Barium L-tartrate

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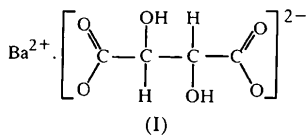
Abstract

Barium L-tartrate, $Ba^{2+} \cdot C_4H_4O_6^{2-}$, has been grown in silica-gel medium for the first time and its structure has been solved. A new coordination of the cation with the tartrate anion is observed. The cation exhibits ninefold coordination without the presence of water molecules and the tartrate groups are linked through $Ba \cdots O$ contacts to form a three-dimensional network.

Comment

This work is part of a research project on the investigation of the dielectric properties of tartrate salts, as related to their crystalline structure. The increased interest is motivated by a desire to provide an explanation for the ferroelectric phase transition in the rochelle salt (potassium sodium tartrate tetrahydrate) through the study of the tartrate anion conformation and the cation environment (Solans *et al.*, 1997).

The structure of barium L-tartrate, (I), has been determined (Fig. 1). Bond lengths and angles in the

$$Ba^{2+} \cdot \left[\begin{matrix} O \\ \diagdown \\ O \end{matrix} C - \overset{OH}{\underset{H}{C}} - \overset{H}{\underset{OH}{C}} - C \overset{O}{\diagup} \overset{}{\diagdown} O \right]^{2-}$$

(I)

tartrate anion (Table 3) are normal and do not deviate significantly from those of other reported tartrates with divalent cations, *i.e.* Ca^{2+} (Hawthorne *et al.*, 1982; Ambady, 1968), Sr^{2+} (Ambady, 1968), Ni^{2+} (Bostelaar *et al.*, 1984), Zn^{2+} (Templeton *et al.*, 1985) and Mn^{2+} (Ruiz-Pérez *et al.*, 1996). The two halves of the tartrate ion, each consisting of a carboxylate group, a tetrahedral C and a hydroxy O atom, are individually

planar [maximum deviation 0.045 (3) Å for C3] and the four C atoms assume a typical zigzag planar conformation [C1—C2—C3—C4 178.1 (3)°]. The angle between the C2/O3/C1/O1/O2 and C3/O4/C4/O5/O6 planes is 67.2 (2)°, which is close to the usual value of about 60° found in tartrates.
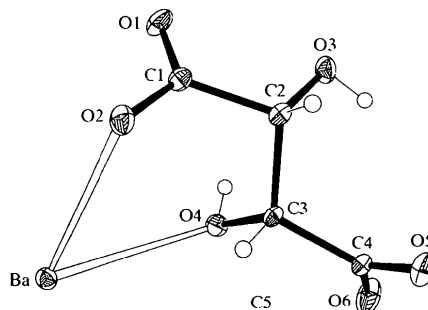

Fig. 1. The molecular structure of the title compound showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level for non-H atoms.
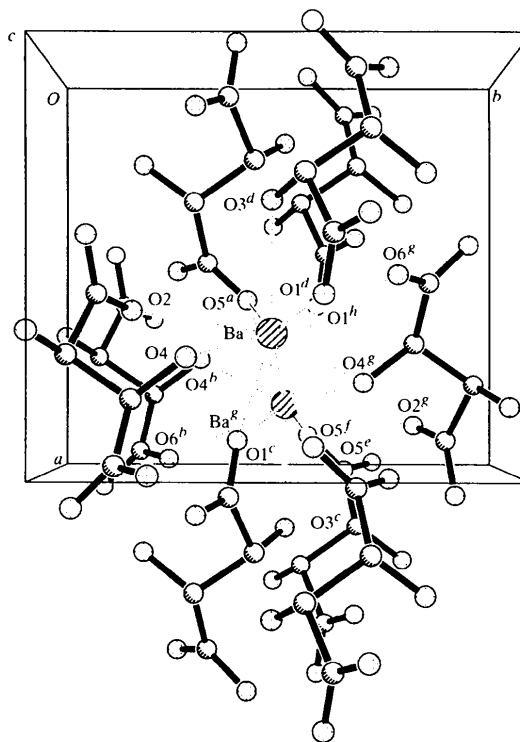

Fig. 2. Packing diagram of the title compound viewed down the *c* axis, showing the nine-coordination sphere of Ba^{2+}. H atoms have been omitted for clarity. O atoms are labelled with the following symmetry codes: (*a*) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (*b*) $x, y, z - 1$; (*c*) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (*d*) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (*e*) $2 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (*f*) $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (*g*) $\frac{3}{2} - x, 1 - y, z - \frac{1}{2}$; (*h*) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.

