the formation of N—H$\cdots$O hydrogen bonds, but none of the N atoms acts as an acceptor of intermolecular hydrogen bonds. The anions, by contrast, act only as acceptors of intermolecular hydrogen bonds and each anion is a fourfold acceptor in N—H$\cdots$O hydrogen bonds, consonant with the 1:2 stoichiometry of (IV). Thus, apart from the two types of intramolecular hydrogen bond, all the hydrogen bonds contributing to the supramolecular structure are of the N—H$\cdots$O type.

The supramolecular structure of (IV) is surprisingly similar to that of the corresponding [(cyclam)H$_2$]$^{2+}$ salt (Ferguson *et al.*, 1999), namely a chain of fused rings. The hydrogen bonds formed by the pendent amino groups serve to reinforce this basic architecture rather than to modify it in any material way; in particular, the amino groups do not lead to the formation of a supramolecular structure having dimensionality greater than one. The supramolecular structure is thus most conveniently described in terms of the amino-induced modification of the fused-ring structure reported previously (Ferguson *et al.*, 1999).

Atoms N1 and N4, both at ($x$, $y$, $z$), act as donors to the anionic O2 atoms in the anions at ($x$, $y$, $z$) and ($1 + x$, $y$, $z$) respectively; at the same time, the symmetry-related N1 and N4 atoms in the same cation, which are at ($1 - x$, $1 - y$, $1 - z$), act as donors to the O2 atoms in the anions at ($1 - x$, $1 - y$, $-z$) and ($-x$, $1 - y$, $1 - z$), respectively. These hydrogen bonds, together with the intramolecular N—H$\cdots$N hydrogen bonds within the cations, generate a chain of fused $R_2^2(10)$ and $R_6^4(12)$ rings running parallel to the [100] direction. The $R_2^2(10)$ rings are centred at ($n + \frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) and the $R_6^4(12)$ rings at ($n$, $\frac{1}{2}$, $\frac{1}{2}$) ($n$ = zero or integer). Each cation is thus linked to four different anions, and the two pendent amino groups in each cation form further N—H$\cdots$O hydrogen bonds to the same four anions. N6 at ($x$, $y$, $z$) acts as a donor to the anions at ($1 + x$, $y$, $z$) and ($1 - x$, $1 - y$, $1 - z$) *via* H6*B* and H6*A*,

respectively, while the symmetry-related N6 atom in the same cation at ($1 - x$, $1 - y$, $1 - z$) similarly acts as a donor to the anions at ($x$, $y$, $z$) and ($-x$, $1 - y$, $1 - z$). Each cation therefore acts as a double donor of N—H$\cdots$O hydrogen bonds to each of four anions, and each anion acts as a double acceptor from each of two cations; the anion at ($x$, $y$, $z$) is the acceptor from the cations centred at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) and ($-\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$).

The $R_6^4(12)$ motif common to both (IV) and its [(cyclam)-H$_2$]$^{2+}$ analogue contains no C atoms; an alternative circuit, about the same centre of inversion but incorporating atoms C5, C6 and C7, has graph-set descriptor $R_4^2(16)$. A third motif about the same centre of inversion, of $R_4^2(14)$ type, includes the paired N6—H6*B*$\cdots$O2 hydrogen bonds (Fig. 2); in both the $R_4^2(16)$ and $R_4^2(14)$ rings, the sole acceptor is the anionic O2.

**Figure 2**
Stereoview of part of the crystal structure of (IV), showing the chain of fused rings parallel to [100].
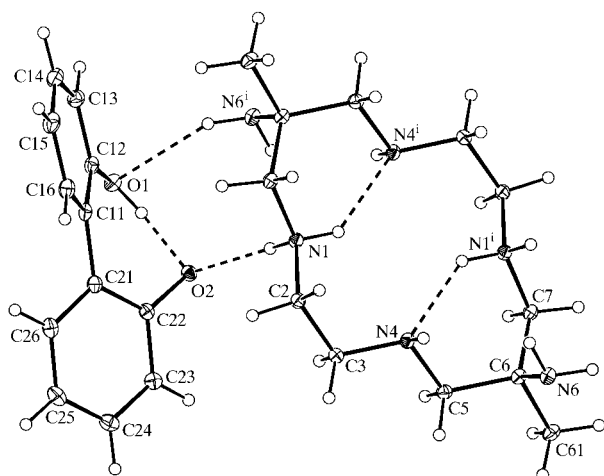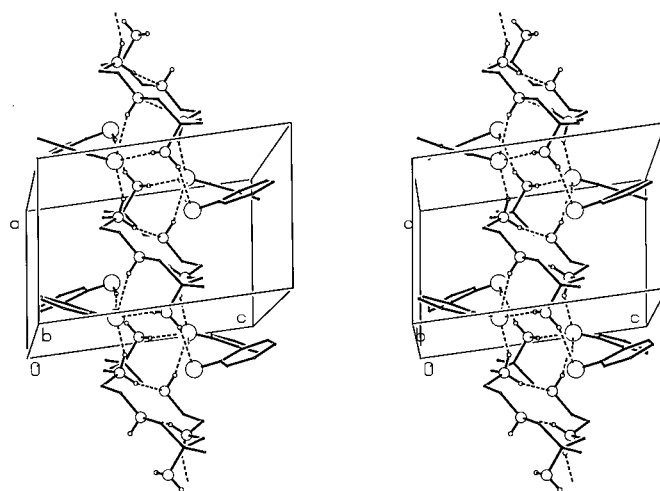
**Figure 1**
The molecular components of (IV) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Symmetry-related atoms (i) are at $1 - x$, $1 - y$, $1 - z$.

