intermolecular H-atom transfer from O(3*B*) to O(1*B*) is easily accomplished.

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References

BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142–146.

DECLERCQ, J. P., GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1973). *Acta Cryst.* A**29**, 231–234.

DELMAS, M., GORRICHON, J. P., GASET, A., ROQUES, R., DECLERCQ, J. P. & GERMAIN, G. (1981). *Acta Cryst.* B**37**, 621–625.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

JOHNSON, C. K. (1976). *ORTEP* II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

KOBAYASHI, Y. & IITAKA, Y. (1977). *Acta Cryst.* B**33**, 925–928.

MARCH, J. (1977). In *Advanced Organic Chemistry*, 2nd ed. New York: McGraw-Hill.

RUDMAN, R. (1981). *Trans. Am. Crystallogr. Assoc.* **17**, 31–41.

SAKE GOWDA, D. S. & RUDMAN, R. (1982). *J. Chem. Phys.* **77**, 4671–4677.

SANTORO, E. & CHIAVARINI, M. (1978). *J. Chem. Soc. Perkin Trans.* 2, pp. 189–192.

SHOJA, M. & WHITE, J. G. (1979). *Acta Cryst.* B**35**, 206–208.

SILVER, L. & RUDMAN, R. (1970). *J. Phys. Chem.* **74**, 3134–3139.

WENZEL, J. (1976). *J. Non-Cryst. Solids*, **21**, 263–270.

Acta Cryst. (1983). C**39**, 1267–1271

Polymorphism of Crystalline Poly(hydroxymethyl) Compounds. VIII.* Structures of the Tris(hydroxymethyl)aminomethane Hydrogenhalides,† $(HOH_2C)_3CNH_3^+.X^-$ (X=F,Cl,Br,I)

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Abstract. Three of the title compounds, TrisH$^+$.X^- (X = F,Cl,Br), are isostructural: rhombohedral, $R\bar{3}$ (H), $Z = 6$. At 294 K the crystal data are: TrisH$^+$.F$^-$: $M_r = 141{\cdot}2$, $a = 7{\cdot}123$ (6), $c = 22{\cdot}47$ (2) Å, $V = 987{\cdot}3$ Å^3, $D_x = 1{\cdot}425$, $D_m = 1{\cdot}418$ Mg m^{-3}, μ(Cu $K\alpha$) = 1·21 mm^{-1} (only crystal data were obtained for this compound). TrisH$^+$.Cl$^-$: $M_r = 157{\cdot}6$, $a = 7{\cdot}569$ (1), $c = 24{\cdot}694$ (4) Å, $V = 1225{\cdot}2$ Å^3, $D_x = 1{\cdot}278$, $D_m = 1{\cdot}275$ Mg m^{-3}, μ(Cu $K\alpha$) = 3·78 mm^{-1}, $F(000) = 504$; final $R = 0{\cdot}072$ for 266 unique reflections. TrisH$^+$.Br$^-$: $M_r = 202{\cdot}1$, $a = 7{\cdot}701$ (2), $c = 25{\cdot}447$ (8) Å, $V = 1306{\cdot}9$ Å^3, $D_x = 1{\cdot}540$, $D_m = 1{\cdot}537$ Mg m^{-3}, μ(Cu $K\alpha$) = 6·74 mm^{-1}, $F(000) = 612$; final $R = 0{\cdot}032$ for 508 unique reflections. The fourth title compound, TrisH$^+$.I$^-$, $M_r = 249{\cdot}1$, is cubic, $I2_13$, $a = 11{\cdot}627$ (3) Å, $V = 1571{\cdot}8$ Å^3, $Z = 8$, $D_x = 2{\cdot}105$, $D_m = 2{\cdot}089$ Mg m^{-3}, μ(Cu $K\alpha$) = 32·28 mm^{-1} at 294 K, $F(000) = 960$; final $R = 0{\cdot}056$ for 210 unique reflections. All data were collected with Ni-filtered Cu K radiation ($\lambda_{K_{\alpha 1}} = 1{\cdot}54051$ Å). In the chloride and bromide structures, the halide anions lie on both sides of a hydrogen-bonded double layer of TrisH$^+$ cations formed with the $-NH_3^+$ moieties facing toward each other, such that the $X\cdots$N distances are greater than the X$\cdots$C(C) (central carbon) distances. The resulting anion–anion repulsion explains the unusually low density and high cleavability of these crystals. The iodide structure has a normal density with $X\cdots$N less than $X\cdots$C(C), but is distinguished by crystallizing in a space group rarely found for an organic compound.

