1-(Methyl-α-D-glucopyranosid-6-yl)-3-vinylimidazolium iodide dimethylformamide monosolvate

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The title solvated molecular salt, [MeGluVIm]I (MeGluVIm = 1-(methyl-α-D-glucopyranosid-6-yl)-3-vinylimidazolium), or C_{12}H_{19}N_{2}O_{5}^+\cdot I^-\cdot C_{3}H_{7}NO, was synthesized from methyl-α-D-6-iodoglucopyranoside and vinylimidazole in DMF. It crystallizes through precipitation from ethyl acetate solution directly after the reaction procedure. The crystal structure consists of an iodide anion and a [MeGluVIm] cation. Furthermore, the crystal structure contains one molecule of DMF, which accepts two O—H⋯H hydrogen bonds from the OH groups of the glucopyranoside.

Structure description

[MeGluVIm]I is part of a sub-category of ionic liquids, called carbohydrate-based ionic liquids (CHILs; Jopp, 2020). These molecules are defined as ionic organic compounds in which either the cation or the anion consists of an intact carbohydrate moiety. Our group has recently discovered a straightforward synthetic strategy for CHILs, in which methyl-α-D-glucopyranoside is transformed into methyl-α-D-6-iodoglucopyranoside in the first step (Skaanderup et al., 2002) and then in the second step quarternized with an N-substituted imidazole of choice to achieve a carbohydrate-based ionic liquid (Schnegas & Jopp, 2021). The title compound [MeGluVIm]I contains a vinylimidazolium ring bound to atom C6 of the glucopyranoside. Fig. 1 shows the asymmetric unit, including one molecule of dimethylformamide, which was used as the reaction solvent. The title compound crystallizes in a monoclinic unit cell. The crystal structure contains three classical hydrogen bonds and additional C—H⋯O/I interactions (Table 1). One hydrogen bond is formed between O3—H3A of the glucopyranoside and O7 of DMF.
acetate (80 ml) was added and the flask was stored in a fridge with an H⋯H length of 2.09 (4) Å. Two additional hydrogen bonds exists between the [MeGluVIm] cation and the iodide anion, which are O4—H4⋯I1 with 2.71 (5) Å and O5—H5⋯I1 with 2.75 (5) Å. Fig. 2 gives an alternative view of the cation, indicating the distinctive chair conformation of the glucopyranoside as well as the overall stereochemistry of the compound. The configurations of the stereogenic centres in the chosen cation are S (C1), R (C2), S (C3), S (C4) and R (C5).

Synthesis and crystallization

Methyl-6-iodo-d-glucopyranoside (1.824 g; 6 mmol) and 1-vinylimidazole (0.821 g; 10 mmol) were dissolved in DMF (10 ml) and stirred at 95 °C for 24 h. After cooling down, ethyl acetate (80 ml) was added and the flask was stored in a fridge overnight. The solvent was decanted and the precipitated solid was washed with ethyl acetate (3 × 40 ml) and dried under high vacuum to achieve the product as a beige solid (1.752 g; yield 73%). Single crystals of the compound were formed during the precipitation (m.p.: 448–453 K; Td: 509 K).

1H NMR (300 MHz, D2O): δ = 3.21–3.30 (m, 3H, OCH3); 3.58 (dd, 1H, J = 9.77, J = 3.77, H-2); 3.66–3.75 (m, 1H); 3.95 (dd, 1H, J = 6.3, J = 3.72); 4.50 (dd, 1H, J = 14.55, J = 7.38, H-6a); 4.70 (dd, 1H, J = 14.55, J = 2.55, H-6 b); 4.85 (d, 1H, J = 3.77, H-1); 5.49 (dd, 1H, J = 8.68, J = 2.84, vinyl-CH);
5.86 (dd, 1H, \(^3J = 15.58, ^3J = 2.85\), vinyl-CH\(_2\) – a); 7.2 (dd, 1H, 
\(^3J = 15.58, ^3J = 8.70\), vinyl-CH\(_2\) – b); 7.70 (d, 1H, \(^3J = 2.0\), H\(_{\text{Ar}}\)); 
7.86 (d, 1H, \(^3J = 2.0\), H\(_{\text{Ar}}\)); 9.16 (s, 1H).

\(^{13}\text{C}\) NMR (300 MHz, D\(_2\)O): \delta m= 36.9 (NCH); 50.2 (C-6); 
55.1 (OCH\(_3\)); 69.2, 40.5, 71.0, 72.8 (C-2, C-3, C-4, C-5); 99.3 (C-1); 109.8 (CH\(_2\)); 119.4, 123.8, 128.1 (CH\(_{\text{Ar}}\)).

