IUCrData

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5,7,7,12,14,14-Hexamethyl-4,11-diaza-1,8-diazoniacyclotetradeca-4,11-diene bis(methanesulfonate)

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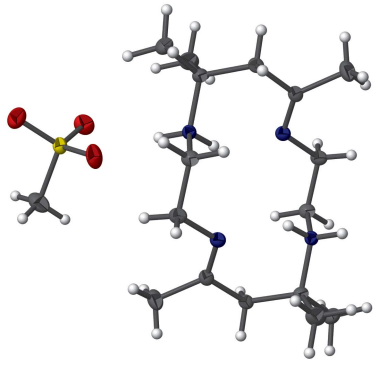
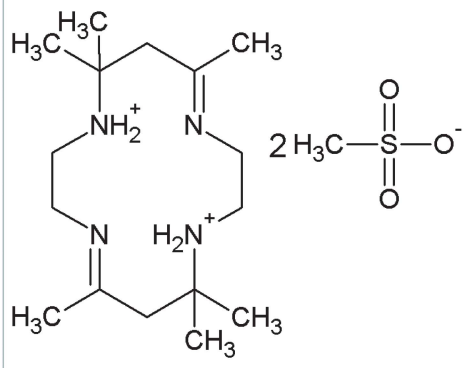
Structural data: full structural data are available from iucrdata.iucr.org

In the title molecular salt, $C_{16}H_{34}N_4^{2+}\cdot 2CH_3SO_3^-$, the centrosymmetric macrocyclic molecule has all four N atoms oriented towards the inside of the cavity, similar to its conformation in metal complexes. The conformation of the ethylenediamine fragment is *trans–gauche–trans* and the conformation of the propylenediamine group is *trans–cis–gauche–gauche*. In the crystal, each protonated N atom makes a strong hydrogen bond with a sulfonate O atom and another intramolecular hydrogen bond connects two N atoms of the same macrocyclic ring to generate ensembles of one dication and two anions.

3D view



Chemical scheme



Structure description

The title salt belongs to a class of widely studied azamacrocycles discovered by Curtis (1960). The reaction between ethylenediamine and acetone after addition of perchloric acid (Curtis, 1968) is, perhaps, the simplest known macrocyclic synthesis. However, the potentially hazardous nature of perchloric acid prevents its use in an undergraduate laboratory. Several alternatives to $HClO_4$ were suggested (Curtis, 1968; Tait & Busch, 1978), requiring more complicated preparations. We report here the synthesis of the Curtis macrocycle in the presence of methanesulfonic acid. Its availability in an anhydrous liquid form favors a condensation reaction.

In the crystal structure of the title salt, the centrosymmetric macrocyclic molecule has all four N atoms oriented towards the inside of the cavity, similar to its conformation in metal complexes (Fig. 1). The conformations of the ethylenediamine fragments are *trans–gauche–trans* and the conformations of the propylenediamine fragments are *trans–cis–gauche–gauche* (see Table 1). The diprotonated tetramine macrocycle forms a neutral salt with two methanesulfonate ions. Each protonated N atom makes a strong hydrogen bond

Table 1
Selected torsion angles (°).

C6—N1—C5—C4	179.58 (8)	C6^{i}—C2—C3—N2	18.86 (14)
N2—C4—C5—N1	64.44 (11)	N1—C6—C2^{i}—C3^{i}	54.12 (11)
C3—N2—C4—C5	−153.05 (9)	C5—N1—C6—C2^{i}	67.30 (11)
C4—N2—C3—C2	−177.43 (9)		

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···N2^{i}	0.908 (16)	1.993 (16)	2.7572 (13)	140.9 (13)
N1—H1B···O1	0.880 (15)	1.875 (15)	2.7453 (12)	169.5 (14)