Introduction. Many compounds with approximately spherical molecules undergo solid–solid phase transitions, with the phase stable just below the melting point referred to as the orientationally disordered, or plastic, crystalline state. As part of our continuing effort to define the sphericity of the molecular envelope needed for the formation of the plastic state, a series of poly(hydroxymethyl) compounds is being investigated. The variation of the hydrogen-bonding schemes in these compounds, as a function of molecular substituents, is also of interest.

The structures of the ordered and plastic phases of tris(hydroxymethyl)aminomethane were reported previously (Eilerman & Rudman, 1980). This compound is a widely used buffering agent, commonly known as Tris. The possibility that the Tris–hydrogen-halide (TrisH$^+$.X^-) salts also form orientationally disordered phases (in a manner analogous to NH_4Cl) was investigated and is reported here. A preliminary report on TrisH$^+$.Cl$^-$ was reported earlier (Rudman, Lippman & Eilerman, 1979).

Experimental. Single crystals of the TrisH$^+$.X^- compounds were prepared by crystallizing them (by slow

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[*] Part VII: Eilerman, Lippman & Rudman (1983).

[†] (1,3-Dihydroxy-2-hydroxymethyl-2-propyl)ammonium halides.

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evaporation) from a solution of Tris dissolved in the appropriate concentrated or dilute (1:1 aqueous, by volume) hydrohalic acid, followed by recrystallization from a very dilute aqueous HX solution. Crystals of all the compounds were transparent, forming white powders when ground; TrisH$^+$.I$^-$ grew both as flakes and needles, the others grew in hexagonal platelets. Examination with a polarizing microscope revealed that TrisH$^+$.X^- (X = F,Cl,Br) crystals were uniaxial and TrisH$^+$.I$^-$ crystals were isotropic. A Syntex $P2_1$ diffractometer was used for all data collection.

TrisH$^+$.F$^-$: D_m from flotation in xylene–carbon tetrachloride mixture; lattice parameters from 12 reflections (11° $< 2\theta <$ 58°). All crystals examined had ω-scan FWHM > 2° and were twinned; intensity data not collected.

TrisH$^+$.Cl$^-$: D_m from flotation in xylene–carbon tetrachloride mixture; irregularly shaped crystal; maximum dimension 0·2 mm; lattice parameters from 14 reflections (11° $< 2\theta <$ 27°). Data collection: 1628 (full sphere to $2\theta = 100°$, $h_{\rm max} = k_{\rm max} = 7$, $l_{\rm max} = 24$), three standards (21$\bar{2}$,101,1$\bar{2}$0) every 25 reflections (2% variation), 272 independent, 266 with $F^2 > 3\sigma(F^2)$, Lp correction applied; Patterson and ΔF methods, anisotropic full matrix, H (from calculation and ΔF synthesis) fixed isotropic, based on F, final cycle: 41 parameters, $R = 0{\cdot}072$, $R_w = 0{\cdot}111$ (defined in Eilerman & Rudman, 1980), $\Delta/\sigma_{\rm max} = 0{\cdot}28$, $S = 6{\cdot}9$, $w^{-1} = \sigma^2(F) + (pF)^2$, $p = 0$, $\sigma(F) = \sigma(F^2)/(2F)$, $\sigma(F^2)$ based on counting statistics; final ΔF map featureless (maximum height 0·18 e Å^{-3}), secondary-extinction value of 1·71 (31). Calculations performed using Adelphi University Library of Crystallographic Programs, with atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

