Bis(imidazolium) galactarate dihydrate

Graham Smith and Urs D. Wermuth

Acta Cryst. (2010). E66, o2399

This open-access article is distributed under the terms of the Creative Commons Attribution Licence http://creativecommons.org/licenses/by/2.0/uk/legalcode, which permits unrestricted use, distribution, and reproduction in any medium, provided the original authors and source are cited.

Acta Crystallographica Section E: Structure Reports Online is the IUCr's highly popular open-access structural journal. It provides a simple and easily accessible publication mechanism for the growing number of inorganic, metal-organic and organic crystal structure determinations. The electronic submission, validation, refereeing and publication facilities of the journal ensure very rapid and high-quality publication, whilst key indicators and validation reports provide measures of structural reliability. In 2007, the journal published over 5000 structures. The average publication time is less than one month.

Crystallography Journals Online is available from journals.iucr.org
Bis(imidazolium) galactarate dihydrate

Graham Smith* and Urs D. Wermuth

Faculty of Science and Technology, Queensland University of Technology, GPO Box 2434, Brisbane, Queensland 4001, Australia

Correspondence e-mail: g.smith@qut.edu.au

Received 19 August 2010; accepted 19 August 2010

Key indicators: single-crystal X-ray study; T = 200 K; mean s(C–C) = 0.002 Å; R factor = 0.030; wR factor = 0.082; data-to-parameter ratio = 11.7.

In the structure of the title salt, 2C₃H₆N₂⁺·C₆H₅O₈₂⁻·2H₂O, the galactarate dianions have crystallographic inversion symmetry and together with the water molecules of solvation form hydrogen-bonded sheet substructures which extend along (110). The imidazolium cations link these sheets peripherally down c through carboxylate O—H—N and N—H···O hydroxy bridges, giving a three-dimensional framework structure.

Related literature

For mention of mucic acid in the Merck Index, see: O’Neil (2001). For the structures of imidazolium hydrogen salts of aliphatic dicarboxylic acids, see: James & Matsushima (1976); MacDonald et al. (2001); Aakeröy & Hitchcock (1993); Fuller et al. (1995); Fukunaga & Ishida (2003); Trivedi et al. (2003). For the structures of galactaric acid, ammonium H galactarate, diammonium galactarate and copper(II) galactarate dihydrate, see: Jeffrey & Wood (1982), Bontchev & Moore (2005), Benetollo et al. (1993) and Ferrier et al. (1998) respectively. For graph-set analysis, see: Etter et al. (1990).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG5021).

References

Aakeröy, C. B. & Hitchcock, P. B. (1993). Chem. Mater., 5, 1129–1135.
Allomare, A., Casarano, G., Giaquazza, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). J. Appl. Cryst. 27, 435.
Benetollo, F., Bombieri, G., Liang, H., Liao, H., Shi, N. & Wu, J. (1993). J. Cryst. Growth Spec. Proc. 3, 171–175.
Bontchev, R. P. & Moore, R. C. (2005). Carbohydr. Res. 340, 2195–2200.
Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). Acta Cryst. B46, 256–262.
Farrugia, L. J. (1999). J. Appl. Cryst. 32, 837–838.
Ferrier, F., Avezou, A., Terzian, G. & Benlian, D. (1998). J. Mol. Struct. 442, 281–284.
Fukunaga, T. & Ishida, H. (2003). Acta Cryst. E59, o1869–o1871.
Fuller, J., Carlin, R. T., Simpson, L. J. & Furtak, T. E. (1995). Chem. Mater. 7, 909–919.
James, M. N. G. & Matsushima, M. (1976). Acta Cryst. B32, 1708–1713.
Jeffrey, G. A. & Wood, R. A. (1982). Carbohydr. Res. 158, 205–211.
MacDonald, J. C., Dorrsett, P. C. & Pilley, M. M. (2001). Cryst. Growth Des. 1, 29–35.
O’Neil, M. J. (2001). The Merck Index, 13th ed., p. 769. Whitehouse Station, New Jersey: Merck & Co.
Oxford Diffraction (2010). CrystAlis PRO. Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
Sheldrick, G. M. (2008). Acta Cryst. A64, 112–122.
Spek, A. L. (2009). Acta Cryst. D65, 144–152.
Trivedi, D. R., Ballabh, A. & Dastidar, P. (2003). CrystEngComm, 5, 358–367.

