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Disodium Hexadecahydrate Diprotonated Form of 1,4,8,11-Tetra(2-carboxy)ethyl-1,4,8,11-tetraazacyclotetradecane $(H_2TETP)^{2-}$ at 110 K†

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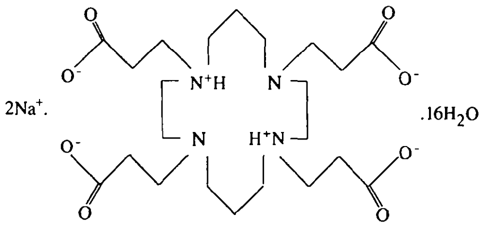
Abstract

The diprotonated $(H_2TETP)^{2-}$ macrocycle in the title compound, $2Na^+.C_{22}H_{38}N_4O_8^{2-}.16H_2O$ or $2Na^+.(H_2TETP)^{2-}.16H_2O$, possesses a [3434] conformation, the propionate arms all being deprotonated. Two are extended and the other two are folded towards two protonated N atoms. The crystal structure is stabilized by a complex hydrogen-bonding scheme since the unit cell contains 16 water molecules.

Comment

The structure of the diprotonated form of 1,4,8,11-tetra(2-carboxy)ethyl-1,4,8,11-tetraazacyclotetradecane, $(H_2TETP)^{2-}$, (I), has been investigated as part of a study of the different conformations of the TETP ligand according to its protonation state (Dahaoui-Gindrey *et al.*, 1995; Dahaoui-Gindrey, 1995).



(I)

As in other TETP forms, the structure is centrosymmetric so only half of the atoms of the chemical formula are unique (Fig. 1). Atoms N1 and N1′ in *trans* positions are protonated, the N—C bond distances of these N atoms being on average longer than those involving the non-protonated N2 and N2′ atoms [1.503 (4) and 1.470 (4) Å, respectively]. The C—O bond lengths, which are statistically equal [1.254 (1)–1.270 (1) Å], are appropriate for deprotonated carboxyl groups. Thus, the TETP ligand is diprotonated bearing two negative charges, and consequently is formulated as $(H_2TETP)^{2-}$. Both negative charges of the ligand are neutralized by the positive charges of two Na^+ ions.

The cyclam skeleton of this compound has a [3434] conformation according to Dale's nomenclature (Dale, 1980), with a methylene group located at each corner of the macrocycle to give an endodentate geometry, as was also reported for H_4TETP and H_5TETP^+ (Dahaoui-Gindrey *et al.*, 1995). $(H_2TETP)^{2-}$ has two of the propionate groups extended outside of the ring and two others folded inside forming an intramolecular three-centre hydrogen bond between the HN1—N1 donor group, and the O3 and N2 acceptors. The sum of the intramolecular angles involving the HN1 atom as the central atom is exactly 360°. The $(H_2TETP)^{2-}$ torsion angles (Table 1) are close to those found in H_4TETP except for the extremity of the folded propionate chain: in particular, the O3 and O4 atoms of $(H_2TETP)^{2-}$ exhibit perfect *cis* and *trans* positions, respectively, with regard to the C10—C11 bond [whereas in H_4TETP, the N2—C9—C10—C11, C9—C10—C11—O3 and C9—C10—C11—O4 torsion angles are −49.8 (7), −45.9 (9) and 132.3 (6)°, respectively].

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† Alternative name: disodium 4,11-diaza-1,8-diazoniatetradecane-1,4,8,11-tetrayltetrakis(3-propionate) hexadecahydrate.

