Discussion. As seen from Fig. 1 which includes projections down the x and y axes, $NC(CH_2)_3CN$ acts as a bridging ligand between two $TiCl_4$ units such that the 1:1 $TiCl_4$–$NC(CH_2)_3CN$ adduct is one-dimensionally polymeric in the solid state. Ti atoms are octahedrally coordinated with the N atoms being in the *cis* configuration. It should also be noted that C(3) is required to sit on a crystallographic twofold axis so that one half of $NC(CH_2)_2CN$ is related to the other half by the twofold symmetry.

The conformation of $NC(CH_2)_3CN$ in the adduct is *trans,trans* for the four C—C single bonds connecting C(1)—C(2)—C(3)—C(2)—C(1). The $NC(CH_2)_3CN$ molecule is nearly planar. The Ti—Cl distances of 2·225–2·266 Å are comparable to those obtained in previous works on $TiCl_4$ adducts, *e.g.* 2·174–2·190 Å in $(TiCl_4$–$NCCOOC_2H_5)_2$ (Constant, Cubaynes, Daran & Jeannin, 1974) and 2·226 Å in $TiCl_4$–$(NCH_2)_2$ (Constant, Daran & Jeannin, 1971). The Ti—N distance of 2·188 Å is similar to those found in $TiCl_4$–$(NCH_2)_2$, 2·198 Å, and $(TiCl_4$–$NCCOOC_2H_5)_2$, 2·240 Å. The C≡N triple-bond distance of 1·134 Å is slightly shorter than the 1·155 Å length observed in the equilibrium C≡N distance in CH_3CN (Cooney & Fraser, 1974). Such a shortening is expected because the C≡N bond strength increases upon coordination (Storhoff & Lewis, 1977). The N—C(1)—C(2) fragment is nearly linear as it should be [∠N—C(1)—C(2) 176·2°]. The departure from the ideal 180° of the Ti—N—C(1) angle (171·3°) is presumably a manifestation of crystal-packing effects caused primarily by the rigid nature of the N—C(1)—C(2) framework. It is noted that the linearity of the Ti—N—C(1)—C(2) segment prevents both ends of the dinitrile molecules from coordinating with the same Ti atom. To explain the slightly short C(1)—C(2) distance (1·466 Å) as compared to a typical C—C single-bond length of 1·54 Å, we may safely assume that there is a partial double-bond character due to the neighboring —C≡N group.

The financial support from the National Science Council of the Republic of China is acknowledged.

References

Constant, G., Cubaynes, J. J., Daran, J. C. & Jeannin, Y. (1974). *J. Coord. Chem.* **4**, 71–75.

Constant, G., Daran, J. C. & Jeannin, Y. (1971). *Acta Cryst.* B**27**, 2388–2392.

Cooney, R. P. & Fraser, D. B. (1974). *Aust. J. Chem.* **27**, 1855–1875.

Cotton, F. A. & Wilkinson, G. (1980). In *Advanced Inorganic Chemistry*, 4th ed. New York: Interscience.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Jain, S. C. & Rivest, R. (1963). *Can. J. Chem.* **41**, 2130–2136.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Lee, F. L. & Gabe, E. J. (1978). *The NRC PDP-*11 *Crystal Structure System*. National Research Council of Canada, Ottawa.

Perrin, D. D., Armarego, W. L. F. & Perrin, D. R. (1980). In *Purification of Laboratory Chemicals*, 2nd ed. Oxford: Pergamon Press.

Storhoff, B. N. & Lewis, H. C. Jr (1977). *Coord. Chem. Rev.* **23**, 1–29.

Acta Cryst. (1986). C**42**, 291–293

Conformational Aspects of *meso*-Tartaric Acid. X.* Structure of Sodium Trihydrogen Di-*meso*-tartrate

By A. J. A. R. Blankensteyn and J. Kroon†

Laboratorium voor Kristal- en Structuurchemie, Rijksuniversiteit, Padualaan 8, 3584 *CH Utrecht, The Netherlands*

(*Received* 24 *July* 1985; *accepted* 28 *October* 1985)

Abstract. $Na^+.C_8H_{11}O_{12}^-$, $M_r = 322·16$, monoclinic, $P2_1/n$, $a = 6·514$ (1), $b = 9·193$ (4), $c = 9·440$ (3) Å, $\beta = 96·38$ (2)°, $V = 561·8$ (4) Å^3, $Z = 2$, $D_x = 1·904$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 2·01$ mm^{-1}, $F(000) = 330$, $T = 295$ K, $R = 0·058$ for 989 diffractometer data with $I > 2·5\sigma(I)$. In this super-acid salt, the *meso*-tartrate anion adopts a dissymmetric conformation. The heavy atoms in one half of the anion are approximately coplanar, whereas the other glycolic-acid part is rather distorted from planarity owing to intermolecular H bonding. The H-bond scheme concerning the carboxyl-group coupling is of the mixed *A*/*B* type. The sodium-ion coordination is pseudo cubic with Na—O distances in the range 2·468–2·607 Å.