Acta Cryst. (2010). E66, o2399

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer

Absorption correction: multi-scan

(CrysAlis PRO; Oxford Diffraction, 2010)

Tmin = 0.965, Tmax = 0.980

Refinement

R[F² > 2σ(F²)] = 0.030

wR(F²) = 0.082

S = 1.13

1657 reflections

142 parameters

H atoms treated by a mixture of independent and constrained refinement

Δρ(max) = 0.30 e Å⁻³

Δρ(min) = −0.20 e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

D—H···A

D—H

H···A

D···A

D—H···A

N11—H111···O21 0.89 (2) 1.84 (2) 2.7311 (15) 175.9 (19)
N31—H31···O12 0.89 (2) 1.785 (19) 2.6810 (14) 174 (2)
O21—H22···O1W 0.87 (2) 1.76 (2) 2.6324 (15) 177 (2)
O31—H32···O12 0.83 (2) 1.89 (2) 2.7014 (13) 170.9 (16)
O1W—H11W···O11 0.87 (3) 1.82 (3) 2.6799 (14) 170.9 (18)
O1W—H12W···O31 0.86 (3) 1.94 (3) 2.7373 (15) 164.4 (19)

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

Data collection: CrysAlis PRO (Oxford Diffraction, 2010); cell refinement: CrysAlis PRO; program(s) used to solve structure: SIR2004 (Altomare et al., 1994); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008) within WinGX (Farrugia, 1999); molecular graphics: PLATON (Spek, 2009); software used to prepare material for publication: PLATON.

The authors acknowledge financial support from the Australian Research Committee and the Faculty of Science and Technology, Queensland University of Technology.

Experimental

Crystal data

2C₃H₆N₂⁺·C₆H₅O₈₂⁻·2H₂O

Mr = 382.34

Triclinic, P̅1

α = 6.9184 (4) Å

b = 7.1336 (4) Å

γ = 105.835 (6)°

V = 425.06 (5) Å³

Z = 1

Mo Ka radiation

μ = 0.13 mm⁻¹

T = 200 K

μ = 0.13 mm⁻¹

T = 200 K

Published online: 17 November 2010

Acta Cryst. (2010). E66, o2399

DOI: 10.1107/S1600536810033532

Smith & Wermuth o2399

Acta Cryst. (2010). E66, o2399

DOI: 10.1107/S1600536810033532

Smith & Wermuth o2399

Acta Cryst. (2010). E66, o2399

DOI: 10.1107/S1600536810033532

Smith & Wermuth o2399
supplementary materials
supplementary materials

Acta Cryst. (2010). E66, o2399  [doi:10.1107/S1600536810033532 ]

Bis(imidazolium) galactarate dihydrate

G. Smith and U. D. Wermuth

Comment

Galactaric acid (mucic acid) (O’Neil, 2001) is the C6 homologue of tartaric acid but differs from it in being achiral and as well has only a small number of representative crystal structures in the CSD, e.g. the acid itself (Jeffrey & Wood, 1982), ammonium hydrogen galactarate (Bontchev & Moore, 2005), diaminonium galactarate (Benetollo et al., 1993) and some metal complexes, e.g. copper(II) galactarate dihydrate (a fungicide) (Ferrier et al., 1998). Because the imidazolium cation has proved to be an excellent linking molecule for the generation of supramolecular layered structures particularly with dicarboxylic acids, including hydroxy acids (James & Matsushima, 1976; MacDonald et al., 2001; Aakeröy & Hitchcock, 1993; Fuller et al., 1995; Fukunaga & Ishida, 2003; Trivedi et al., 2003), we carried out a 1:2 stoichiometric reaction of galactaric acid with imidazole in aqueous ethanol and obtained large relatively hard, chemically stable crystals of the title compound, 2(CH$_3$N$_3$)$^+$ C$_4$H$_8$O$_8^{2^-}$. 2H$_2$O (I), and the structure is reported here.

In the structure of (I) (Fig. 1), the galactarate anions lie across crystallographic inversion centres which is also the case in the structure of the parent acid (Jeffrey & Wood, 1982). Hydrogen-bonded anion-water sheets extending across the <100> planes in the unit cell (Fig. 2) are formed through hydroxyl O31–H…O12$^{iii}$ carboxyl and water-bridging O31…O11$^{iv}$ carboxyl interactions (for symmetry codes, see Table 1). These include $R_2^2$(12) and $R_3^3$(12) cyclic motifs (Etter et al., 1990). The layered substructures are linked peripherally down the $c$ cell direction by the imidazolium cations through carboxyl O…H—N$^+$—H…O' hydroxyl bridges giving a three-dimensional framework structure (Fig. 3). The structure of (I) differs from those of the anhydrous 1:1 salts of the hydrogen dicarboxylates (MacDonald et al., 2001) in which the bridging imidazolium cations are incorporated within two-dimensional layered structures.

