

Monoclinic
 $P2_1$
 $a = 8.056 (1) \text{ \AA}$
 $b = 13.552 (1) \text{ \AA}$
 $c = 10.822 (1) \text{ \AA}$
 $\beta = 111.53 (1)^\circ$
 $V = 1099.1 (2) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.210 \text{ Mg m}^{-3}$
 D_m not measured

Cell parameters from 25 reflections
 $\theta = 10\text{--}15^\circ$
 $\mu = 0.077 \text{ mm}^{-1}$
 $T = 300 \text{ K}$
 Prism
 $0.5 \times 0.3 \times 0.2 \text{ mm}$
 Colourless

Data collection

Rigaku AFC-5 diffractometer
 θ - 2θ scans
 Absorption correction: none
 2817 measured reflections
 2638 independent reflections
 1542 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.014$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = 0 \rightarrow 10$
 $k = 0 \rightarrow 17$
 $l = -14 \rightarrow 14$
 3 standard reflections every 100 reflections
 intensity decay: none

Refinement

Refinement on F
 $R = 0.056$
 $wR = 0.065$
 $S = 1.00$
 2263 reflections
 270 parameters
 H atoms riding
 $w = 1/[\sigma^2(F) + 0.0009F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.01$
 $\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 3. Selected geometric parameters (\AA , $^\circ$) for (II)

O1—C5	1.357 (5)	C5—C14	1.371 (5)
O2—C24	1.348 (5)	C14—C15	1.497 (5)
N3—C25	1.476 (5)	C15—C24	1.368 (6)
N4—C30	1.491 (6)	C23—C24	1.422 (6)
C5—C6	1.416 (5)	C25—C30	1.512 (6)
O1—C5—C6	115.2 (4)	O2—C24—C15	124.5 (4)
O1—C5—C14	124.2 (3)	O2—C24—C23	115.2 (4)
C5—C14—C15	120.7 (4)	N3—C25—C30	109.2 (4)
C14—C15—C24	120.9 (3)	N4—C30—C25	109.9 (4)
C5—C14—C15—C24	79.4 (5)	N3—C25—C30—N4	-63.9 (4)

Table 4. Hydrogen-bonding geometry (\AA , $^\circ$) for (II)

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
O1—H1 \cdots N3 ⁱ	0.960	1.845	2.737 (4)	153.2
O2—H2 \cdots N4 ⁱⁱ	0.960	1.877	2.813 (4)	164.4

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, 1 - z$; (ii) $2 - x, y - \frac{1}{2}, 1 - z$.

The refinements were carried out based on all reflections without $|F_o| = 0$. The threshold $I > 2\sigma(I)$ was used only for calculation of the R factor. The H atoms bonded to N and O atoms were located from difference syntheses and the positions of those bonded to C atoms were calculated geometrically. A riding model (N—H, O—H and C—H 0.96 \AA) was used for all H atoms in (I) and (II). In (I), the toluene molecule lies near the twofold axis, showing orientational disorder. The position of the C16 atom was fixed on the twofold axis, and the other six C atoms, C17—C22, were introduced with site-occupation factors of 50%.

For both compounds, data collection: *AFCIMSC Diffractometer Control System* (Rigaku Corporation, 1993); cell refinement: *AFCIMSC Diffractometer Control System*; data re-

duction: local programs; program(s) used to solve structures: *CRYSTAN-GM* (Edwards *et al.*, 1996); program(s) used to refine structures: *CRYSTAN-GM*; molecular graphics: *CRYSTAN-GM*; software used to prepare material for publication: *CRYSTAN-GM*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1035). Services for accessing these data are described at the back of the journal.

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1,3-Diamino-5-ammonio-1,3,5-trideoxy-cis-inositol iodide

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Abstract

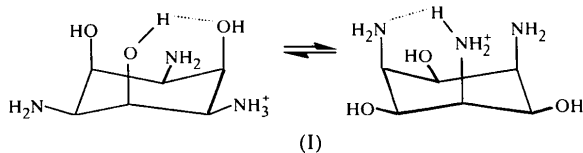
The cation in 1,3-diamino-5-ammonio-1,3,5-trideoxy-cis-inositol iodide (HtaciI, $\text{C}_6\text{H}_{16}\text{N}_3\text{O}_3^+\text{I}^-$) adopts a chair conformation with the three N atoms in equatorial positions and the three O atoms in axial positions. The Htaci⁺ cation displays an intramolecular O—H \cdots O hydrogen bond. A complex network of N—H \cdots O and O—H \cdots N hydrogen bonds generates a complex structure with channels along [001] which are filled with the iodide counter-ions coordinated by N—H \cdots I hydrogen bonds.