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

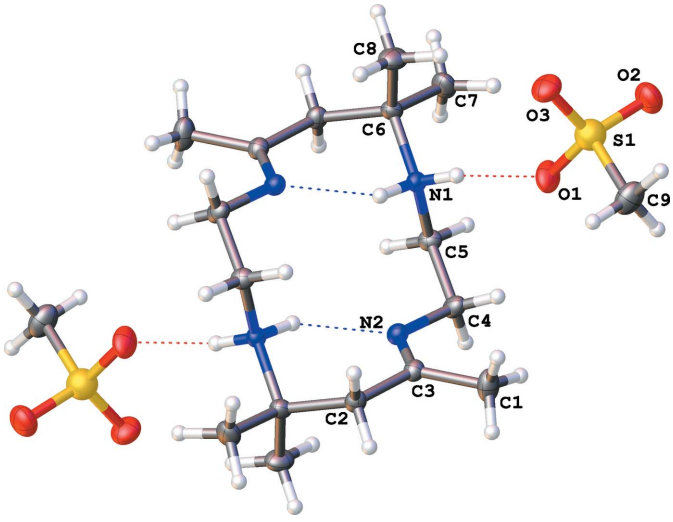


Figure 1
The molecular structure of the title compound, showing the atom-labeling scheme and 50% probability displacement ellipsoids.

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{34}N_4^{2+}\cdot 2CH_3O_3S^-$
M_r	472.66
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	173
a, b, c (Å)	9.7931 (12), 8.6816 (11), 14.1098 (17)
β (°)	94.003 (4)
V (Å^3)	1196.7 (3)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.26
Crystal size (mm)	0.59 × 0.42 × 0.22
Data collection	
Diffractometer	Bruker PHOTON 100 CMOS
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.893, 0.952
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	62436, 5245, 3974
R_{int}	0.052
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.806
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.110, 1.05
No. of reflections	5245
No. of parameters	206
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.51, −0.38

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

with one of the O atoms of the sulfonate group (Table 2, Fig. 2). Another hydrogen bond connects two N atoms of the same macrocyclic ring (Fig. 3).

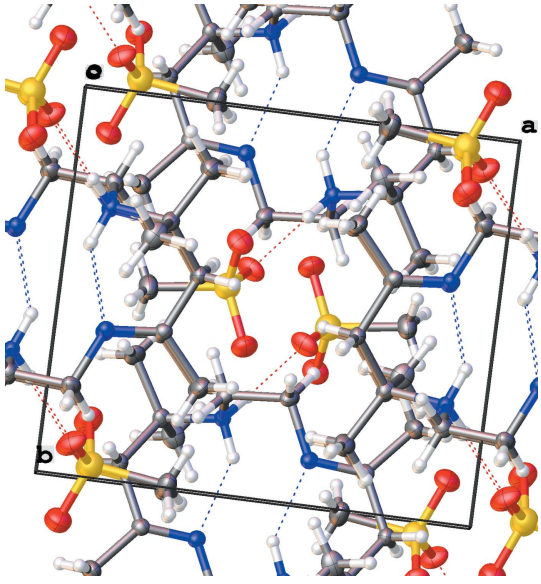


Figure 2
Packing diagram (view along the *c* axis).

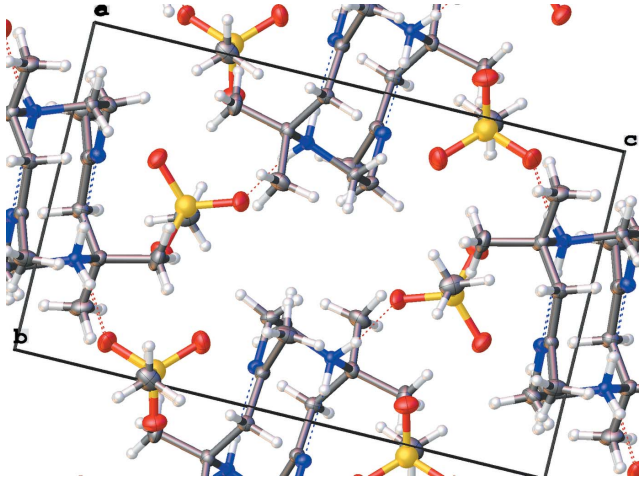


Figure 3
Packing diagram (view along the *a* axis).

Synthesis and crystallization

The title compound was prepared in a manner similar to a known procedure with perchloric acid (Tait & Busch, 1978) by slow addition of 0.96 g (0.01 mol) methanesulfonic acid to a solution of ethylenediamine (0.6 g, 0.01 mol) in 20 ml of acetone. (**Caution!** Potentially violent neutralization reaction.) Colorless crystals were collected after several hours. Some of these crystals appeared to be suitable for X-ray crystallography analysis. The bulk product reacts with Cu^{II} ions yielding a solution of the well-known red macrocyclic complex.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3.

