Poly[[(μ4-1,3,5-triamino-1,3,5-trideoxy-cis-inositol)sodium] bromide]

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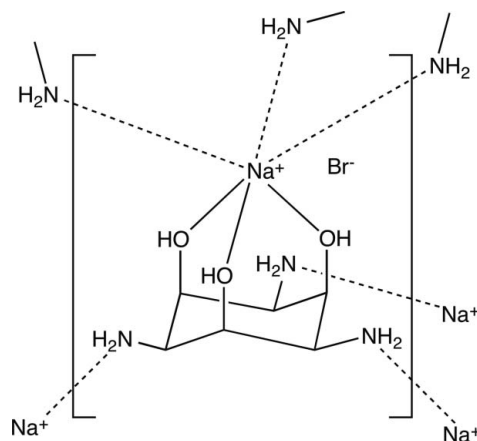Correspondence e-mail: hegetschweiler@mx.uni-saarland.de

In the structure of the title compound, $\{[Na(C_6H_{15}N_3O_3)]Br\}_n$, the sodium cation and the bromide anion are both located on threefold rotation axes. The sodium cation is bonded to the three hydroxy groups of one 1,3,5-triamino-1,3,5-trideoxy-cis-inositol (taci) ligand, with the taci ligand residing around the same threefold rotation axis as the sodium ion. The coordination sphere of the sodium ion is completed by three amino groups of three neighbouring taci molecules. Hence, this type of coordination constitutes a three-dimensional open framework with channels along the c axis which are filled with the bromide counter-anions. Each bromide ion forms three symmetry-related hydrogen bonds to both the hydroxy and the amino groups of neighbouring taci ligands.

Related literature

The crystal structure of an Na–bis-taci complex has been reported by Bartholomä et al. (2010). Puckering parameters were calculated according to Cremer & Pople (1975). For a preliminary preparation and characterization of the title compound, see: Egli (1994). For a general overview of the coordination chemistry of taci, see: Hegetschweiler (1999). The crystal structure of a Cu^{II}–taci complex has been reported by Reiss et al. (1998). For the crystal structure of a mono-protonated taci salt, see: Reiss et al. (1999).

Experimental

Crystal data

$[Na(C_6H_{15}N_3O_3)]Br$	$Z = 2$
$M_r = 280.10$	Mo $K\alpha$ radiation
Trigonal, $P31c$	$\mu = 4.15$ mm^{-1}
$a = 8.0491$ (10) Å	$T = 153$ K
$c = 8.8953$ (18) Å	$0.57 \times 0.45 \times 0.28$ mm
$V = 499.10$ (13) Å^3	

Data collection

Siemens P4 diffractometer	690 independent reflections
Absorption correction: integration (XPREP; Bruker, 2008) using indexed faces	682 reflections with $I > 2\sigma(I)$
$T_{min} = 0.101$, $T_{max} = 0.331$	$R_{int} = 0.077$
3954 measured reflections	3 standard reflections every 100 reflections
	intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.078$	
$S = 1.05$	$\Delta\rho_{max} = 0.42$ e Å^{-3}
690 reflections	$\Delta\rho_{min} = -0.55$ e Å^{-3}
59 parameters	Absolute structure: Flack (1983), 340 Friedel pairs
3 restraints	Flack parameter: −0.03 (3)

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$O\cdots$Br	0.82	2.46	3.278 (3)	175
N1—H2$N\cdots$Br^i	0.90 (1)	2.91 (3)	3.696 (4)	147 (5)

Symmetry code: (i) $y, x, z + \frac{1}{2}$.

Data collection: XSCANS (Siemens, 1994); cell refinement: XSCANS; data reduction: XSCANS and XPREP (Bruker, 2008); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 2012); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2009).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2727).

metal-organic compounds

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supporting information

Poly[[(*μ*$_4$-1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol)sodium] bromide]

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S1. Comment

The coordination ability of 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (= taci) attracted attention owing to the two distinct chair conformations of this ligand, allowing metal binding either *via* three axial nitrogen or three axial oxygen donors (Hegetschweiler, 1999). For the free taci ligand and its protonation products, a chair conformation with axial hydroxy groups has been asserted (Reiss *et al.*, 1999). However, binding of divalent transition metal cations such as Cu^{2+} usually occurs *via* three axial amino groups (Reiss *et al.*, 1998). The binding of Na$^+$ to a protonated bis-taci unit (where two taci-moieties are connected *via* a O—CH$_2$—CH$_2$—O bridge) occurred *via* the axial hydroxy groups (Bartholomä *et al.*, 2010).