TrisH$^+$.Br$^-$: D_m from flotation in xylene–carbon tetrachloride mixture; rectangular plate, 0·27 × 0·14 × 0·056 mm, lattice parameters from 15 reflections (14° $< 2\theta <$ 27°), ω-scan FWHM = 0·15°. Data collection: 1157 ($h,k,\pm l$ up to $2\theta = 136°$, $h_{\rm max} = 8$, $k_{\rm max} = 8$, $|l_{\rm max}| = 31$), automatic recentering every 200 reflections, four standard reflections (10$\bar{2}$, 110, 1$\bar{1}$2, 2$\bar{1}\bar{3}$) every 46 reflections (2·3% variation), 518 independent, 508 with $F > 3\sigma(F)$, Lp and empirical absorption (11 curves, transmission-factor range 1–0·639) corrections applied; refined as isostructural with TrisH$^+$.Cl$^-$, anisotropic full matrix, H (from calculation and ΔF synthesis) isotropic, based on F, final cycle: 44 parameters, $\Delta/\sigma_{\rm max} = 0{\cdot}06$, $R = 0{\cdot}032$, $R_w = 0{\cdot}050$ (for all data $R = 0{\cdot}033$, $R_w = 0{\cdot}051$), $S = 1{\cdot}595$, w as for TrisH$^+$.Cl$^-$ with $p = 0{\cdot}030$, final ΔF synthesis featureless aside from some residual electron density (approximately $\frac{1}{12}$ that of the Br peak) in the vicinity of the Br peak. Lattice parameters calculated with *CELREF*, all other calculations performed with the Syntex (1973) *XTL* programs [which utilize atomic scattering factors based on the analytical expressions found in *International Tables for X-ray Crystallography* (1974)]. Anomalous-dispersion correction for Br applied.

TrisH$^+$.I$^-$: D_m from flotation in methyl iodide–carbon tetrachloride mixture; irregularly shaped crystal, maximum dimension 0·11 mm; color initially transparent, changing to reddish-brown after 4 d exposure to X-rays; lattice parameters from 18 reflections ($15 < 2\theta < 105°$). Data collection: 627 (one octant, $2\theta_{\rm max} = 115°$, $h_{\rm max} = 12$), four standard reflections (051, 134, 781, 842) every 45 reflections (irregular effect noted: 051 increased in intensity nearly 19%, others showed a slight increase and then levelled off, also note color change described above, no decay-correction applied), 210 independent (all used in refinement), Lp and empirical absorption (12 curves, transmission-factor range 1–0·386) corrections applied; Patterson and ΔF synthesis, anisotropic full matrix for non-hydrogen atoms, methylene H positions calculated but not refined with fixed isotropic B, other H atoms not found, final cycle: 28 parameters, $\Delta/\sigma_{\rm max} = 0{\cdot}00$, $R = 0{\cdot}056$, $R_w = 0{\cdot}074$, $S = 4{\cdot}64$, w as for TrisH$^+$.Cl$^-$ with $p = 0{\cdot}015$, final ΔF synthesis featureless. Programs as for TrisH$^+$.Br$^-$; anomalous-dispersion correction for iodine applied.

The structure of TrisH$^+$.Cl$^-$ was initially treated as a general triclinic system with $Z = 2$. Data were collected and the structure was solved in $P\bar{1}$, with one complete molecule in the asymmetric unit. The resulting molecular model showed threefold symmetry consistent with two centrosymmetric rhombohedral space groups: $R\bar{3}$ and $R\bar{3}m$. The positional parameters found in the triclinic setting were transformed to the hexagonal setting of the rhombohedral unit cell using the inverse transpose of the triclinic→hexagonal transformation matrix (101/00$\bar{1}$/132). Since the C(1) and O atoms were not in special positions, refinement was continued in $R\bar{3}$. In the case of TrisH$^+$.I$^-$, only three space groups are consistent with the observed systematic absences and the molecular site symmetry. The first Patterson map was prepared in $I23$, where it was immediately apparent that the peaks were consistent with a structure in $I2_13$. Further ΔF syntheses and least-squares refinement were continued in $I2_13$.