Comment

The inositols (cyclohexane-1,2,3,4,5,6-hexols) are widespread in biological systems and play an important

role as precursors and storage forms for messenger molecules that mediate calcium release in cells (Shears, 1989; Majerus *et al.*, 1988). As a consequence, the binding of Ca^{2+} and of other metal cations to the different isomers of inositol and inositol phosphates has been the subject of various investigations (Angyal & Hickman, 1975; Bieth *et al.*, 1990; Schmitt *et al.*, 1992).

Among the eight possible diastereomeric forms, *cis*-inositol showed a particularly high affinity towards metal ions. The crystal structure of its monohydrate has been reported recently (Freeman *et al.*, 1996). The metal binding properties of this compound can be further enhanced by replacing three of the six hydroxy groups by amino groups. The resulting 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (*taci*) proved to be a versatile ligand towards a variety of metal cations (Ghisletta *et al.*, 1998).



However, in contrast to *cis*-inositol, the two possible chair conformations of *taci*, with either three hydroxy or three amino groups in the axial positions, are of different energy. Since the three axial substituents represent a

pre-organized donor set for metal binding, it is of particular interest to know which of the two conformers will predominate. A variety of different effects such as 1,3-diaxial repulsion, intra- and intermolecular hydrogen bonding, and electrostatic interactions in the protonated forms account for this difference in energy. It has been shown that the form with three axial hydroxy groups is exclusively formed for the free *taci* and the triply protonated H_3taci^{3+} species (Hegetschweiler *et al.*, 1993; Ghisletta *et al.*, 1992). This finding can be explained by the poor intramolecular N—H...N hydrogen bonds in the former and the strong electrostatic repulsion energy between the positively charged ammonium groups in the latter species. However, for the partially protonated $Htaci^+$ and H_2taci^{2+} , intramolecular hydrogen bonds between an ammonium group and an amino group should result in a significant stabilization of the conformer with the three N atoms in axial positions and it is thus less clear which conformer would be the more stable.

The $Htaci^+$ cation, (I), of the title compound exhibits a chair conformation with the O atoms in axial and the N atoms in equatorial positions. All C—C, C—O, C—N and X—H distances, as well as all bond angles, fall in the expected ranges derived from other aminoinositols (Reiß *et al.*, 1998). With regard to hydrogen-bond formation, the hydroxy and amino groups may act either as proton donors or acceptors. The iodide

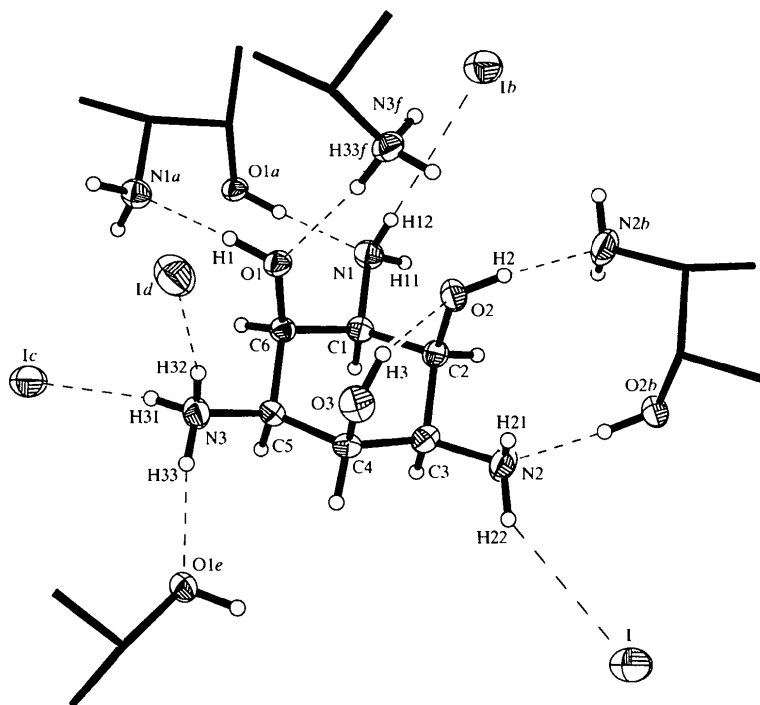


Fig. 1. Diagram showing the $Htaci^+$ cation with its hydrogen-bonding environment. Displacement ellipsoids are at the 50% probability level. For clarity, only those parts of the neighbouring cations that are relevant to hydrogen bonding are shown. [Symmetry codes: (a) $1-x, -1-y, 2-z$; (b) $1-x, -1-y, 3-z$; (c) $x, y, -1+z$; (d) $x+\frac{1}{2}, -\frac{1}{2}-y, -\frac{1}{2}+z$; (e) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{5}{2}-z$; (f) $\frac{3}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$.]