In the title compound, [Na(C$_6$H$_{15}$N$_3$O$_3$)]$^+$Br$^-$, the cation, anion and the taci ligand have site symmetry 3. The taci ligand also adopts a chair conformation with axial hydroxy groups, which bind to the Na$^+$ cation (Na—O distance: 2.409 (4)Å). The puckering parameters (Cremer & Pople, 1975) of the cyclohexane ring are Q = 0.531Å, φ = 0.0°, θ = 180.0°. Interlinking of the Na$^+$ cation to three equatorial amino groups of three neighbouring taci ligands (Na—N distance: 2.556 (4)Å) generates a distorted octahedral coordination geometry around the sodium ion. Due to symmetry, the three oxygen and the three nitrogen donors form each two parallel, equilateral triangles with a twist angle τ of 56.4°. This value indicates that the *fac*-NaO$_3$N$_3$ coordination geometry adopts C_{3v} symmetry quite closely. The bromide anion is hydrogen-bonded to three hydroxy groups of three adjacent taci ligands. Additionally, three N—H⋯Br contacts are formed (see Table 1). These N—H⋯Br contacts may be interpreted as weak hydrogen bonds. The three (N—)H and the three (O—)H hydrogen atoms form again two parallel, equilateral triangles with a twist angle τ = 32.4°. The six hydrogen atoms, which encapsulate the bromide ion, constitute thus a polyhedron which is just an intermediate form between a trigonal prism (τ = 0°) and a trigonal antiprism (τ = 60°). Notably, the bromide ion is not located in the centre of this polyhedron. It is significantly displaced towards the three (O—)H hydrogen atoms. Inspection of the structure further reveals an intermolecular N⋯O separation of 2.831 (6)Å, a value which falls in a range expected for N—H⋯O hydrogen bonding. However, the corresponding N—H⋯O angle of 110 (6)° is very acute and would not be in agreement with such an interpretation.

S2. Experimental

The title compound was first isolated unintentionally by Egli (1994) in the reaction of K$_2$ReBr$_6$, NaOCH$_3$ and taci. In our study, it was prepared by adding equimolar amounts of NaBr and taci in small portions to boiling MeOH until a saturated solution was obtained. The solution was filtered hot and was allowed to cool slowly to room temperature, yielding colourless single crystals suitable for crystal structure analysis.

S3. Refinement

All hydrogen atoms were identified in difference syntheses. In the latest stages of refinement, the coordinates of the N– and C– bonded hydrogen atoms were refined, whereas the coordinates of the (O—)H hydrogen atom had to be