All of the TrisH$^+$.X^- molecules lie on threefold axes, so that the asymmetric unit is limited to X, N, and C(C) (the central carbon atom) lying along the threefold axis, with one H(N) and one hydroxymethyl group ($-$CH$_2$OH) off the axis; the final positional parameters and equivalent isotropic thermal parameters are listed in Table 1.*

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* Lists of structure factors, anisotropic thermal parameters, bond angles, and H-atom bond lengths have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38627 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters in fractional coordinates for atoms in* TrisH$^+$.X^- (X = Cl, Br, I) ($\times 10^5$ *for* X, $\times 10^4$ *for* O, N, C) *and their* $B_{\rm eq}$ ($=\frac{1}{3}\sum_i\sum_j B_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j$) *values, with e.s.d.'s in parentheses*

(*a*) Non-hydrogen atoms

	Cl	Br	I
X x	0	0	4271 (9)
y	0	0	x
z	11136 (5)	11303 (2)	x
$B_{\rm eq}$ (Å^2)	3·05	2·62	2·72
O x	3169 (4)	3059 (3)	4315 (8)
y	3258 (3)	3217 (3)	1385 (9)
z	2837 (1)	2868 (1)	2405 (11)
$B_{\rm eq}$(Å^2)	3·55	2·66	2·34
N x	0	0	3434 (10)
y	0	0	x
z	3320 (2)	3338 (2)	x
$B_{\rm eq}$(Å^2)	2·63	2·16	1·42
C(C)x	0	0	2690 (12)
y	0	0	x
z	2724 (2)	2749 (2)	x
$B_{\rm eq}$(Å^2)	2·78	2·34	1·52
C(1) x	1271 (5)	1272 (4)	3125 (15)
y	2207 (5)	2176 (4)	1465 (14)
z	2523 (1)	2565 (1)	2741 (14)
$B_{\rm eq}$(Å^2)	3·19	2·63	1·84

(*b*) Hydrogen atoms (x,y,z $\times 10^3$ for X = Cl, Br, $\times 10^4$ for X = I)

	Cl	Br	I
H(1) x	56 (6)	50 (4)	3020†
y	288 (5)	289 (4)	1157
z	261 (2)	259 (1)	3535
B(Å^2)	4·0*	1·80 (44)	3·0*
H(2) x	151 (5)	145 (4)	2635†
y	220 (5)	207 (4)	991
z	211 (2)	224 (1)	2199
B(Å^2)	4·0*	3·35 (60)	3·0*
H(N) x	89 (5)	117 (5)	‡
y	12 (6)	15 (4)	
z	343 (1)	346 (1)	
B(Å^2)	4·0*	3·88 (64)	
H(O) x	320 (5)	368 (5)	‡
y	314 (6)	310 (5)	
z	254 (2)	275 (1)	
B(Å^2)	4·0*	3·47 (82)	

* Not refined.
† Calculated position, not refined.
‡ Not found.

Differential scanning calorimetry (*DSC*). A Perkin Elmer DSC-1B calorimeter was used to investigate the thermal behavior of the TrisH$^+$.X^- compounds. TrisH$^+$.F$^-$ was studied from 230 to 400 K, while the other three were examined over the temperature interval 140 to 470 K. No phase transitions were observed for any of the compounds. The F$^-$ salt decomposes at 390 K and the Cl$^-$ salt at 421 K (lit. value 422 K), while the Br$^-$ salt melts at 413 K and the I$^-$ salt at 463 K (lit. value 462 K).