HRMS (ESI, m/z): calculated for C\(_{12}\)H\(_{19}\)N\(_2\)O\(_5\)+, 271.1299; measured 271.1306. Calculated for \(\Gamma^-\), 126.9040; measured 126.9045.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The crystal studied was refined as a two-component inversion twin.

Funding information

We acknowledge financial support by the Deutsche Forschungsgemeinschaft and the University of Rostock within the funding programme Open Access Publishing.

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full crystallographic data

*IUCrData* (2022). 7, x220265  [https://doi.org/10.1107/S2414314622002656]

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3-Ethenyl-1-((methyl-α-D-glucopyranosid-6-yl)imidazolium iodide dimethylformamide monosolvate

Crystal data

| Parameter          | Value                          |
|--------------------|--------------------------------|
| C<sub>12</sub>H<sub>19</sub>N<sub>2</sub>O<sub>5</sub>·I<sup>−</sup>·C<sub>3</sub>H<sub>7</sub>NO |                          |
| Mr                 | 471.29                         |
| Monoclinic, P<sub>2</sub><sup>1</sup> |                                |
| a                  | 10.816 (2) Å                   |
| b                  | 7.0106 (15) Å                  |
| c                  | 13.169 (3) Å                   |
| β                  | 106.833 (4)°                   |
| V                  | 955.7 (3) Å³                   |
| Z                  | 2                              |

Data collection

- Bruker Kappa APEXII CCD diffractometer
- Radiation source: sealed tube
- Detector resolution: 10.4167 pixels mm<sup>−1</sup>
- phi and ω scans
- Absorption correction: multi-scan (SADABS; Bruker, 2003)
- T<sub>min</sub> = 0.629, T<sub>max</sub> = 0.746

Refinement

- Refinement on F<sup>2</sup>
- Least-squares matrix: full
- R[F<sup>2</sup> > 2σ(F<sup>2</sup>)] = 0.028
- wR(F<sup>2</sup>) = 0.060
- S = 1.03
- 6072 reflections
- 242 parameters
- 1 restraint
- H atoms treated by a mixture of independent and constrained refinement

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
**Refinement.** All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.98 (methyl groups), 0.99Å (methylene groups), 1.00Å (methine groups) or 0.95 Å (aryl CH) and with $U_{iso}(H) = 1.5$ times $U_{eq}(C)$ (methyl groups) or with $U_{iso}(H) = 1.2$ times $U_{eq}(C)$ (methylene groups, aryl CH, methine groups). Torsion angles of all methyl groups were allowed to refine.

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 $F^2 > 2\sigma(F^2)$ 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.

Refined as a two-component inversion twin.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\AA^2$)*