Acknowledgements

Financial support from the State University of New York for the acquisition and maintenance of the X-ray diffractometer is gratefully acknowledged.

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full crystallographic data

IUCrData (2016). **1**, x161033 [doi:10.1107/S2414314616010336]

5,7,7,12,14,14-Hexamethyl-4,11-diaza-1,8-diazoniacyclotetradeca-4,11-diene bis(methanesulfonate)

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5,7,7,12,14,14-Hexamethyl-4,11-diaza-1,8-diazoniacyclotetradeca-4,11-diene bis(methanesulfonate)

Crystal data

$C_{16}H_{34}N_4^{2+}\cdot 2CH_3O_3S^-$
M_r = 472.66
Monoclinic, $P2_1/n$
a = 9.7931 (12) Å
b = 8.6816 (11) Å
c = 14.1098 (17) Å
β = 94.003 (4)°
V = 1196.7 (3) Å^3
Z = 2
$F(000)$ = 512
D_x = 1.312 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9910 reflections
θ = 3.1–33.8°
μ = 0.26 mm^{-1}
T = 173 K
Block, colourless
0.59 × 0.42 × 0.22 mm

Data collection

Bruker PHOTON 100 CMOS diffractometer
Radiation source: sealedtube
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
T_{min} = 0.893, T_{max} = 0.952
62436 measured reflections
5245 independent reflections
3974 reflections with $I > 2\sigma(I)$
R_{int} = 0.052
θ_{max} = 35.0°, θ_{min} = 2.9°
h = −15→15
k = −14→14
l = −22→22

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.110
S = 1.05
5245 reflections
206 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0567P)^2 + 0.2818P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.51 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

Special details

Experimental. SADABS-2014/5 (Bruker,2014/5) was used for absorption correction. wR2(int) was 0.0555 before and 0.0536 after correction. The Ratio of minimum to maximum transmission is 0.9378. The $\lambda/2$ correction factor is 0.00150.

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.59253 (8)	0.19791 (10)	0.43144 (6)	0.01580 (14)
H1A	0.5572 (15)	0.1012 (18)	0.4307 (10)	0.026 (4)*
H1B	0.5421 (14)	0.2614 (18)	0.3951 (11)	0.024 (3)*
N2	0.38388 (9)	0.11848 (10)	0.56274 (6)	0.01794 (15)
C1	0.15447 (12)	0.23278 (13)	0.52301 (10)	0.0294 (2)
H1C	0.0816 (8)	0.2253 (7)	0.5587 (6)	0.035*
H1D	0.1260 (8)	0.2250 (6)	0.4608 (6)	0.035*
H1E	0.1961 (5)	0.3248 (9)	0.5338 (6)	0.035*
C2	0.18794 (10)	−0.05125 (11)	0.55689 (7)	0.01856 (17)
H2A	0.1594 (15)	−0.0847 (17)	0.4937 (11)	0.024 (3)*
H2B	0.1079 (17)	−0.0392 (18)	0.5879 (11)	0.032 (4)*
C3	0.25378 (10)	0.10527 (11)	0.54911 (7)	0.01759 (17)
C4	0.44688 (11)	0.27092 (12)	0.55915 (8)	0.02115 (19)
H4A	0.3995 (15)	0.3410 (18)	0.5181 (11)	0.028 (4)*
H4B	0.4501 (16)	0.3166 (19)	0.6210 (12)	0.033 (4)*
C5	0.59251 (10)	0.25877 (12)	0.53033 (7)	0.01873 (17)
H5A	0.6330 (15)	0.3588 (18)	0.5318 (10)	0.026 (4)*
H5B	0.6485 (15)	0.1925 (17)	0.5700 (10)	0.024 (3)*
C6	0.73047 (10)	0.17883 (12)	0.38985 (7)	0.01878 (17)
C7	0.80936 (12)	0.33048 (14)	0.39918 (10)	0.0276 (2)
H7A	0.8375 (15)	0.3512 (17)	0.4650 (11)	0.025 (4)*
H7B	0.8870 (17)	0.324 (2)	0.3631 (12)	0.038 (4)*
H7C	0.7508 (16)	0.4143 (19)	0.3701 (11)	0.033 (4)*
C8	0.69890 (13)	0.13881 (16)	0.28543 (8)	0.0286 (2)
H8A	0.6461 (17)	0.218 (2)	0.2539 (12)	0.041 (4)*
H8B	0.7831 (17)	0.125 (2)	0.2553 (12)	0.040 (4)*
H8C	0.6453 (17)	0.0418 (18)	0.2775 (11)	0.031 (4)*
S1	0.37838 (3)	0.46573 (3)	0.24372 (2)	0.01973 (7)
O1	0.42782 (10)	0.41405 (11)	0.33881 (6)	0.03133 (19)
O2	0.43476 (10)	0.61414 (11)	0.22043 (7)	0.0351 (2)
O3	0.39480 (10)	0.34887 (11)	0.17162 (6)	0.0320 (2)
C9	0.20072 (13)	0.49311 (18)	0.24961 (11)	0.0343 (3)
H9A	0.1624 (19)	0.399 (2)	0.2635 (12)	0.045 (5)*
H9B	0.1858 (18)	0.566 (2)	0.2955 (13)	0.042 (5)*
H9C	0.1639 (19)	0.533 (2)	0.1860 (14)	0.043 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0155 (3)	0.0160 (3)	0.0158 (3)	0.0005 (3)	0.0003 (3)	0.0006 (3)
N2	0.0177 (4)	0.0166 (3)	0.0197 (4)	−0.0006 (3)	0.0025 (3)	−0.0016 (3)
C1	0.0221 (5)	0.0214 (5)	0.0437 (7)	0.0030 (4)	−0.0044 (4)	0.0033 (5)
C2	0.0148 (4)	0.0184 (4)	0.0224 (4)	−0.0002 (3)	0.0008 (3)	0.0001 (3)
C3	0.0187 (4)	0.0170 (4)	0.0169 (4)	0.0009 (3)	0.0001 (3)	−0.0018 (3)
C4	0.0211 (4)	0.0172 (4)	0.0259 (5)	−0.0018 (3)	0.0061 (4)	−0.0046 (4)