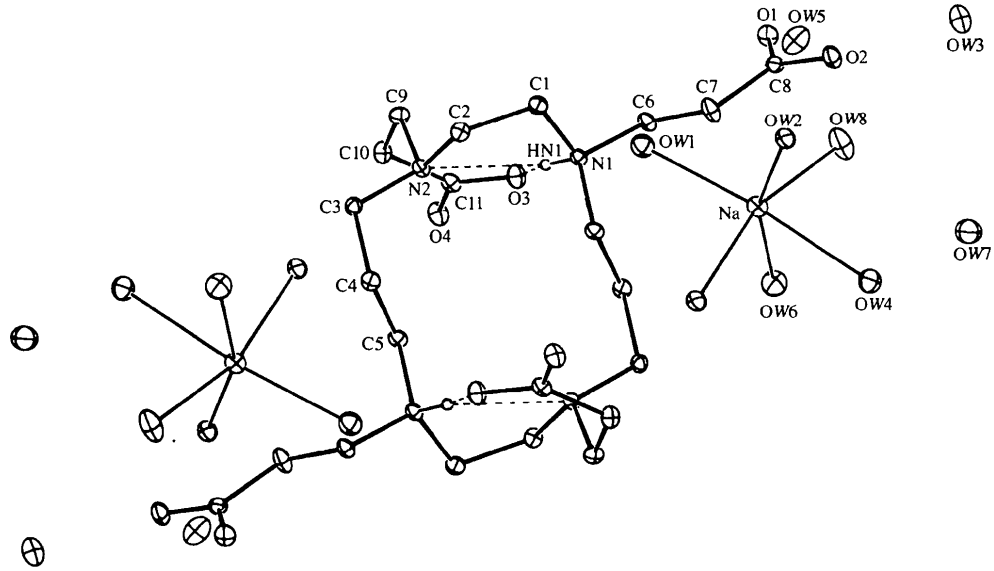

Fig. 1. The molecular structure of the title complex showing the labelling scheme. Only H atoms bonded to N1 and its symmetry equivalent are shown. Hydrogen bonds are indicated by dashed lines. Displacement ellipsoids are plotted at the 50% probability level and H atoms have been assigned arbitrary radii.

All 16 H atoms of the eight water molecules of hydration in the asymmetric unit are involved in a very complex hydrogen-bonding scheme (Table 2). Each O atom of the deprotonated carboxyl groups is hydrogen bonded to three water molecules, except for O3, which is already involved in an intramolecular hydrogen bond. The Na^+ ion does not interact with the macrocyclic ligand but with six water molecules [Na···O 2.3778 (9)–2.4706 (9) Å], resulting in a distorted octahedron; the major deviations from regular octahedral coordination are angles O*W*8—Na—O*W*6 and O*W*2—Na—O*W*6 of 71.89 (3) and 160.82 (3)°, respectively. Two O*W*2 atoms related by an inversion centre bridge two Na^+ ions in a nearly square conformation, with Na—O*W*2 bond distances and an O*W*2—Na—O*W*2 angle of 2.3899 (7) and 2.4094 (8) Å, and 90.02 (3)°, respectively. Despite the very high number of hydration water molecules in the unit cell, neither crystal instability nor disorder in the crystal structure was found as each water molecule participates strongly in the crystal packing, either with Na^+ ion interactions or through hydrogen bonding as for O*W*7 which is involved in four hydrogen bonds.

Experimental

For the preparation of the title compound, two equivalents of NaOH were added to a saturated solution of the tetraprotonated form of 1,4,8,11-tetra(2-carboxy)ethyl-1,4,8,11-tetraazacyclotetradecane, H_4TETP (Dahaoui-Gindrey *et al.*, 1995). Colourless crystals of $2Na^+.(H_2TETP)^{2-}.16H_2O$ were obtained by slow evaporation of this solution at room temperature. Analysis: calculated for $C_{22}H_{38}N_4Na_2O_8H_{38}.16H_2O$: C 32.19, H 8.60, N 6.83, Na 5.60%; found: C 31.9, H 8.9, N 6.7, Na 5.6%.

Crystal data

$2Na^+.C_{22}H_{38}N_4O_8^{2-}.16H_2O$
M_r = 820.79
Triclinic
$P\bar{1}$
a = 8.779 (1) Å
b = 9.942 (2) Å
c = 12.385 (2) Å
α = 71.84 (1)°
β = 74.20 (1)°
γ = 87.29 (1)°
V = 987.5 (2) Å^3
Z = 1
D_x = 1.38 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 7.8–16.3°
μ = 0.13 mm^{-1}
T = 110 (3) K
Prism
0.40 × 0.34 × 0.24 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
6238 measured reflections
5706 independent reflections
4907 reflections with $I > 3\sigma(I)$

R_{int} = 0.023
θ_{max} = 30.0°
$h = -12 \rightarrow +12$
$k = -13 \rightarrow +13$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity decay: 2%

Refinement

Refinement on F
R = 0.030
wR = 0.036
S = 1.59
4907 reflections
375 parameters
All H atoms refined
$w = 1/[\sigma^2(F) + 0.0004F^2]$

$(\Delta/\sigma)_{max}$ = 0.060
$\Delta\rho_{max}$ = 0.490 e Å^{-3}
$\Delta\rho_{min}$ = −0.240 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