|    | x     | y     | z     | $U_{iso}$/$U_{eq}$ |
|----|-------|-------|-------|--------------------|
| N1 | 0.1863 (3) | 1.0859 (4) | 0.3364 (2) | 0.0151 (5) |
| N2 | 0.1065 (3) | 1.1296 (4) | 0.1676 (2) | 0.0179 (6) |
| O1 | 0.3511 (2) | 0.8245 (4) | 0.4934 (2) | 0.0146 (5) |
| O2 | 0.3182 (3) | 0.5032 (4) | 0.4445 (2) | 0.0184 (5) |
| O3 | 0.4060 (3) | 0.3939 (4) | 0.6541 (3) | 0.0222 (6) |
| O4 | 0.2120 (3) | 0.5948 (4) | 0.7282 (2) | 0.0197 (5) |
| O5 | 0.0572 (2) | 0.8579 (4) | 0.5786 (2) | 0.0169 (5) |
| C1 | 0.3882 (3) | 0.6322 (5) | 0.5202 (3) | 0.0150 (7) |
| H1 | 0.4821 | 0.6180 | 0.5263 | 0.018* |
| C2 | 0.3673 (3) | 0.5847 (5) | 0.6269 (3) | 0.0156 (6) |
| H2 | 0.4240 | 0.6703 | 0.6816 | 0.019* |
| C3 | 0.2266 (3) | 0.6217 (5) | 0.6246 (3) | 0.0137 (6) |
| H3 | 0.1679 | 0.5327 | 0.5733 | 0.016* |
| C4 | 0.1910 (3) | 0.8273 (5) | 0.5914 (3) | 0.0129 (6) |
| H4 | 0.2438 | 0.9163 | 0.6464 | 0.015* |
| C5 | 0.2174 (3) | 0.8639 (4) | 0.4853 (3) | 0.0123 (6) |
| H5 | 0.1607 | 0.7793 | 0.4299 | 0.015* |
| C6 | 0.1951 (3) | 1.0688 (4) | 0.4498 (3) | 0.0139 (6) |
| H6A | 0.1141 | 1.1156 | 0.4618 | 0.017* |
| H6B | 0.2671 | 1.1487 | 0.4921 | 0.017* |
| C7 | 0.3439 (4) | 0.5229 (5) | 0.3446 (3) | 0.0238 (8) |
| H7A | 0.3086 | 0.4128 | 0.2997 | 0.036* |
| H7B | 0.4374 | 0.5295 | 0.3558 | 0.036* |
| H7C | 0.3033 | 0.6400 | 0.3097 | 0.036* |
| C8 | 0.0831 (3) | 1.1454 (4) | 0.2617 (3) | 0.0153 (7) |
| H8 | 0.0055 | 1.1915 | 0.2729 | 0.018* |
| C9 | 0.2788 (3) | 1.0274 (5) | 0.2893 (3) | 0.0174 (7) |
| H9 | 0.3618 | 0.9775 | 0.3244 | 0.021* |
| C10 | 0.2286 (4) | 1.0547 (5) | 0.1843 (3) | 0.0200 (7) |
| H10 | 0.2698 | 1.0273 | 0.1313 | 0.024* |
| C11 | 0.0197 (3) | 1.1684 (9) | 0.0656 (3) | 0.0238 (7) |
| H11 | 0.0524 | 1.1636 | 0.0060 | 0.029* |
| C12 | −0.1014 (4) | 1.2099 (7) | 0.0494 (3) | 0.0322 (11) |
| H12A | −0.1368 | 1.2158 | 0.1075 | 0.039* |
| H12B | −0.1547 | 1.2344 | −0.0205 | 0.039* |
| H3A | 0.426 (4) | 0.391 (7) | 0.711 (3) | 0.014 (12)* |
|       | U_{11}   | U_{22}   | U_{33}   | U_{12}   | U_{13}   | U_{23}   |
|-------|----------|----------|----------|----------|----------|----------|
| N1    | 0.0161   | 0.0129   | 0.0185   | -0.0016  | 0.0086   | -0.0002  |
| N2    | 0.0226   | 0.0170   | 0.0156   | -0.0010  | 0.0079   | 0.0006   |
| O1    | 0.0115   | 0.0128   | 0.0203   | -0.0008  | 0.0061   | 0.0012   |
| O2    | 0.0274   | 0.0139   | 0.0178   | -0.0039  | 0.0125   | -0.0033  |
| O3    | 0.0272   | 0.0191   | 0.0205   | 0.0079   | 0.0072   | 0.0051   |
| O4    | 0.0252   | 0.0200   | 0.0170   | 0.0001   | 0.0109   | 0.0032   |
| O5    | 0.0146   | 0.0199   | 0.0185   | 0.0001   | 0.0081   | -0.0027  |
| C1    | 0.0138   | 0.0141   | 0.0181   | 0.0027   | 0.0064   | 0.0005   |
| C2    | 0.0163   | 0.0147   | 0.0158   | 0.0024   | 0.0049   | 0.0002   |
| C3    | 0.0156   | 0.0140   | 0.0132   | -0.0010  | 0.0065   | -0.0021  |
| C4    | 0.0130   | 0.0130   | 0.0135   | 0.0004   | 0.0052   | -0.0024  |
| C5    | 0.0108   | 0.0131   | 0.0137   | -0.0002  | 0.0047   | -0.0014  |
| C6    | 0.0170   | 0.0132   | 0.0135   | 0.0008   | 0.0075   | -0.0004  |
| C7    | 0.038    | 0.0196   | 0.0184   | -0.0027  | 0.0156   | -0.0031  |
| C8    | 0.0205   | 0.0111   | 0.0169   | -0.0008  | 0.0085   | 0.0021   |
| C9    | 0.0175   | 0.0153   | 0.0237   | -0.0017  | 0.0129   | -0.0021  |
| C10   | 0.0234   | 0.0175   | 0.0241   | -0.0043  | 0.0149   | -0.0032  |
| C11   | 0.0362   | 0.0203   | 0.0148   | 0.0011   | 0.0072   | 0.005    |
| C12   | 0.042    | 0.030    | 0.0215   | 0.0067   | 0.0031   | 0.0061   |
| I1    | 0.02599  | 0.01685  | 0.01752  | 0.00241  | 0.00673  | 0.00025  |
| N3    | 0.0222   | 0.0241   | 0.0226   | -0.0012  | 0.0040   | 0.0042   |
| O7    | 0.0305   | 0.0392   | 0.0239   | 0.0009   | 0.0108   | 0.0044   |
| C13   | 0.028    | 0.041    | 0.024    | 0.003    | -0.0027  | 0.0025   |
| C14   | 0.033    | 0.042    | 0.031    | -0.0034  | 0.0139   | 0.005    |
| C15   | 0.022    | 0.0260   | 0.022    | -0.0009  | 0.0021   | 0.0034   |