anion is an exclusive acceptor and the ammonium group an exclusive donor. Out of the nine different donor-acceptor combinations, only five were observed in this structure. The iodide anion interacts with the H atoms of the amino groups (N1 and N2) and with the two H atoms of the ammonium group (N3). The ammonium group also acts as a donor towards a hydroxy group (O1). In addition, two hydroxy groups (O1 and O2) form hydrogen bonds with the NH_2 groups of two adjacent molecules. Such $\text{O}-\text{H}\cdots\text{NH}_2$ interactions have recently been described as a basic structural motif for alcohol-amine adducts (Ermer & Eling, 1994; Hanessian *et al.*, 1995). The third OH group (O3) forms an intramolecular hydrogen bond to a neighbouring hydroxy group, a feature that is well known for amino-substituted inositols (Schmalle & Hegetschweiler, 1996) and is also predicted for the inositols themselves, as indicated by some recently performed *ab initio* calculations (Liang *et al.*, 1994). The entire hydrogen-bonding network can be separated into two different structural motifs, as follows:

(i) the Htaci^+ cations form a zigzag chain along [001]. The symmetry-equivalent cations are connected to each other by two of the above-mentioned $\text{O}-\text{H}\cdots\text{NH}_2$ bonds (Fig. 2 and Table 1). In terms of the graph-set analysis, this motif can be classified as $R_2^2(10)$ (Etter, 1990).

(ii) Each of these zigzag chains is further hydrogen bonded *via* $\text{N}-\text{H}\cdots\text{O}$ bonds to four neighbouring chains through the NH_3^+ group (N3) and an OH group (O1) (Fig. 1, e.g. $\text{N3}-\text{H33}\cdots\text{O1e}$). The resulting infinite array can be described as a structure with channels

along [001] that are centrosymmetrically filled with the iodide counter-ions coordinated by $\text{N}-\text{H}\cdots\text{I}$ hydrogen bonds (Fig. 2 and Table 1).

According to the donor-acceptor distances, the strongest hydrogen bonds correspond to the intermolecular $\text{N}-\text{H}\cdots\text{O}$ interactions. Intramolecular hydrogen bonding between hydroxy groups in a 1,3-diaxial arrangement was also observed in the title compound, however, as mentioned above, it is to be expected that the reversed chair conformation would also be stabilized by an $\text{N}-\text{H}\cdots\text{N}$ interaction between the axial ammonium and amino groups (see Scheme). The predominance of the conformation with axial hydroxy groups for the title compound must thus be attributed to the more favourable intermolecular interactions. It is likely that similar interactions are also present in aqueous solution, where water molecules may replace the alcoholic hydroxy groups of a neighbouring Htaci^+ cation. The result of our present study thus underlines further the importance of such intermolecular interactions in discussing the conformation of the inositols and related compounds (Liang *et al.*, 1994).

Experimental

1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol (100 mg, 0.56 mmol) was dissolved in 10 ml of methanol. Potassium iodide (44.5 mg, 0.28 mmol) dissolved in 1 ml of methanol was then added. The solution was evaporated *in vacuo* to a total volume of about 8 ml. Besides the main product, $[\text{KH}(\text{taci})_2]_2\cdot\text{H}_2\text{O}$, crystals of HtaciI grew at room temperature within about two weeks.

Crystal data

$\text{C}_6\text{H}_{16}\text{N}_3\text{O}_3\cdot\text{I}^-$
 $M_r = 305.12$
 Monoclinic
 $P2_1/n$
 $a = 10.2987(8) \text{ \AA}$
 $b = 10.1307(6) \text{ \AA}$
 $c = 11.1151(8) \text{ \AA}$
 $\beta = 115.338(7)^\circ$
 $V = 1048.11(13) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.934 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from
 5000 quasi-centered
 reflections automatically
 selected from the data set
 $\mu = 3.040 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Isometric
 $0.8 \times 0.5 \times 0.4 \text{ mm}$
 Colourless

Data collection

Stoe IPDS diffractometer
 ϕ scans
 Absorption correction:
 numerical (*X-RED*; Stoe
 & Cie, 1996)
 $T_{\min} = 0.210$, $T_{\max} = 0.398$
 6611 measured reflections
 1818 independent reflections
 1718 reflections with
 $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$
 $\theta_{\text{max}} = 25^\circ$
 $h = -12 \rightarrow 12$
 $k = -12 \rightarrow 12$
 $l = -13 \rightarrow 13$
 Standard reflections: a
 max. of 50 per image
 intensity decay: none