Experimental

The title compound was synthesized by heating together under reflux for 10 minutes 1 mmol of galactaric acid (mucic acid) and 2 mmol of imidazole in 50 ml of 50% ethanol-water. After concentration to ca 30 ml, partial room temperature evaporation of the hot-filtered solution gave large colourless plates of (I) (m.p. 435 K) from which a suitable analytical specimen was cleaved.

Refinement

Hydrogen atoms potentially involved in hydrogen-bonding interactions were located by difference methods and their positional and isotropic displacement parameters were refined. Other H atoms were included in the refinement in calculated positions (C–H$_{\text{aromatic}}$ = 0.95 Å and others = 1.00 Å) and allowed to ride, with $U_{\text{iso}}$(H) = 1.2$U_{\text{eq}}$(C).
supplementary materials

Figures

Fig. 1. The molecular configuration and atom-numbering scheme for the cation, dianion and water species in (I). The galactarate dianion has inversion symmetry [symmetry code: (i) -x + 1, -y + 1, -z + 2]. Non-H atoms are shown as 50% probability ellipsoids and inter-species hydrogen bonds are shown as dashed lines.

Fig. 2. Hydrogen-bonded anion-water sheet substructures in (I), extending across (110) (imidazolium cations are omitted). For symmetry codes, see Table 1. Hydrogen bonds are shown as dashed lines.

Fig. 3. The three-dimensional structure of (I) viewed down the approximate a cell direction, showing the imidazolium bridges.

Bis(imidazolium) galactarate dihydrate

Crystal data

\[ 2\text{C}_3\text{H}_7\text{N}_2^+\text{C}_6\text{H}_5\text{O}_4^{2-}\cdot2\text{H}_2\text{O} \]

- \( Z = 1 \)
- \( M_r = 382.34 \)
- Triclinic, \( PT \)
- Hall symbol: -\( P \) 1
- \( a = 6.9184 \pm 0.0002 \) Å
- \( b = 7.1336 \pm 0.0002 \) Å
- \( c = 9.3652 \pm 0.0006 \) Å
- \( \alpha = 92.000 (5)^\circ \)
- \( \beta = 100.559 (5)^\circ \)
- \( \gamma = 109.835 (6)^\circ \)
- \( V = 425.06 (5) \) Å\(^3\)

- \( \rho = 1.494 \) Mg m\(^{-3}\)
- Melting point: 435 K
- Mo \( K\alpha \) radiation, \( \lambda = 0.71073 \) Å
- Cell parameters from 3387 reflections
- \( \theta = 3.5-28.7^\circ \)
- \( \mu = 0.13 \) mm\(^{-1}\)
- \( T = 200 \) K
- Plate, colourless
- \( 0.45 \times 0.45 \times 0.30 \) mm

Data collection

- Oxford Diffraction Gemini-S CCD-detector diffractometer
- Radiation source: Enhance (Mo) X-ray source graphite
- \( \omega \) scans
- Absorption correction: multi-scan
- 1657 independent reflections
- 1431 reflections with \( I > 2\sigma(I) \)
- \( R_{int} = 0.019 \)
- \( \theta_{max} = 26.0^\circ \), \( \theta_{min} = 3.5^\circ \)
- \( h = -8 \rightarrow 8 \)

sup-2
(Crystals PRO; Oxford Diffraction, 2010)

\( T_{\text{min}} = 0.965, T_{\text{max}} = 0.980 \)

4949 measured reflections

\( k = -8 \rightarrow 8 \)

\( l = -11 \rightarrow 11 \)

**Refinement**

Refinement on \( F^2 \)

Least-squares matrix: full

Primary atom site location: structure-invariant direct methods

\( R[F^2 > 2\sigma(F^2)] = 0.030 \)

Secondary atom site location: difference Fourier map

\( wR(F^2) = 0.082 \)

Hydrogen site location: inferred from neighbouring sites

\( S = 1.13 \)

H atoms treated by a mixture of independent and constrained refinement

1657 reflections

\( (\Delta\sigma)_{\text{max}} = 0.001 \)

142 parameters

\( \Delta p_{\text{max}} = 0.30 \) e Å\(^{-3} \)

0 restraints

\( \Delta p_{\text{min}} = -0.20 \) e Å\(^{-3} \)