Atomic displacement parameters (Å²)
### Geometric parameters (Å, °)

| Bond/Angle                  | Length/Distance (Å) | Angle (°)  |
|----------------------------|---------------------|------------|
| N1—C8                      | 1.324 (4)           |            |
| N1—C9                      | 1.383 (4)           |            |
| N1—C6                      | 1.472 (4)           |            |
| N2—C8                      | 1.339 (4)           |            |
| N2—C10                     | 1.379 (5)           |            |
| O1—C1                      | 1.421 (4)           |            |
| O1—C5                      | 1.446 (4)           |            |
| O2—C1                      | 1.396 (4)           |            |
| O2—C7                      | 1.428 (5)           |            |
| O3—C2                      | 1.416 (4)           |            |
| O3—H3A                     | 0.72 (4)            |            |
| O4—C3                      | 1.430 (4)           |            |
| O4—H4A                     | 0.78 (5)            |            |
| O5—C4                      | 1.424 (4)           |            |
| O5—H5A                     | 0.74 (5)            |            |
| C1—C2                      | 1.523 (5)           |            |
| C1—O1                      | 1.536 (5)           |            |
| C2—C3                      | 1.523 (5)           |            |
| C3—H3                      | 1.0000              |            |
| C4—C5                      | 1.527 (5)           |            |
| C5—N1—C9                   | 108.9 (3)           |            |
| C8—N1—C9                   | 124.9 (3)           |            |
| C9—N1—C6                   | 126.0 (3)           |            |
| C8—N2—C10                  | 108.2 (3)           |            |
| C8—N2—C11                  | 127.4 (3)           |            |
| C10—N2—C11                 | 124.2 (3)           |            |
| C1—O1—C5                   | 113.8 (3)           |            |
| C2—O2—C7                   | 112.6 (3)           |            |
| C2—O3—H3A                  | 105 (4)             |            |
| C3—O4—H4A                  | 117 (4)             |            |
| C4—O5—H5A                  | 108 (3)             |            |
| O2—C1—O1                   | 112.4 (3)           |            |
| O2—C1—C2                   | 108.8 (3)           |            |
| O1—C1—C2                   | 109.3 (3)           |            |
| O2—C1—H1                   | 108.8               |            |
| O1—C1—H1                   | 108.8               |            |
| C2—C1—H1                   | 108.8               |            |
| O3—C2—C1                   | 109.2 (3)           |            |
| O3—C2—C3                   | 112.5 (3)           |            |
| C1—C2—C3                   | 110.9 (3)           |            |
O3—C2—H2 108.0  C12—C11—H11 118.1
C1—C2—H2 108.0  N2—C11—H11 118.1