N1—C1	1.498 (1)	N2—C9	1.474 (1)
N1—C5^{i}	1.502 (1)	C8—O1	1.254 (1)
N1—C6	1.508 (1)	C8—O2	1.2653 (9)
N2—C2	1.4653 (9)	C11—O3	1.2570 (9)
N2—C3	1.470 (1)	C11—O4	1.270 (1)
N1—C1—C2—N2	−39.3 (1)	N1—C6—C7—C8	−172.01 (9)
C1—C2—N2—C3	169.17 (8)	C6—C7—C8—O1	6.9 (1)
C2—N2—C3—C4	−79.2 (1)	C6—C7—C8—O2	−174.69 (9)
N2—C3—C4—C5	−68.17 (8)	C1—C2—N2—C9	−69.2 (1)
C3—C4—C5—N1^{i}	−179.53 (6)	C2—N2—C9—C10	161.47 (7)
C4—C5—N1^{i}—C1^{i}	−168.91 (6)	C4—C3—N2—C9	157.98 (7)
C5—N1^{i}—C1^{i}—C2^{i}	63.34 (8)	C3—N2—C9—C10	−77.05 (9)
C2—C1—N1—C6	167.46 (7)	N2—C9—C10—C11	−72.1 (1)
C1—N1—C6—C7	71.5 (1)	C9—C10—C11—O3	0.1 (1)
C4^{i}—C5^{i}—N1—C6	−63.70 (8)	C9—C10—C11—O4	−179.42 (9)
C5^{i}—N1—C6—C7	−57.0 (1)		
Na···OW1^{ii}	2.3778 (9)	Na···OW2^{iii}	2.4094 (8)
Na···OW8	2.3891 (9)	Na···OW6	2.4341 (9)
Na···OW2^{ii}	2.3899 (7)	Na···OW4^{iii}	2.4706 (9)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—HN1···O3	0.93 (1)	1.84 (1)	2.7222 (8)	157 (1)
N1—HN1···N2	0.93 (1)	2.38 (1)	2.806 (1)	108 (1)
OW2—H1W2···O1	0.81 (2)	2.00 (2)	2.804 (1)	175 (1)
OW5—H2W5···O1	0.80 (2)	2.07 (2)	2.845 (1)	161 (2)
OW4—H1W4···O1	0.91 (2)	2.11 (2)	3.001 (1)	165 (2)
OW3—H1W3···O2	0.85 (2)	1.98 (2)	2.8028 (9)	163 (1)
OW8—H1W8···O2	0.84 (2)	1.97 (2)	2.811 (1)	173 (2)
OW1—H1W1···O2	0.83 (2)	2.02 (2)	2.846 (1)	176 (1)
OW5^{i}—H1W5^{i}···O3	0.83 (2)	1.98 (2)	2.795 (1)	167 (1)
OW2^{ii}—H2W2^{ii}···O4	0.84 (2)	1.92 (2)	2.7634 (9)	175 (2)
OW7^{iii}—H1W7^{iii}···O4	0.91 (2)	1.90 (2)	2.765 (1)	159 (1)
OW3^{i}—H2W3^{i}···O4	0.78 (2)	2.14 (2)	2.886 (1)	158 (2)
OW1—H2W1···OW7	0.87 (2)	1.92 (2)	2.778 (1)	168 (2)
OW8^{iv}—H2W8^{iv}···OW3	0.83 (2)	1.92 (2)	2.7468 (9)	169 (2)
OW7^{v}—H2W7^{v}···OW4	0.83 (2)	2.04 (2)	2.837 (1)	160 (2)
OW4—H2W4···OW7	0.91 (1)	2.06 (1)	2.9703 (9)	179 (2)
OW6^{vi}—H1W6^{vi}···OW5	0.84 (2)	1.98 (2)	2.803 (1)	170 (2)
OW6—H2W6···OW8	0.82 (2)	2.14 (2)	2.832 (1)	142 (2)

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

All H atoms were located from difference Fourier maps and were refined isotropically.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *DREAM* (Blessing, 1987). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP* (Johnson, 1970).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1178). Services for accessing these data are described at the back of the journal.

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Octacarbonyl-μ-chloro-μ-dicyclohexylphosphido-dimanganese

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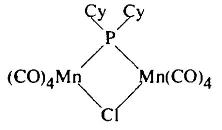
Abstract

The title compound, $[Mn_2(\mu\text{-}Cl)\{\mu\text{-}P(C_6H_{11})_2\}(CO)_8]$, has as central molecular fragment, a planar Mn_2ClP ring, with Mn—Cl and Mn—P bond lengths of 2.4010 (12) and 2.4134 (11) Å, respectively.

Comment

The title compound, (I), is the first example of a structurally characterized μ-Cl- and μ-P-bridged dimanganese–carbonyl complex. The centre of the molecule lies on a crystallographic twofold axis that runs through the Cl and P atoms.



(I)

Both the Mn atoms attain slightly distorted octahedral coordination *via* the bridging Cl and P atoms, and the four carbonyl groups. The latter show an almost eclipsed arrangement at the manganese centres, with torsion angles C3—Mn1—Mn1*A*–C2*A* −0.2 (2), C1—Mn1—Mn1*A*—C1*A* −0.8 (3) and C4—Mn1—Mn1*A*—C4*A* −2.0 (2)°. According to the twofold axis, the central Mn_2ClP ring is planar, with a non-bonding Mn···Mn distance of 3.648 (1) Å. The short Mn—Cl bond length of 2.4010 (12) Å may be compared with values of 2.395 (1) Å for $[Mn_2(\mu\text{-}Cl)_2(CO)_8]$ (Clegg & Morton, 1978) and 2.397 (2) Å for $[Mn_2(\mu\text{-}Cl)_2(CO)_6(thf)_2]$ (Van Derveer & Burlitch, 1980). The Mn—P bond length of 2.4134 (11) Å is equal to that