constrained using the AFIX 83 option of the *SHELXL* program. The N—H bond lengths were restrained to 0.90Å. All U_{iso} values, besides those of the CH groups, were refined freely.
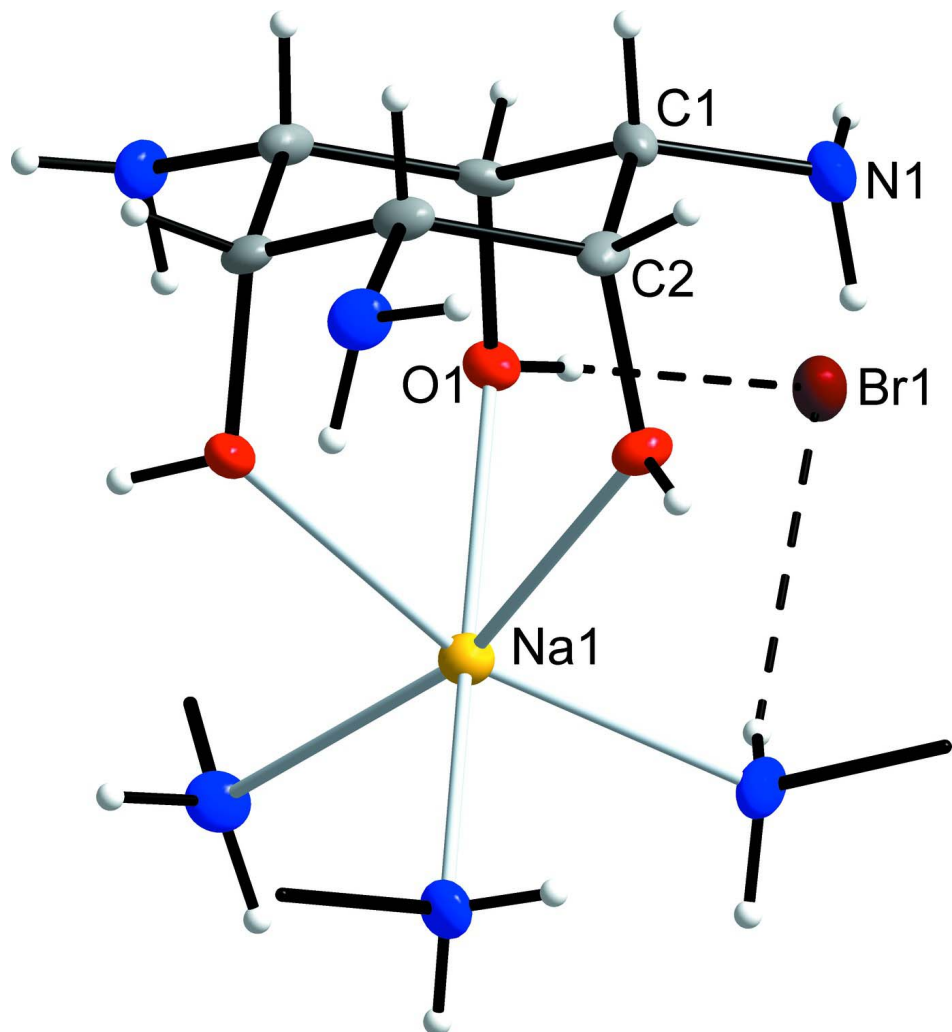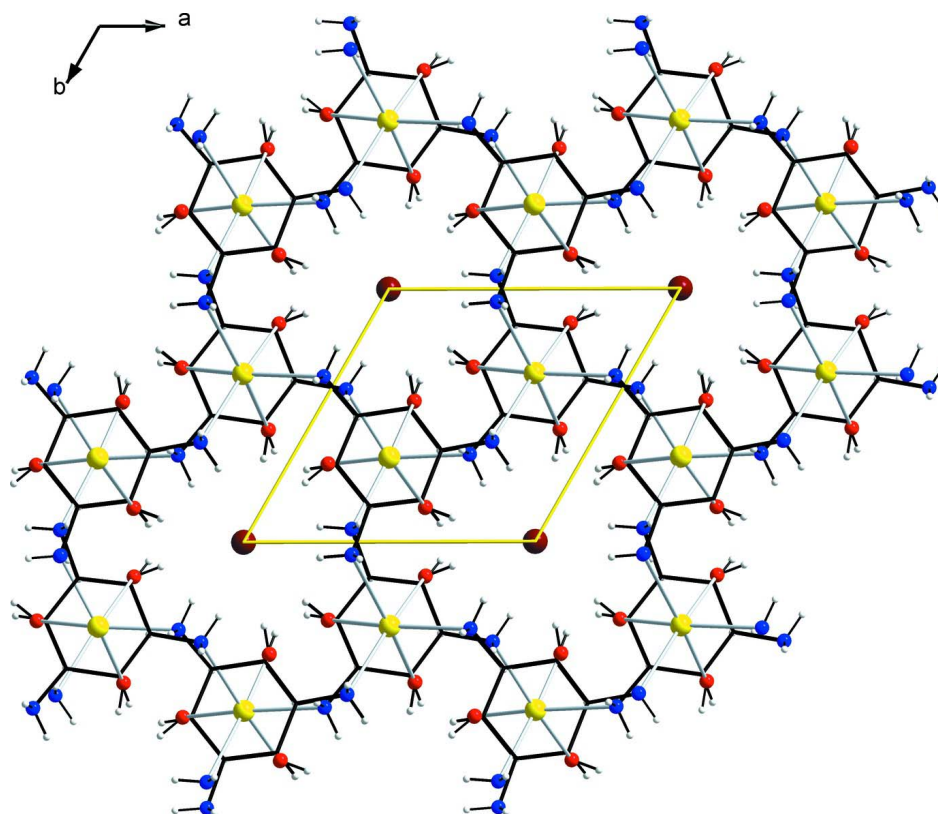

Figure 1

Ellipsoid plot and numbering scheme of a Br anion and an Na(taci) moiety together with the coordinating amino groups of three additional, neighbouring taci units. Displacement parameters are given at the 50% probability level.