During the first heating scan of the F$^-$ and Cl$^-$ salts, only one endotherm is observed, corresponding to the temperature of (partial) decomposition. On subsequent runs of the same sample, several other peaks, in addition to the decomposition peak, appear on the thermogram. The Br$^-$ and I$^-$ salts demonstrate normal, reproducible melting points with no indication of any decomposition. On the other hand, visual observation of the melting behavior of these compounds in a standard melting-point apparatus offers conflicting observations. The F$^-$ and Cl$^-$ salts do not visibly decompose and melt at temperatures somewhat higher than those found in the DSC; the Br$^-$ salt softens and shifts position (possibly indicating a solid–solid phase transition) at 413 K, but actually melts at 444 K; while the white I$^-$ salt becomes discolored to form a reddish-brown liquid, which darkens in color upon subsequent re-melting. It is noted that Tris is known to be thermally stable and forms a plastic crystal at 407·3 K before melting at 446·0 K (Eilerman & Rudman, 1980). The discrepancy between the DSC and visual observations may be due to the pressure that is built up in the hermetically sealed DSC Al sample pan. Any HX vapor that is released as TrisH$^+$.X^- is heated would be trapped in the DSC sample pan and result in the formation of equilibrium between TrisH$^+$.X^-, HX, and Tris, while in the open m.p. tube, HX can escape. The sensitivity of thermal decomposition to pressure will be investigated. However, our present understanding is that, contrary to the behavior of the ammonium halides (Parsonage & Staveley, 1978), the TrisH$^+$.X^- compounds melt or decompose before undergoing any solid–solid phase transitions.

Discussion. *Tris*H$^+$ *ion*. From the three intramolecular distances observed in the compounds listed in Table 2, it is apparent that the C—N distance is lengthened when the N atom is quadrivalent, while the C—C and C—O distances do not change appreciably. The exception to this appears to be TrisH$^+$.Cl$^-$, where a short C—N distance is counterbalanced by a long C—O distance. This may be due to a strong Cl$^-\cdots$O interaction (see below) or it may be an artifact of the refinement. The TrisH$^+$ ions in TrisH$^+$.X^- have threefold symmetry (Fig. 1), while in Tris, the molecules lie on pseudo-mirror planes.

Table 2. *Intramolecular distances* (Å) *involving non-hydrogen atoms in Tris*H$^+$.X^- *and related compounds*

The C—C and C—O distances for the last three compounds are average values; e.s.d.'s are in parentheses.

	C(C)—N	C(C)—C(1)	C(1)—O	Reference
TrisH$^+$.Cl	1·471 (8)	1·535 (4)	1·468 (5)	(*a*)
TrisH$^+$.Br	1·498 (6)	1·532 (3)	1·425 (4)	(*a*)
TrisH$^+$.I	1·497 (11)	1·512 (17)	1·440 (20)	(*a*)
TrisH$^+$ ADP salt	1·498 (8)	1·531 (12)	1·423 (11)	(*b*)
Tris*	1·492 (6)	1·533 (6)	1·429 (6)	(*c*)
Tris	1·469 (2)	1·526 (2)	1·420 (2)	(*d*)

References: (*a*) this work; (*b*) Shakked, Viswamitra & Kennard (1980); (*c*) Ivarsson (1982); (*d*) Eilerman & Rudman (1980).

* As a ligand through O and N.

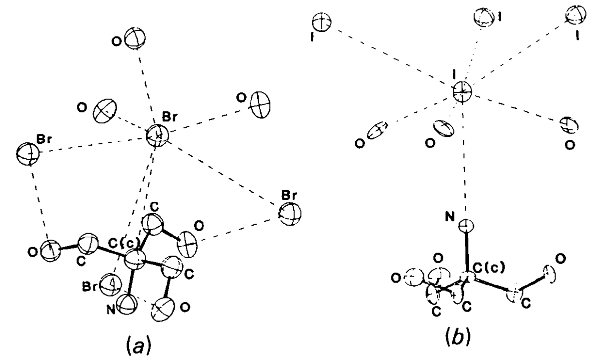

Fig. 1. TrisH$^+$ cations and sevenfold environment of halide ions; the closest *X*, O, and TrisH$^+$ are shown. (*a*) TrisH$^+$.Br$^-$: the Br$\cdots$C(*C*) distance is shown. Note that the nearest-neighbor Br$^-$ ions are on the same side of the central Br$^-$ ion as is the TrisH$^+$ cation. As a consequence, this view has been rotated [relative to that in (*b*)], so as to reduce overlap in the figure. (*b*) TrisH$^+$.I$^-$: I$\cdots$N is shorter than I$\cdots$C(*C*) and the nearest-neighbor I$^-$ atoms are on the side opposite to the TrisH$^+$ cation. This view is perpendicular to I$\cdots$N—C(*C*).