C5	0.0187 (4)	0.0198 (4)	0.0177 (4)	−0.0028 (3)	0.0011 (3)	−0.0031 (3)
C6	0.0178 (4)	0.0204 (4)	0.0185 (4)	0.0004 (3)	0.0042 (3)	0.0025 (3)
C7	0.0239 (5)	0.0221 (5)	0.0376 (6)	−0.0033 (4)	0.0078 (4)	0.0066 (4)
C8	0.0309 (6)	0.0383 (6)	0.0168 (4)	0.0053 (5)	0.0042 (4)	0.0015 (4)
S1	0.02069 (12)	0.01985 (12)	0.01816 (11)	0.00210 (8)	−0.00218 (8)	0.00111 (8)
O1	0.0413 (5)	0.0299 (4)	0.0213 (4)	0.0110 (4)	−0.0083 (3)	0.0019 (3)
O2	0.0368 (5)	0.0267 (4)	0.0421 (5)	−0.0053 (4)	0.0046 (4)	0.0071 (4)
O3	0.0383 (5)	0.0340 (5)	0.0239 (4)	0.0045 (4)	0.0023 (3)	−0.0075 (3)
C9	0.0221 (5)	0.0346 (6)	0.0456 (7)	0.0035 (5)	−0.0018 (5)	−0.0082 (6)

Geometric parameters (Å, º)