**Special details**

**Geometry.** Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles.

**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\(^2\))**

|     | \( x \)    | \( y \)    | \( z \)    | \( U_{\text{iso}}/U_{\text{eq}} \) |
|-----|-------------|-------------|-------------|---------------------------------|
| O11 | 0.18384 (15)| -0.07229 (13)| 0.80626 (9) | 0.0234 (3)                      |
| O12 | 0.26773 (14)| -0.02982 (13)| 1.04961 (9) | 0.0207 (3)                      |
| O21 | 0.19607 (14)| 0.29951 (14) | 0.78260 (9) | 0.0203 (3)                      |
| O31 | 0.62559 (14)| 0.35914 (13) | 0.90945 (10)| 0.0197 (3)                      |
| C1  | 0.23436 (18)| 0.03283 (17) | 0.92558 (13)| 0.0154 (3)                      |
| C2  | 0.25848 (18)| 0.25478 (17) | 0.92684 (12)| 0.0151 (3)                      |
| C3  | 0.48566 (18)| 0.38863 (17) | 0.99549 (13)| 0.0153 (3)                      |
| N11 | 0.34766 (19)| 0.22454 (18) | 0.54570 (12)| 0.0261 (4)                      |
| N31 | 0.35478 (19)| 0.13600 (18) | 0.32587 (12)| 0.0265 (4)                      |
| C21 | 0.2302 (2)  | 0.1404 (2)   | 0.41585 (14)| 0.0269 (4)                      |
| C41 | 0.5588 (2)  | 0.2202 (2)   | 0.40018 (15)| 0.0302 (5)                      |
| C51 | 0.5544 (2)  | 0.2764 (2)   | 0.53780 (15)| 0.0285 (4)                      |
| O1W | -0.02769 (16)| 0.53271 (15)| 0.78655 (11)| 0.0244 (3)                      |
| H22 | 0.118 (3)   | 0.373 (3)    | 0.7852 (19) | 0.046 (5)*                      |
| H2  | 0.16380     | 0.28050     | 0.98780     | 0.0180*                         |
supplementary materials

|    | U^11  | U^22  | U^33  | U^12  | U^13  | U^23  |
|----|-------|-------|-------|-------|-------|-------|
| O11| 0.0320 (5) | 0.0168 (5) | 0.0185 (5) | 0.0058 (4) | 0.0047 (4) | −0.0032 (4) |
| O12| 0.0290 (5) | 0.0158 (5) | 0.0174 (4) | 0.0077 (4) | 0.0056 (4) | 0.0024 (3) |
| O21| 0.0257 (5) | 0.0230 (5) | 0.0157 (5) | 0.0135 (4) | 0.0032 (4) | 0.0023 (4) |
| O31| 0.0214 (5) | 0.0149 (5) | 0.0265 (5) | 0.0079 (4) | 0.0113 (4) | 0.0032 (4) |
| C1 | 0.0129 (6) | 0.0148 (6) | 0.0174 (6) | 0.0026 (5) | 0.0051 (4) | 0.0001 (5) |
| C2 | 0.0185 (6) | 0.0143 (6) | 0.0132 (6) | 0.0058 (5) | 0.0049 (5) | 0.0009 (5) |
| C3 | 0.0185 (6) | 0.0136 (6) | 0.0144 (6) | 0.0052 (5) | 0.0054 (5) | 0.0017 (5) |
| N11| 0.0347 (7) | 0.0308 (7) | 0.0175 (6) | 0.0160 (5) | 0.0084 (5) | 0.0031 (5) |
| N31| 0.0379 (7) | 0.0260 (6) | 0.0152 (6) | 0.0116 (5) | 0.0044 (5) | 0.0010 (5) |
| C21| 0.0273 (7) | 0.0304 (8) | 0.0230 (7) | 0.0104 (6) | 0.0043 (6) | 0.0070 (6) |
| C41| 0.0311 (8) | 0.0336 (8) | 0.0301 (8) | 0.0134 (6) | 0.0120 (6) | 0.0064 (6) |
| C51| 0.0286 (7) | 0.0294 (8) | 0.0241 (7) | 0.0085 (6) | 0.0007 (6) | 0.0004 (6) |
| O1W| 0.0231 (5) | 0.0180 (5) | 0.0325 (6) | 0.0063 (4) | 0.0095 (4) | −0.0005 (4) |