* Part IX: Moerman, Ouwerkerk & Kroon (1985).

† To whom correspondence should be addressed.

0108-2701/86/030291-03$01.50

Introduction. This work is part of a series of structural investigations on *meso*-tartaric acid compounds. Points of interest are the molecular conformations of the *meso*-tartaric acid molecule and the patterns of hydrogen bonding.

In a previous paper we reported the structure determination of sodium *meso*-tartrate (Blankensteyn & Kroon, 1985). The *meso*-tartrate dianion of that structure adopts a centrosymmetric conformation, which is exceptional for complexes of *meso*-tartaric acid.

In this paper we describe the crystal structure determination of an acid sodium salt of *meso*-tartaric acid.

Experimental. Flat regular crystal, dimensions approximately 0·5 × 0·3 × 0·3 mm, grown from aqueous solution of sodium carbonate and *meso*-tartaric acid mixture in 1 mol to 2 mol ratio. Enraf–Nonius CAD-4 diffractometer, Cu $K\alpha$ radiation, cell measurement with setting angles of 17 reflections, ranging from $\theta = 13{\cdot}6$ to 28·4°; $\omega/2\theta$ scan of width 2·50° and variable speed; $2\theta_{max} = 163{\cdot}0°$, $h = -7$ to 7, $k = 0$ to 11, $l = -11$ to 11; no systematic fluctuations in standard reflections ($\bar{4}00$, $0\bar{3}2$ and $1\bar{1}4$); 2171 reflections measured, 1017 unique, 992 of which considered observed [$I > 2{\cdot}5\sigma(I)$], $R_{int} = 0{\cdot}059$. Lp corrections, no absorption correction. Structure solved by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Anisotropic refinement on F by full-matrix least squares with *SHELX*76 (Sheldrick, 1976). Hydrogen atoms located from three-dimensional difference Fourier map and by stereochemical considerations; their positional parameters subsequently refined, but isotropic thermal parameters put equal to those of their carrier atoms and kept fixed; unit weights; number of refined parameters: 112. Three reflections (020, $\bar{1}03$ and $\bar{1}23$) appeared to suffer from extinction and were removed from refinement. Convergence at $R = 0{\cdot}058$. $wR = 0{\cdot}056$, $S = 0{\cdot}74$. $(\Delta/\sigma)_{max} = 0{\cdot}1$; max. and min. peaks on final $\Delta\rho$ map 0·34 and −0·48 e Å^{-3}. Calculations carried out on the CDC-Cyber 175 computer of the University of Utrecht with programs of *APOLLO* (data reduction and correction) by A. L. Spek and *EUCLID* [calculation of geometrical data and illustrations (Spek, 1982)]. Scattering factors for Na^+, O and C from Cromer & Mann (1968) and for hydrogen from Stewart, Davidson & Simpson (1965).

Discussion. In Table 1 the final atomic coordinates and equivalent isotropic temperature factors are listed.* In Fig. 1 a perspective view and the numbering of the anion is shown. Table 2 gives bond lengths, bond angles, selected torsion angles, the hydrogen-bond geometries and the Na^+ coordination. In sodium *meso*-tartrate the anions are situated at the centres of symmetry (Blankensteyn & Kroon, 1985), while the sodium ions are in general positions. In the title compound this situation is reversed.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42607 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and isotropic thermal parameters* (Å^2)