The molecular packing of the title compound is shown in Fig. 2. The Ba^{2+} ion is surrounded by six tartrate groups and is linked to nine O atoms (Table 1). Six of these O atoms are involved in the formation of five- and six-membered chelate rings. The average Ba^{2+}—O distance observed in (I) is 2.816 (3) Å, which agrees with the values reported in other examples of nine-coordinate barium, *e.g.* 2.83 Å in $BaCs_4(PO_3)_6$ (Averbuch-Pouchot & Durif, 1986), 2.831 Å in $BaAl_2O_4 \cdot H_2O$ (Ahmed *et al.*, 1973), 2.90 Å in $BaAl_2Ge_2O_8$ (Calleri & Gazzoni, 1977) and 2.844 Å in $Ba_4YbCu_3O_9$ (Vallino *et al.*, 1991). The tartrate groups are linked through Ba$\cdots$O contacts to form a three-dimensional network which is further stabilized by O—H$\cdots$O intermolecular hydrogen bonds (Table 2). Within this network, adjacent Ba^{2+} ions share six O atoms, forming a hexagonal-shaped cavity perpendicular to the *c* axis. This arrangement has not been observed previously in tartrate salts with divalent cations, which usually appear with various numbers of water molecules in the crystal packing.

Experimental

Single crystals of barium L-tartrate were grown in silica-gel medium using the techniques described by Henisch (1970). An approximate 1 *M* solution of sodium metasilicate nonahydrate was added to 1 *M* L-tartaric acid (pH 4–5). The mixture was introduced into test tubes, covered, and allowed to set for 48 h at room temperature. A 1 *M* solution of barium chloride was introduced above the gel and the tubes were stored at 313 K. Crystals appeared at the gel interface within about one week, and well formed crystals had grown after about two weeks.

Crystal data

$Ba^{2+} \cdot C_4H_4O_6^{2-}$	Mo $K\alpha$ radiation
$M_r = 285.41$	$\lambda = 0.71069$ Å
Orthorhombic	Cell parameters from 25
$P2_12_12_1$	reflections
$a = 8.181 (2)$ Å	$\theta = 12.03$–$18.39°$
$b = 9.036 (2)$ Å	$\mu = 6.379$ mm^{-1}
$c = 8.392 (1)$ Å	$T = 293 (2)$ K
$V = 620.4 (2)$ Å^3	Prism
$Z = 4$	$0.60 \times 0.25 \times 0.15$ mm
$D_x = 3.056$ Mg m^{-3}	Pale pink
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	1813 reflections with $I > 2\sigma(I)$
ω–2θ scans	$R_{int} = 0.023$
Absorption correction:	$\theta_{max} = 30°$
empirical *via* azimuthal	$h = -11 \rightarrow 11$
(ψ) scans (North *et al.*,	$k = -4 \rightarrow 12$
1968)	$l = -11 \rightarrow 0$
$T_{min} = 0.159$, $T_{max} = 0.384$	3 standard reflections
2045 measured reflections	frequency: 120 min
1067 independent reflections	intensity decay: 1%
(plus 746 Friedel-related reflections)	

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.761$ e Å^{-3}
$R(F) = 0.019$	$\Delta\rho_{min} = -0.644$ e Å^{-3}
$wR(F^2) = 0.048$	Extinction correction:
$S = 1.210$	SHELXL97
1813 reflections	Extinction coefficient:
101 parameters	0.0022 (5)
H-atom parameters	Scattering factors from
constrained	*International Tables for*
$w = 1/[\sigma^2(F_o^2) + (0.0256P)^2$	*Crystallography* (Vol. C)
$+ 1.3377P]$	Absolute structure:
where $P = (F_o^2 + 2F_c^2)/3$	Flack (1983)
$(\Delta/\sigma)_{max} = 0.001$	Flack parameter = -0.01 (2)

Table 1. *Selected bond distances (Å)*

Ba—O3^i	2.769 (3)	Ba—O4^{iii}	2.809 (3)
Ba—O5^{ii}	2.773 (3)	Ba—O1^{iv}	2.837 (3)
Ba—O1^i	2.798 (3)	Ba—O4	2.870 (3)
Ba—O6^{iii}	2.805 (3)	Ba—O5^v	2.876 (3)
Ba—O2	2.805 (3)	Ba$\cdots$Ba^{vi}	4.4590 (5)