Figure 2

Section of the extended network of the title compound viewed along the *c* axis.

Poly[[(*µ₄*-1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol)sodium] bromide]

Crystal data

[Na(C₆H₁₅N₃O₃)]Br	$D_x = 1.864$ Mg m⁻³
$M_r = 280.10$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Trigonal, $P31c$	Cell parameters from 99 reflections
Hall symbol: P 3 -2c	$\theta = 6.6–14.9°$
$a = 8.0491$ (10) Å	$\mu = 4.15$ mm⁻¹
$c = 8.8953$ (18) Å	$T = 153$ K
$V = 499.10$ (13) Å³	Block, colorless
$Z = 2$	$0.57 \times 0.45 \times 0.28$ mm
$F(000) = 284$	

Data collection

Siemens P4 diffractometer	690 independent reflections
Radiation source: fine-focus sealed tube	682 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.077$
ω scan	$\theta_{max} = 26.5°$, $\theta_{min} = 2.9°$
Absorption correction: integration	$h = -9{\rightarrow}9$
(*XPREP*; Bruker, 2008) using indexed faces	$k = -10{\rightarrow}10$
$T_{min} = 0.101$, $T_{max} = 0.331$	$l = -11{\rightarrow}11$
3954 measured reflections	3 standard reflections every 100 reflections
	intensity decay: none

Refinement

Refinement on F^2	H atoms treated by a mixture of independent
Least-squares matrix: full	and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.036$	$w = 1/[\sigma^2(F_o^2) + (0.015P)^2 + 2.P]$
$wR(F^2) = 0.078$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
690 reflections	$\Delta\rho_{max} = 0.42$ e Å^{-3}
59 parameters	$\Delta\rho_{min} = -0.55$ e Å^{-3}
3 restraints	Extinction correction: *SHELXL97* (Sheldrick,
Primary atom site location: structure-invariant	2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
direct methods	Extinction coefficient: 0.024 (4)
Secondary atom site location: difference Fourier	Absolute structure: Flack (1983), 340 Friedel
map	pairs
Hydrogen site location: inferred from	Absolute structure parameter: −0.03 (3)
neighbouring sites	

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Na	0.3333	0.6667	0.1288 (3)	0.0163 (6)
Br	1.0000	1.0000	0.22830 (19)	0.0196 (3)
N1	0.6544 (6)	0.6032 (6)	0.4871 (4)	0.0180 (8)
H1N	0.638 (9)	0.569 (8)	0.390 (2)	0.027 (15)*
H2N	0.768 (4)	0.707 (5)	0.508 (7)	0.024 (14)*
C1	0.4981 (6)	0.6393 (6)	0.5290 (5)	0.0141 (9)
H1	0.494 (8)	0.637 (8)	0.627 (5)	0.017*
C2	0.5288 (6)	0.8341 (6)	0.4803 (5)	0.0144 (9)
H2	0.638 (8)	0.926 (8)	0.526 (6)	0.017*
O1	0.5558 (4)	0.8645 (5)	0.3206 (3)	0.0155 (6)
H1O	0.6689	0.9049	0.2998	0.023 (15)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Na	0.0170 (9)	0.0170 (9)	0.0148 (13)	0.0085 (5)	0.000	0.000
Br	0.0178 (3)	0.0178 (3)	0.0232 (4)	0.00892 (14)	0.000	0.000
N1	0.0150 (18)	0.023 (2)	0.0201 (19)	0.0123 (16)	−0.0004 (16)	0.0018 (17)
C1	0.016 (2)	0.021 (2)	0.0103 (19)	0.0130 (19)	0.0007 (17)	0.0021 (18)
C2	0.016 (2)	0.015 (2)	0.0085 (18)	0.0055 (18)	−0.0035 (17)	−0.0003 (17)
O1	0.0137 (16)	0.0197 (16)	0.0122 (13)	0.0076 (14)	0.0021 (13)	0.0031 (12)