## Experimental

Equimolar quantities of diammac dihydrate and 2,2′-biphenol were separately dissolved in methanol. The solutions were mixed and the mixture was set aside to crystallize, producing analytically pure (IV). Analysis: found C 68.1, H 8.2, N 13.5%; C$_{36}$H$_{50}$N$_6$O$_4$ requires C 68.5, H 8.0, N 13.3%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

*Crystal data*

| | |
|---|---|
| C$_{12}$H$_{32}$N$_6^{2+}$·2C$_{12}$H$_9$O$_2^-$ | $D_x = 1.291$ Mg m$^{-3}$ |
| $M_r = 630.82$ | Mo $K\alpha$ radiation |
| Triclinic, $P\bar{1}$ | $\lambda = 0.71073$ Å |
| $a = 7.3994$ (3) Å | Cell parameters from 4644 |
| $b = 9.9179$ (4) Å | reflections |
| $c = 11.3987$ (6) Å | $\theta = 2.65$–$30.03°$ |
| $\alpha = 83.841$ (2)° | $\mu = 0.085$ mm$^{-1}$ |
| $\beta = 82.063$ (2)° | $T = 100$ (1) K |
| $\gamma = 79.433$ (3)° | Plate, colourless |
| $V = 811.56$ (6) Å$^3$ | $0.20 \times 0.20 \times 0.12$ mm |
| $Z = 1$ | |

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| N1—C2 | 1.4908 (14) | C7—N1$^i$ | 1.4960 (14) |
| C2—C3 | 1.5142 (16) | C6—N6 | 1.4668 (15) |
| C3—N4 | 1.4713 (14) | C6—C61 | 1.5317 (15) |
| N4—C5 | 1.4748 (14) | O1—C12 | 1.3590 (14) |
| C5—C6 | 1.5343 (15) | C11—C21 | 1.4927 (16) |
| C6—C7 | 1.5436 (16) | O2—C22 | 1.3490 (14) |
| | | | |
| C7$^i$—N1—C2—C3 | −169.63 (9) | N4—C5—C6—N6 | 63.65 (12) |
| N1—C2—C3—N4 | 71.01 (12) | N4—C5—C6—C61 | −179.35 (10) |
| C2—C3—N4—C5 | −176.37 (9) | C12—C11—C21—C22 | 42.59 (16) |
| C3—N4—C5—C6 | 176.69 (9) | C16—C11—C21—C26 | 39.40 (15) |
| N4—C5—C6—C7 | −62.80 (13) | C12—C11—C21—C26 | −138.12 (12) |
| C5—C6—C7—N1$^i$ | 65.56 (12) | C16—C11—C21—C22 | −139.89 (12) |
| C6—C7—N1$^i$—C2$^i$ | 168.45 (9) | | |

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

*Data collection*

| | |
|---|---|
| Nonius KappaCCD diffractometer | 3615 reflections with $I > 2\sigma(I)$ |
| $\varphi$ and $\omega$ scans with $\kappa$ offsets | $R_{int} = 0.025$ |
| Absorption correction: multi-scan | $\theta_{max} = 30.03°$ |
| (*DENZO-SMN*; Otwinowski & | $h = 0 \rightarrow 10$ |
| Minor, 1997) | $k = -13 \rightarrow 13$ |
| $T_{min} = 0.983$, $T_{max} = 0.990$ | $l = -15 \rightarrow 16$ |
| 15 144 measured reflections | Intensity decay: negligible |
| 4644 independent reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0461P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.045$ | $+ 0.2179P]$ |
| $wR(F^2) = 0.117$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.045$ | $(\Delta/\sigma)_{max} = 0.001$ |
| 4644 reflections | $\Delta\rho_{max} = 0.31$ e Å$^{-3}$ |
| 211 parameters | $\Delta\rho_{min} = -0.26$ e Å$^{-3}$ |
| H-atom parameters constrained | |

**Table 2**
Hydrogen-bonding geometry (Å, °).

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| O1—H1$\cdots$O2 | 0.84 | 1.65 | 2.4656 (11) | 164 |
| N1—H1$A\cdots$O2 | 0.92 | 1.88 | 2.7238 (12) | 152 |
| N1—H1$B\cdots$N4$^i$ | 0.92 | 2.07 | 2.8290 (13) | 139 |
| N4—H4$A\cdots$O2$^{ii}$ | 0.92 | 2.45 | 3.3091 (13) | 155 |
| N6—H6$A\cdots$O1$^i$ | 0.91 | 2.39 | 3.1938 (13) | 148 |
| N6—H6$B\cdots$O2$^{ii}$ | 0.91 | 2.25 | 3.1248 (13) | 160 |

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 + x, y, z$.

Compound (IV) crystallized in the triclinic system; space group $P\bar{1}$ was assumed and confirmed by the analysis. H atoms were treated as riding atoms with C—H = 0.95–0.99 Å, N—H = 0.91 and 0.92 Å, and O—H = 0.84 Å. Examination of the structure with *PLATON* (Spek, 2000) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 2000); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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