For non H-atoms, $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}/U_{iso}
Na	½	½	0	0·0332 (6)
O(1)	−0·0446 (3)	0·1235 (2)	0·0341 (2)	0·0319 (6)
O(2)	0·2896 (3)	0·1512 (2)	0·1113 (2)	0·0289 (6)
O(3)	0·2278 (3)	0·4324 (3)	0·1660 (3)	0·0310 (6)
O(4)	0·1080 (4)	0·2331 (3)	0·3866 (2)	0·0314 (6)
O(5)	−0·3783 (3)	0·3086 (3)	0·1953 (3)	0·0328 (6)
O(6)	−0·2685 (4)	0·1251 (3)	0·3394 (3)	0·0341 (6)
C(1)	0·1099 (5)	0·1974 (3)	0·0941 (3)	0·0240 (6)
C(2)	0·0497 (5)	0·3433 (3)	0·1505 (3)	0·0233 (8)
C(3)	−0·0321 (5)	0·3180 (3)	0·2955 (3)	0·0239 (8)
C(4)	−0·2374 (5)	0·2380 (4)	0·2799 (3)	0·0260 (10)
H(1)	−0·060 (5)	0·386 (4)	0·082 (3)	0·022
H(2)	−0·051 (5)	0·417 (4)	0·343 (3)	0·023
H(3)	0	0	0	0·031
H(4)	0·213 (6)	0·502 (4)	0·204 (4)	0·030
H(5)	0·196 (6)	0·287 (4)	0·417 (4)	0·031
H(6)	−0·498 (6)	0·256 (4)	0·172 (4)	0·032

In contrast with its conformation in sodium *meso*-tartrate, in this acid salt the anion adopts a dissymmetric conformation. This is in concert with the general behaviour of the *meso*-tartrate molecule established in a number of crystal structures (Kroon, 1982). The non-hydrogen atoms in one half of the anion are nearly coplanar, whereas in the second half the carboxyl group is rotated more than 20° out of the plane with the α-hydroxyl O atom. This large deviation from planarity is due to a torque exerted by two H bonds which are more or less perpendicular to the carboxyl-group plane.

As in potassium hydrogen *meso*-tartrate (Kroon & Kanters, 1972), the carboxyl-group coupling is of the mixed A/B H-bond type (Speakman, 1972). The B-type H bond of 2·650 (3) Å is abnormally long. In this type of H bond a distance of 2·55 Å is usually found. This elongation is probably caused by the less-favourable acceptance scheme, the donor proton being in the bonded region of the carboxyl group, which is moreover also involved in the A-type bond. A similar H-bonding scheme is found in the crystal structure of (3,6-dithiaoctanedioato-S,S')(3,6-dithiaoctanedioic acid-S,S')copper(I) (Helder, Birker, Verschoor & Reedijk, 1984); this also has a rather large H-bond length of 2·609 (2) Å.

The oxygen coordination of the sodium ion is eightfold and is distorted cubic (see Fig. 2); distances are given in Table 2. Fig. 3 shows the crystal packing viewed along the a axis.

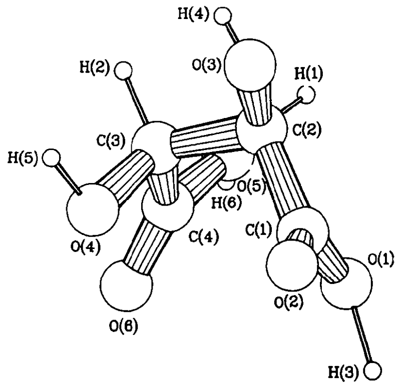

Fig. 1. Stereochemistry and atom numbering of the *meso*-tartaric ion.

Table 2. *Bond distances* (Å), *bond angles* (°), *selected torsion angles* (°), H-*bond geometry and* Na *coordination* (Å)

C(1)–O(1)	1·292 (4)	C(3)–C(4)	1·519 (4)
C(1)–O(2)	1·239 (4)	C(4)–O(6)	1·208 (4)
C(1)–C(2)	1·511 (4)	C(4)–O(5)	1·318 (4)
C(2)–O(3)	1·414 (4)	O(1)–H(3)	1·224 (2)
C(2)–C(3)	1·541 (4)	O(3)–H(4)	0·75 (4)
C(2)–H(1)	0·99 (3)	O(4)–H(5)	0·79 (4)
C(3)–H(2)	1·03 (2)	O(5)–H(6)	0·92 (4)
C(3)–O(4)	1·417 (4)		