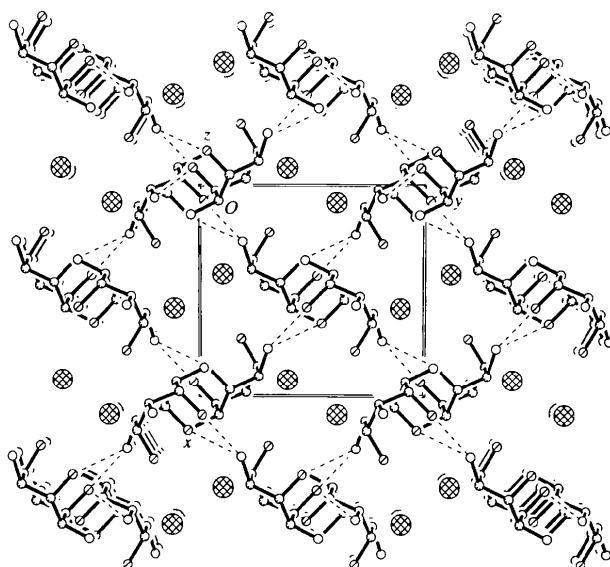


Fig. 2. Diagram showing the nearly tetragonal packing of the Htaci^+ cations along [001], with the iodide counter-ions centrosymmetrically occupying the channels (H atoms have been omitted for clarity).

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\max} = 0.009$
$R[F^2 > 2\sigma(F^2)] = 0.025$	$\Delta\rho_{\max} = 1.155 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.058$	$\Delta\rho_{\min} = -0.875 \text{ e } \text{\AA}^{-3}$
$S = 1.079$	Extinction correction:
1818 reflections	<i>SHELXL97</i>
177 parameters	Extinction coefficient:
H atoms: see below	0.0041 (6)
$w = 1/[\sigma^2(F_o^2) + (0.017P)^2 + 2.630P]$	Scattering factors from
where $P = (F_o^2 + 2F_c^2)/3$	<i>International Tables for Crystallography</i> (Vol. C)

Table 1. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1...N1 ⁱ	0.895 (10)	1.843 (12)	2.730 (3)	171 (4)
O2—H2...N2 ⁱⁱ	0.892 (10)	1.897 (15)	2.765 (4)	164 (4)
O3—H3...O2	0.890 (10)	2.12 (3)	2.865 (3)	140 (4)
N1—H12...I ⁱⁱⁱ	0.894 (10)	3.01 (2)	3.782 (3)	145 (3)
N3—H31...I ⁱⁱⁱⁱ	0.892 (10)	2.914 (13)	3.788 (3)	167 (3)
N3—H32...I ^v	0.896 (10)	2.944 (15)	3.807 (3)	162 (3)
N3—H33...O ^v	0.896 (10)	2.019 (12)	2.908 (3)	171 (4)
N2—H22...I	0.894 (10)	2.96 (3)	3.729 (3)	145 (4)

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $1-x, 1-y, 1-z$; (iii) $x, y, z-1$; (iv) $\frac{1}{2}+x, \frac{3}{2}-y, z-\frac{1}{2}$; (v) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

400 exposures were taken in the $0-360^\circ$ φ range with a crystal-to-detector distance of 60 mm and an exposure time of 1 min. Constant-circle profiles (17 pixels) without allowing overlap were used for integration, yielding a 92.8% completeness of data. A numerical absorption correction (Stoe & Cie, 1996) was applied using optically determined crystal faces (Stoe & Cie, 1997). The refined maximum and minimum difference electron densities of 1.155 and $-0.875 \text{ e } \text{\AA}^{-3}$ were located only 0.79 and 0.72 \AA from the iodide counter-ion, respectively. The atomic coordinates of all H atoms were taken from difference Fourier syntheses. The atomic coordinates and individual U_{iso} values were refined for the two NH₂, the NH₃ and the OH group with the X—H distances restrained to plausible values. The atomic coordinates of H atoms bonded to C atoms were refined with the C—H distance restrained to a plausible value and the U_{iso} value set to $1.2U_{\text{eq}}(\text{C})$.

Data collection: *IPDS Software* (Stoe & Cie, 1997). Cell refinement: *IPDS Software*. Data reduction: *IPDS Software*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997b). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1992). Software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1311). Services for accessing these data are described at the back of the journal.

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Intramolecular N—H...O, intermolecular O—H...O, C—H...O and Csp^3 —H... π_{arene} interactions in (2*S*)-2-[(2*R*)-2-hydroxy-2-phenylethanoyl]amino}-4-methylpentanoic acid

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Abstract

The title compound, C₁₄H₁₉NO₄, forms a hydrogen-bonded network in the solid state, consisting of one intramolecular N—H...O [N...O 2.569 (3) \AA] and two intermolecular O—H...O=C [O...O 2.704 (2) and