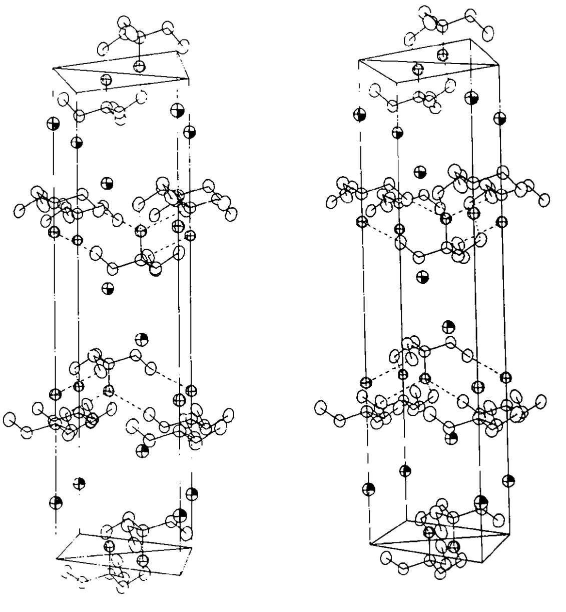

Fig. 2. Stereoview of the TrisH$^+$.Br$^-$ unit cell. The Br$^-$ ions are shown with shaded ellipses, while the N atoms have unshaded ellipses. The hydrogen-bonded (dashed lines) double layers of cations are separated by the halide ions.

*Tris*H$^+$.*X*$^-$ (*X* = F,Cl,Br) *crystal structures.* These compounds form an unusual crystal structure (Fig. 2) which consists of infinite sheets ~5·7 Å thick (for the Cl$^-$ salt) separated by an essentially empty layer ~2·5 Å thick. Consequently, the crystals are exceptionally easy to cleave (mica-like), easily deformed, and grow as twins. This explains why the ω scans of the F$^-$ salt were so broad and suitable intensity data could not be obtained. Similarly, the Cl$^-$ salt data were also not of sufficient quality for a fully satisfactory refinement. This open structure and the ease with which these materials form intercalation compounds were also exhibited when crystals of TrisH$^+$.Br$^-$ were placed in a desiccator together with I_2 crystals. After several hours the I_2 vapor was heavily absorbed by the TrisH$^+$.Br$^-$ crystals. The I_2 vapor was then removed by heating the crystals in an oven at 363 K.

The structure of the infinite sheets is also of interest, consisting of an inner portion formed by strong hydrogen bonding (Table 3) between a double layer of TrisH$^+$ ions arranged in such a manner that the C—N vectors of half the molecules are inverted with respect to the other half, with the —NH$_3^+$ groups *facing* each other. The *X*$^-$ ions are located on both sides of this double cation layer, with C(*C*)$\cdots$*X* shorter than N$\cdots$*X* (Table 3). The system seems to be stabilized by a balance between the *X*$^-\cdots$H—O hydrogen-bond forces (through the hydroxymethyl groups) and the repulsive forces of the *X*$^-\cdots$*X*$^-$ nearest-neighbor interactions across the ~2·5 Å layers of essentially empty space. This open structure explains why the densities of TrisH$^+$.Cl$^-$ and TrisH$^+$.Br$^-$ are unusually low [*e.g.* compare $D_x = 1\cdot54$ Mg m^{-3} for $BrNO_2C(CH_2OH)_2$ (Sake Gowda & Rudman, 1982), a compound with nearly the same molecular weight and types of atoms].