O(1)–C(1)–O(2)	123·8 (3)	C(2)–C(3)–H(2)	109 (2)
O(1)–C(1)–C(2)	113·7 (3)	O(4)–C(3)–C(4)	107·0 (2)
O(2)–C(1)–C(2)	122·5 (3)	O(4)–C(3)–H(2)	109 (2)
C(1)–C(2)–C(3)	107·9 (2)	H(2)–C(3)–C(4)	109 (2)
C(1)–C(2)–O(3)	108·0 (3)	C(3)–C(4)–O(5)	111·5 (2)
O(3)–C(2)–C(3)	110·9 (2)	C(3)–C(4)–O(6)	124·2 (3)
C(1)–C(2)–H(1)	109 (2)	O(5)–C(4)–O(6)	124·3 (3)
O(3)–C(2)–H(1)	111 (2)	C(1)–O(1)–H(3)	114·0 (2)
C(3)–C(2)–H(1)	110 (2)	C(2)–O(3)–H(4)	113 (3)
C(2)–C(3)–C(4)	112·0 (2)	C(3)–O(4)–H(5)	106 (3)
C(4)–C(3)–H(2)	109 (2)	C(4)–O(5)–H(6)	114 (2)
C(2)–C(3)–O(4)	111·1 (2)		

C(1)–C(2)–C(3)–C(4)	−68·8 (3)
O(2)–C(1)–C(2)–O(3)	24·1 (4)
O(4)–C(3)–C(4)–O(6)	1·7 (4)
H(3)–O(1)–C(1)–O(2)	2·7 (4)
H(6)–O(5)–C(4)–O(6)	−10 (3)
H(4)–O(3)–C(2)–C(1)	−171 (3)
H(5)–O(4)–C(3)–C(4)	−159 (3)

	O–H(Å)	H···O(Å)	O···O(Å)	O–H···O(°)
O(1)–H(3)···O(1^{i})	1·224 (2)	1·224 (2)	2·448 (4)	180
O(3)–H(4)···O(2^{ii})	0·75 (4)	2·22 (4)	2·921 (3)	157 (4)
O(4)–H(5)···O(1^{iii})	0·79 (4)	2·08 (4)	2·845 (3)	163 (4)
O(5)–H(6)···O(2^{iv})	0·92 (4)	1·73 (4)	2·650 (3)	174 (4)

Na···O(3) Na···O(3^{v})	2·570 (2)	Na···O(5^{vii}) Na···O(5^{viii})	2·607 (3)
Na···O(4^{vi}) Na···O(4^{ii})	2·530 (3)	Na···O(6^{vi}) Na···O(6^{ii})	2·468 (3)

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

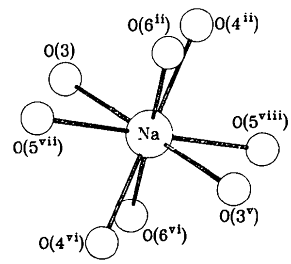

Fig. 2. A perspective view of the coordination sphere of the sodium ion. Superscripts in the atom numbering refer to the symmetry code given in Table 2.

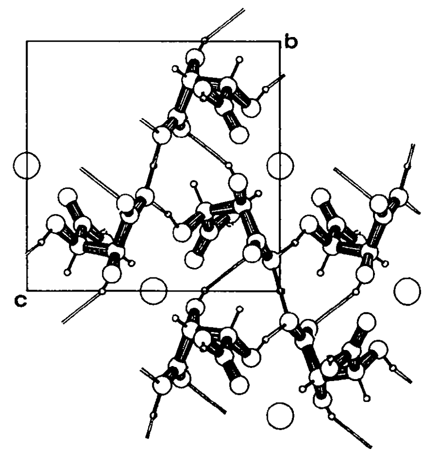

Fig. 3. Projection of the unit-cell contents down the *a* axis. The sodium ions are represented by large spheres; hydrogen bonds are indicated by open sticks (for reasons of clarity the H bond connecting two molecules separated by a translation in the direction of the *a* axis has been omitted).

References

BLANKENSTEYN, A. J. A. R. & KROON, J. (1985). *Acta Cryst.* C**41**, 182–184.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

HELDER, J., BIRKER, P. J. M. W. L., VERSCHOOR, G. C. & REEDIJK, J. (1984). *Inorg. Chim. Acta*, **85**, 169–173.

KROON, J. (1982). *Molecular Structure and Biological Activity*, edited by J. F. GRIFFIN & W. L. DUAX, pp. 151–163. New York: Elsevier Biomedical.

KROON, J. & KANTERS, J. A. (1972). *Acta Cryst.* B**28**, 714–722.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

MOERMAN, W., OUWERKERK, M. & KROON, J. (1985). *Acta Cryst.* C**41**, 1205–1208.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

SPEAKMAN, J. C. (1972). *Struct. Bonding* (*Berlin*), **12**, 141–199.

SPEK, A. L. (1982). The *EUCLID* package. In *Computational Crystallography*, edited by D. SAYRE, p. 528. Oxford: Clarendon Press.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.