N1—H1A	0.908 (16)	C5—H5B	0.950 (15)
N1—H1B	0.880 (15)	C6—C2^{i}	1.5316 (14)
N1—C5	1.4921 (12)	C6—C7	1.5275 (15)
N1—C6	1.5190 (13)	C6—C8	1.5242 (15)
N2—C3	1.2803 (13)	C7—H7A	0.966 (15)
N2—C4	1.4625 (13)	C7—H7B	0.946 (17)
C1—H1C	0.905 (9)	C7—H7C	0.997 (17)
C1—H1D	0.905 (9)	C8—H8A	0.952 (18)
C1—H1E	0.905 (9)	C8—H8B	0.962 (17)
C1—C3	1.5023 (15)	C8—H8C	0.994 (16)
C2—H2A	0.960 (15)	S1—O1	1.4647 (9)
C2—H2B	0.930 (16)	S1—O2	1.4485 (9)
C2—C3	1.5113 (14)	S1—O3	1.4536 (9)
C2—C6^{i}	1.5317 (14)	S1—C9	1.7637 (13)
C4—H4A	0.940 (16)	C9—H9A	0.92 (2)
C4—H4B	0.956 (17)	C9—H9B	0.925 (18)
C4—C5	1.5137 (14)	C9—H9C	1.006 (19)
C5—H5A	0.954 (15)		
H1A—N1—H1B	112.0 (13)	C4—C5—H5B	113.6 (8)
C5—N1—H1A	108.3 (9)	H5A—C5—H5B	108.5 (12)
C5—N1—H1B	106.6 (10)	N1—C6—C2^{i}	109.68 (8)
C5—N1—C6	117.26 (8)	N1—C6—C7	109.32 (8)
C6—N1—H1A	104.1 (9)	N1—C6—C8	105.81 (8)
C6—N1—H1B	108.8 (9)	C7—C6—C2^{i}	109.73 (9)
C3—N2—C4	119.58 (9)	C8—C6—C2^{i}	111.91 (9)
H1C—C1—H1D	109.5	C8—C6—C7	110.30 (9)
H1C—C1—H1E	109.5	C6—C7—H7A	110.6 (9)
H1D—C1—H1E	109.5	C6—C7—H7B	108.8 (11)
C3—C1—H1C	109.5	C6—C7—H7C	108.7 (9)
C3—C1—H1D	109.5	H7A—C7—H7B	110.0 (14)
C3—C1—H1E	109.5	H7A—C7—H7C	112.1 (13)
H2A—C2—H2B	105.7 (13)	H7B—C7—H7C	106.5 (13)
C3—C2—H2A	107.6 (9)	C6—C8—H8A	110.7 (10)
C3—C2—H2B	108.1 (10)	C6—C8—H8B	109.5 (10)
C3—C2—C6^{i}	118.37 (8)	C6—C8—H8C	111.8 (9)

C6^{i}—C2—H2A	110.2 (9)	H8A—C8—H8B	109.8 (14)
C6^{i}—C2—H2B	106.2 (10)	H8A—C8—H8C	107.1 (14)
N2—C3—C1	126.24 (9)	H8B—C8—H8C	107.8 (14)
N2—C3—C2	119.65 (9)	O1—S1—C9	105.20 (7)
C1—C3—C2	114.09 (8)	O2—S1—O1	111.93 (6)
N2—C4—H4A	114.6 (9)	O2—S1—O3	113.55 (6)
N2—C4—H4B	109.3 (10)	O2—S1—C9	106.48 (7)
N2—C4—C5	110.73 (8)	O3—S1—O1	112.43 (5)
H4A—C4—H4B	106.1 (13)	O3—S1—C9	106.54 (6)
C5—C4—H4A	108.2 (9)	S1—C9—H9A	107.9 (12)
C5—C4—H4B	107.6 (9)	S1—C9—H9B	109.3 (11)
N1—C5—C4	109.73 (8)	S1—C9—H9C	107.3 (10)
N1—C5—H5A	108.4 (9)	H9A—C9—H9B	111.6 (15)
N1—C5—H5B	107.4 (9)	H9A—C9—H9C	111.6 (16)
C4—C5—H5A	109.2 (9)	H9B—C9—H9C	108.9 (15)
C6—N1—C5—C4	179.58 (8)	C5—N1—C6—C8	−171.83 (9)
N2—C4—C5—N1	64.44 (11)	C6^{i}—C2—C3—N2	18.86 (14)
C3—N2—C4—C5	−153.05 (9)	C6^{i}—C2—C3—C1	−162.42 (9)
C4—N2—C3—C1	4.03 (16)	N1—C6—C2^{i}—C3^{i}	54.12 (11)
C4—N2—C3—C2	−177.43 (9)	C5—N1—C6—C2^{i}	67.30 (11)
C5—N1—C6—C7	−53.05 (11)		

Symmetry code: (i) −*x*+1, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···N2^{i}	0.908 (16)	1.993 (16)	2.7572 (13)	140.9 (13)
N1—H1*B*···O1	0.880 (15)	1.875 (15)	2.7453 (12)	169.5 (14)

Symmetry code: (i) −*x*+1, −*y*, −*z*+1.