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

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

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D$$\cdots$$A$	D—H$\cdots$$A$
O3—H3O$\cdots$O2^i	0.820	2.109	2.697 (4)	128.6
O4—H4O$\cdots$O6^{ii}	0.820	1.861	2.653 (4)	162.1

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

Table 3. *Average geometry values (Å, °) for the tartrate ligand*

C—C	1.535 (5)
C—O (hydroxy)	1.421 (4)
C—O (carboxyl)	1.255 (5)
C—C—C	110.2 (3)
C—C—O (hydroxy)	111.5 (3)
C—C—O (carboxyl)	116.9 (3)
O—C—O	126.1 (3)

The positions of the H atoms were idealized geometrically and refined with fixed individual isotropic displacement parameters [$U_{iso} = 1.2U_{eq}(C)$ and $1.5U_{eq}$(hydroxy O)] using a riding model with C—H distances of 0.98 Å and O—H distances of 0.82 Å. The positions obtained for the hydroxy H atoms were consistent with the intermolecular hydrogen bonding. The Flack (1983) parameter confirmed the absolute configuration of the title molecule, which was synthesized from a substance of known chirality.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *XCAD4* (Harms, 1996). Program(s) used to solve structure: *SIR97* (Giacovazzo *et al.*, 1999). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *PARST95* (Nardelli, 1995).

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of tris(2-aminoethyl)amine (tren) and pyridinecarboxaldehyde, *i.e.* [Mn(py₃tren)](ClO₄)₂ [py₃tren is tris-(2-pyridylmethyleneaminoethyl)amine, $C_{24}H_{27}N_7$], is a seven-coordinate monocapped trigonal antiprism with C_3 symmetry.

Comment

Tripodal metal complexes of transition metals and their derivatives have been widely investigated (Riley *et al.*, 1991; Sanyal *et al.*, 1995). Many potentially tripodal heptadentate ligands have been reported; most of them are imine-type ligands resulting from the condensation of tren, $N(CH_2CH_2NH_2)_3$, and various aromatic aldehydes or ketones (Kirchner *et al.*, 1987; Alcock *et al.*, 1980; Sim & Sinn, 1978). X-ray crystal structures of the BF_4^- and PF_6^- salts of $[M(py_3tren)]^{2+}$ [py₃tren is tris(2-pyridylmethylene-aminoethyl)amine] demonstrated that the distances between the metal atom and the bridgehead N atom are longer than the sum of the van der Waals radii (Kirchner *et al.*, 1987). These are described as a trigonal antiprism distorted towards a trigonal prism. To date, many seven-coordinate complexes of tripodal ligands, such as $[Mn(pyo_3tren)]^{2+}$ [pyo₃tren is tris(2-pyridyl-*N*-oxide-methyleneaminoethyl)amine; Gou *et al.*, 1993] and Mn–TPAA [TPAA is tris(2-pyridylmethylaminoethyl)amine; Deroche *et al.*, 1996], have been reported. In the course of preparing polyamine intermediates for macrocyclic condensation reactions, we obtained the title complex, (I).

(I)

[Tris(2-pyridyl-κN-methyleneamino-κN-ethyl)amine-κN]manganese(II) diperchlorate

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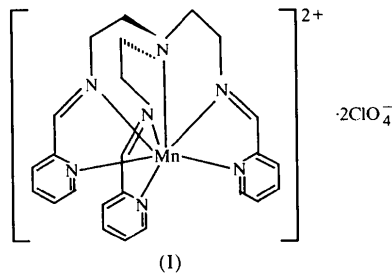(*Received 14 September 1998; accepted 15 December 1998*)

Abstract

The Mn^{II} complex of a tripodal ligand containing one tertiary N atom, three pyridine N atoms and three Schiff base moieties derived from the condensation

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The title complex crystallizes in a trigonal system with space group $P\bar{3}1c$. The manganese ion is coordinated by seven N atoms from py₃tren, the hemispheric coordination being best described as a monocapped trigonal antiprism of [MnN₇], in which the bridgehead N atom is bonded to the metal atom. The three imine N atoms and the three pyridine N atoms form two ideal equilateral triangles between which the Mn atom is located. The two triangles, parallel to each other, are staggered by 48.0°, so the geometry is twisted from an ideal antitrigon (60°) by 12° towards a trigonal prism. There are equal bite angles N2—Mn1—N3 of 71.6(2)° and equal bite distances between the chelating imine N2 and pyridine N3 atoms (N2···N3) of 2.716 Å. The complex