Geometric parameters (Å, º)

Na—O1[i]	2.409 (4)	N1—H2N	0.900 (10)
Na—O1	2.409 (4)	C1—C2	1.523 (6)
Na—O1[ii]	2.409 (4)	C1—C2[ii]	1.526 (6)
Na—N1[iii]	2.556 (4)	C1—H1	0.87 (5)
Na—N1[iv]	2.556 (4)	C2—O1	1.440 (5)
Na—N1[v]	2.556 (4)	C2—C1[i]	1.526 (6)
N1—C1	1.473 (5)	C2—H2	0.91 (6)
N1—Na[vi]	2.556 (4)	O1—H1O	0.8200
N1—H1N	0.895 (10)		
O1[i]—Na—O1	75.37 (13)	C1—N1—H2N	110 (4)
O1[i]—Na—O1[ii]	75.37 (13)	Na[vi]—N1—H2N	103 (4)
O1—Na—O1[ii]	75.37 (13)	H1N—N1—H2N	114 (5)
O1[i]—Na—N1[iii]	94.37 (12)	N1—C1—C2	114.6 (4)
O1—Na—N1[iii]	164.19 (15)	N1—C1—C2[ii]	110.1 (4)
O1[ii]—Na—N1[iii]	90.53 (12)	C2—C1—C2[ii]	113.7 (4)
O1[i]—Na—N1[iv]	90.53 (12)	N1—C1—H1	106 (4)
O1—Na—N1[iv]	94.37 (12)	C2—C1—H1	107 (4)
O1[ii]—Na—N1[iv]	164.19 (15)	C2[ii]—C1—H1	105 (4)
N1[iii]—Na—N1[iv]	97.78 (14)	O1—C2—C1	112.9 (3)
O1[i]—Na—N1[v]	164.19 (15)	O1—C2—C1[i]	109.1 (4)
O1—Na—N1[v]	90.53 (12)	C1—C2—C1[i]	110.8 (4)
O1[ii]—Na—N1[v]	94.37 (12)	O1—C2—H2	107 (3)
N1[iii]—Na—N1[v]	97.78 (14)	C1—C2—H2	108 (4)
N1[iv]—Na—N1[v]	97.78 (14)	C1[i]—C2—H2	109 (3)
C1—N1—Na[vi]	116.3 (3)	C2—O1—Na	126.0 (3)
C1—N1—H1N	107 (4)	C2—O1—H1O	109.5
Na[vi]—N1—H1N	106 (4)	Na—O1—H1O	114.4
Na[vi]—N1—C1—C2	162.1 (3)	C1[i]—C2—O1—Na	−65.3 (4)
Na[vi]—N1—C1—C2[ii]	−68.3 (4)	O1[i]—Na—O1—C2	41.5 (3)
N1—C1—C2—O1	57.6 (5)	O1[ii]—Na—O1—C2	−36.9 (3)
C2[ii]—C1—C2—O1	−70.2 (5)	N1[iii]—Na—O1—C2	−9.3 (6)
N1—C1—C2—C1[i]	−179.8 (3)	N1[iv]—Na—O1—C2	130.9 (3)
C2[ii]—C1—C2—C1[i]	52.5 (6)	N1[v]—Na—O1—C2	−131.3 (3)
C1—C2—O1—Na	58.3 (5)		

Symmetry codes: (i) −*y*+1, *x*−*y*+1, *z*; (ii) −*x*+*y*, −*x*+1, *z*; (iii) *x*−*y*, −*y*+1, *z*−1/2; (iv) −*x*+1, −*x*+*y*+1, *z*−1/2; (v) *y*, *x*, *z*−1/2; (vi) *y*, *x*, *z*+1/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···Br	0.82	2.46	3.278 (3)	175
N1—H2*N*···Br[vi]	0.90 (1)	2.91 (3)	3.696 (4)	147 (5)

Symmetry code: (vi) *y*, *x*, *z*+1/2.