Geometric parameters (Å, °)

|    |    |    | N11—H11 |    |    |    |
|----|----|----|---------|----|----|----|
| O11—C1 | 1.2465 (15) | N11—H11 | 0.89 (2) |    |    |    |
| O12—C1 | 1.2690 (15) | N31—H31 | 0.890 (18) |    |    |    |
| O21—C2 | 1.4223 (14) | C1—C2 | 1.5341 (16) |    |    |    |
| O31—C3 | 1.4293 (16) | C2—C3 | 1.5375 (18) |    |    |    |
| O21—H22 | 0.87 (2) | C3—C3 \(^i\) | 1.5303 (16) |    |    |    |
| O31—H32 | 0.83 (2) | C2—H2 | 1.0000 |    |    |    |
| O1W—H11W | 0.87 (3) | C3—H3 | 1.0000 |    |    |    |
| O1W—H12W | 0.86 (3) | C41—C51 | 1.345 (2) |    |    |    |
| N11—C21 | 1.3249 (17) | C21—H21 | 0.9500 |    |    |    |
| N11—C51 | 1.367 (2) | C41—H41 | 0.9500 |    |    |    |
| N31—C21 | 1.3178 (19) | C51—H51 | 0.9500 |    |    |    |
| N31—C41 | 1.369 (2) |    |    |    |    |    |

| C2—O21—H22 | 108.6 (11) | O31—C3—C3 \(^i\) | 107.52 (10) |    |    |    |
| C3—O31—H32 | 110.6 (13) | O21—C2—H2 | 108.00 |    |    |    |
| H11W—O1W—H12W | 111 (2) | C3—C2—H2 | 108.00 |    |    |    |
| C21—N11—C51 | 108.65 (12) | C1—C2—H2 | 108.00 |    |    |    |
| C21—N31—C41 | 108.66 (11) | O31—C3—H3 | 109.00 |    |    |    |
| C51—N11—H11 | 125.3 (14) | C2—C3—H3 | 109.00 |    |    |    |
| C21—N11—H11 | 126.1 (14) | C3 \(^i\)—C3—H3 | 109.00 |    |    |    |
supplementary materials

| Bond | Distance (Å) |
|------|--------------|
| C41–N31–H31 | 123.6 (14) |
| C21–N31–H31 | 127.7 (14) |
| O12–C1–C2 | 116.02 (10) |
| O11–C1–O12 | 124.82 (11) |
| O11–C1–C2 | 119.16 (10) |
| O21–C2–C3 | 111.32 (10) |
| O21–C2–C1 | 110.05 (9) |
| C1–C2–C3 | 110.45 (10) |
| O31–C3–C2 | 109.98 (9) |
| C2–C3–C3\(^i\) | 112.11 (10) |
| C21–N11–C51–C41 | −0.42 (16) |
| C51–N11–C21–N31 | 0.31 (16) |
| C21–N31–C41–C51 | −0.19 (16) |
| C41–N31–C21–N11 | −0.08 (16) |
| O11–C1–C2–O21 | 5.67 (17) |
| O12–C1–C2–O21 | −174.06 (11) |
| O12–C1–C2–C3 | 62.63 (14) |
| O11–C1–C2–C3 | −117.63 (13) |
| O21–C2–C3–O31 | −59.81 (13) |

Symmetry codes: (i) −x+1, −y+1, −z+2.

**Hydrogen-bond geometry (Å, °)**

| D–H···A       | D–H  | H···A | D···A   | D–H·A |
|---------------|------|------|--------|-------|
| N11–H11···O21 | 0.89 (2) | 1.84 (2) | 2.7311 (15) | 175.9 (19) |
| N31–H31···O12\(^{ii}\) | 0.890 (18) | 1.795 (19) | 2.6810 (14) | 174 (2) |
| O21–H22···O1W | 0.87 (2) | 1.76 (2) | 2.6324 (15) | 177 (2) |
| O31–H32···O12\(^{iii}\) | 0.83 (2) | 1.89 (2) | 2.7104 (13) | 170.9 (16) |
| O1W–H11W···O11\(^{iv}\) | 0.87 (3) | 1.82 (3) | 2.6799 (14) | 170.9 (18) |
| O1W–H12W···O31\(^v\) | 0.86 (3) | 1.94 (3) | 2.7763 (15) | 164.4 (19) |
| C21–H21···O11\(^{vi}\) | 0.95 | 2.32 | 3.0935 (17) | 138 |
| C41–H41···O11\(^{vii}\) | 0.95 | 2.42 | 3.2273 (18) | 142 |
| C51–H51···O1W\(^{viii}\) | 0.95 | 2.34 | 3.2827 (18) | 173 |

Symmetry codes: (ii) x, y, z+1; (iii) −x+1, −y, −z+2; (iv) x, y+1, z; (v) x+1, y, z; (vi) −x, −y, −z+1; (vii) −x+1, −y, −z+1; (viii) x+1, y, z.
supplementary materials

Fig. 1

[Chemical structure diagram]

electronic reprint
supplementary materials

Fig. 3