As yet unexplained is the density of TrisH$^+$.F$^-$, which is 'normal' for this type of organic salt, yet abnormally high for a member of this isostructural series. A possible explanation is that the strong hydrogen-bonding character and small size of the F$^-$ ion results in a contraction along the *c* axis which 'closes up' the otherwise open structure of these crystals. Since the structure of the TrisH$^+$ cation is essentially constant, the change in unit-cell dimensions with change in anion is due to their differences in ionic radii. The change in the length of the *c* axis (Δc), as we progress from F$^-$ to Cl$^-$ to Br$^-$ should be equal to $6(r_{X\bar{1}}-r_{X\bar{2}})$, where *r* is the ionic radius. Using $r_{F^-} = 1\cdot19$, $r_{Cl^-} = 1\cdot67$, and $r_{Br^-} = 1\cdot82$ Å, the Δc calculated between TrisH$^+$.Cl$^-$ and TrisH$^+$.Br$^-$ is 0·90 Å, which compares favorably with the observed 0·75 Å. However, Δc calculated for TrisH$^+$.F$^-$ and TrisH$^+$.Cl$^-$ is 2·88 Å, which is considerably larger than the observed 2·22 Å. On the other hand, the change in the *a* axes (Δa), where a nesting effect exists, should be $\sim(\Delta r_{X\bar{1}} - \Delta r_{X\bar{2}})$, as is found: TrisH$^+$.F$^-$ to TrisH$^+$.Cl$^-$, 0·45 Å observed, 0·48 Å calculated; TrisH$^+$.Cl$^-$ to TrisH$^+$.Br$^-$, 0·13 Å observed, 0·15 Å calculated. It thus appears that in the TrisH$^+$.F$^-$ structure the distance between the ionic double layers is proportionately less than it is in the structures of the Cl$^-$ and Br$^-$ salts.

*Tris*H$^+$.I$^-$ *crystal structure.* In this compound, the anion lies closer to the center of positive charge (N) on the cation than it does in the other compounds (Table 3); the density of TrisH$^+$.I$^-$ is also 'normal' for this type of compound. Another indication of the difference in

Table 3. *Shortest interionic distances* (Å) *in* TrisH$^+$.X^-

	TrisH$^+$.Cl$^-$	TrisH$^+$.Br$^-$	TrisH$^+$.I$^-$
N···O*	2·818 (3)	2·812 (3)	2·886 (15)
X···O*	3·031 (3)	3·217 (2)	3·489 (13)
X···H(O)*	2·68 (4)	2·62 (4)	—
X···H(1)	3·28 (4)	3·28 (3)	3·39
X···H(2)	2·88 (3)	3·15 (3)	3·39
X···C(*C*)†	3·977 (5)	4·120 (4)	4·557 (8)
X···N†	5·447 (5)	5·618 (4)	4·015 (7)
X···X	5·154 (1)	5·217 (1)	4·922 (1)

* Hydrogen-bonded distance: for TrisH$^+$.Br$^-$, O–H(O) = 0·61 (4) Å, ∠O–H(O)···Br = 169 (5)°; N–H(N) = 0·91 (4), H(N)···O = 1·93 (4) Å, ∠N–H(N)···O = 164 (3)°; for TrisH$^+$.Cl$^-$, O–H(O) = 0·73 (5), ∠O–H(O)···Cl = 112 (4)°; N–H(N) = 0·69 (3), H(N)···O = 2·14 (3) Å, ∠N–H(N)···O = 167 (4)°.

† Along threefold axis.

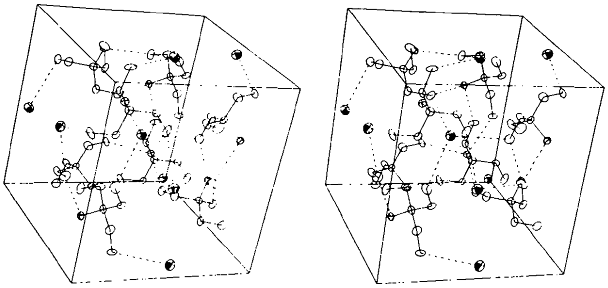

Fig. 3. Stereoview of the TrisH$^+$.I$^-$ unit cell. The I$^-$ ions are shown with shaded ellipses, while the N atoms have unshaded ellipses. The H bonding between N···O as well as the closest I···O and I···N distances are indicated by dashed lines. Focus on the I$^-$ ion closest to the center of the unit cell to observe the threefold symmetry and the iodine environment.

packing found in TrisH$^+$.I$^-$ *vs* TrisH$^+$.Br$^-$, is that the closest X···X distance is significantly shorter in TrisH$^+$.I$^-$ than in either TrisH$^+$.Br$^-$ or TrisH$^+$.Cl$^-$ (Table 3). Each I$^-$ ion lies at the center of a distorted tetrahedron formed by three adjacent I$^-$ ions [at 4·922 (1) Å] and the N atom, with three of the tetrahedral angles equal to 101·4 (4) (1)° and the other three equal to 116·7 (1)°. The sevenfold coordination about the I$^-$ ion is completed by the three nearest-neighbor O atoms (Fig. 1*b*). The structure is stabilized by the N···O hydrogen bonds.

Hydrogen bonding. The TrisH$^+$.X^- compounds are all extensively hydrogen bonded. In TrisH$^+$.I$^-$, a three-dimensional network results (Fig. 3), while in the others a layered compound is formed (Fig. 2). The Y···O distances agree with those reported by Kuleshova & Zorkii (1981): 3·12 Å for Y = Cl, 3·28 Å for Y = Br, and 2·79 Å for Y = N. However, the I···O distance is just equal to the sum of the van der Waals radii for I and O (3·48 Å, Bondi, 1968), so that in the absence of H-atom parameters, the significance of this hydrogen bond cannot be determined.

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References

Bondi, A. (1968). *Physical Properties of Molecular Crystals, Liquids, and Gases*. New York: John Wiley.

Eilerman, D., Lippman, R. & Rudman, R. (1983). *Acta Cryst.* B**39**, 263–266.

Eilerman, D. & Rudman, R. (1980). *J. Chem. Phys.* **72**, 5656–5666.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Ivarsson, G. J. M. (1982). *Acta Cryst.* B**38**, 1828–1831.

Kuleshova, L. N. & Zorkii, P. M. (1981). *Acta Cryst.* B**37**, 1363–1366.

Parsonage, N. G. & Staveley, L. A. K. (1978). *Disorder in Crystals*. Oxford Univ. Press.

Rudman, R., Lippman, R. & Eilerman, D. (1979). *Am. Crystallogr. Assoc. Abstr.* **6**, 73.

Sake Gowda, D. S. & Rudman, R. (1982). *J. Chem. Phys.* **77**, 4666–4670.

Shakked, Z., Viswamitra, M. A. & Kennard, O. (1980). *Biochemistry*, **19**, 2567–2571.

Syntex (1973). *XTL Structure Determination System*. Syntex Analytical Instruments, Cupertino, California.

Acta Cryst. (1983). C**39**, 1271–1273

DL-Glutamic Acid Monohydrate, $C_5H_9NO_4.H_2O$

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Abstract. M_r = 165·15, orthorhombic, *Pbca*, a = 9·119 (3), b = 15·480 (7), c = 10·627 (3) Å, V = 1500·1 Å^3, Z = 8, D_m = 1·46 (1) (by flotation), D_x = 1·46 Mg m^{-3}, Mo $K\alpha$, λ = 0·71069 Å, μ = 0·14 mm^{-1}, $F(000)$ = 704, room temperature. R = 0·049 for 1258 nonzero independent amplitudes. A short intermolecular H-bond with O···O = 2·574 (2) occurs between the α- and γ-carboxyl groups, as is the case in

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