C3—C2—H2 108.0  C11—C12—H12A 120.0
O4—C3—C4 108.1 (3)  C11—C12—H12B 120.0
O4—C3—C2 110.0 (3)  H12A—C12—H12B 120.0
C4—C3—C2 109.4 (3)  C15—N3—C14 121.8 (4)
O4—C3—H3 109.8  C15—N3—C13 121.5 (4)
C3—C4—C5 109.8  C14—N3—C13 116.7 (4)
C2—C3—H3 109.8  N3—C13—H13A 109.5
O5—C4—C3 109.9 (3)  N3—C13—H13B 109.5
O5—C4—C5 108.6 (3)  N3—C13—H13C 109.5
C3—C4—C5 108.9 (3)  H13A—C13—H13B 109.5
O5—C4—H4 109.8  N3—C13—H13C 109.5
C3—C4—H4 109.8  H13B—C13—H13C 109.5
C5—C4—H4 109.8  O7—C15—N3 125.3 (5)
O1—C5—C6 105.7 (3)  N1—C6—C5 110.4 (3)
O1—C5—C4 110.4 (3)  N1—C6—H6A 109.6
C6—C5—C4 112.8 (3)  C7—O2—C1—O1 65.7 (4)
O1—C5—H5 109.3  O5—C4—C5—C6 64.9 (3)
C6—C5—H5 109.3  C3—C4—C5—C6 −175.4 (3)
C4—C5—H5 109.3  C5—O1—C1—O2 61.2 (4)
O7—C15—N3—C14 74.9 (3)
N1—C6—C5—C4 −174.2 (3)
C8—N1—C6—C5 −56.3 (4)
C5—O1—C1—C2 56.3 (3)  C9—N1—C6—C5 −164.3 (3)
C5—O1—C1—O2 −59.7 (3)  C6—N1—C6—C5 −0.8 (4)
C5—O1—C1—C2 −179.2 (3)  C9—N1—C6—C5 −175.6 (3)
O2—C1—C2—O3 −66.8 (3)  C10—N2—C8—N1 0.9 (4)
O2—C1—C2—C3 56.3 (3)  C11—N2—C8—N1 176.6 (4)
O1—C1—C2—C3 −66.8 (3)  C10—N2—C8—N1 176.6 (4)
C3—C2—C3—O4 −174.2 (3)  C11—N2—C8—N1 176.6 (4)
C7—O2—C1—C2 −173.1 (3)  C8—N1—C6—C5 117.5 (3)
C5—O1—C1—O2 −59.7 (3)  C9—N1—C6—C5 −56.3 (4)
C5—O1—C1—C2 −179.2 (3)  O1—C5—C6—N1 74.9 (3)
C5—O1—C1—O2 −59.7 (3)  C4—C5—C6—N1 −164.3 (3)
O2—C1—C2—C3 56.3 (3)  C9—N1—C6—C5 −0.8 (4)
O1—C1—C2—C3 −66.8 (3)  C6—N1—C6—C5 −175.6 (3)
C3—C2—C3—O4 −174.2 (3)  C10—N2—C8—N1 0.9 (4)
C1—C2—C3—O4 63.2 (4)  C11—N2—C8—N1 176.6 (4)
C1—C2—C3—C4 61.2 (4)  C5—O1—C1—O2 61.2 (4)
C1—C2—C3—C4 −59.7 (3)  C8—N1—C6—C5 −56.3 (4)
O3—C2—C3—C4 −178.2 (3)  C9—N1—C6—C5 −164.3 (3)
O3—C2—C3—C4 −178.2 (3)  C6—N1—C6—C5 −0.8 (4)
O4—C3—C4—O5 −55.6 (3)  N1—C9—C10—N2 0.1 (4)
C1—C2—C3—O4 −174.2 (3)  C8—N2—C10—C9 −0.6 (4)
C1—C2—C3—C4 −55.6 (3)  C8—N2—C10—C9 −176.5 (4)
O4—C3—C4—O5 −66.2 (3)  C8—N2—C10—C9 −176.5 (4)
C2—C3—C4—C5 174.1 (3)  C9—N1—C6—C5 175.1 (3)
C2—C3—C4—C5 174.1 (3)  C6—N1—C6—C5 0.5 (4)
C2—C3—C4—C5 −55.3 (3)  C6—N1—C6—C5 0.5 (4)
C1—O1—C5—C6 −176.5 (3)  C8—N1—C6—C5 −175.1 (3)
C1—O1—C5—C4 61.2 (3)  C9—N1—C6—C5 −0.8 (4)
C1—O1—C5—C4 61.2 (3)  N1—C9—C10—N2 0.1 (4)
O5—C4—C5—O1 −177.0 (3)  C8—N2—C10—C9 −0.6 (4)
C3—C4—C5—O1 −57.3 (3)  C8—N2—C10—C9 −176.5 (4)
C3—C4—C5—O1 −57.3 (3)  C9—N1—C6—C5 175.1 (3)
C3—C4—C5—C4 55.3 (3)  C6—N1—C6—C5 0.5 (4)
Hydrogen-bond geometry (Å, °)

|   | D—H···A  | D—H | H···A | D···A | D—H···A  |
|---|----------|-----|-------|-------|---------|
| O3—H3A···O7 | 0.72 (4) | 2.09 (4) | 2.797 (4) | 167 (5) |
| O4—H4A···I1i | 0.78 (5) | 2.71 (5) | 3.482 (3) | 171 (4) |
| O5—H5A···I1 | 0.74 (5) | 2.75 (5) | 3.474 (3) | 165 (4) |
| C6—H6A···O5ii | 0.99 | 2.46 | 3.332 (4) | 147 |
| C8—H8···O4iv | 0.95 | 2.44 | 3.252 (4) | 143 |
| C8—H8···O5ii | 0.95 | 2.53 | 3.285 (4) | 136 |
| C9—H9···O3iii | 0.95 | 2.51 | 3.404 (5) | 156 |
| C10—H10···O7iii | 0.95 | 2.40 | 3.159 (5) | 137 |
| C11—H11···I1iv | 0.95 | 3.02 | 3.925 (3) | 161 |
| C15—H15···O4 | 0.95 | 2.58 | 3.297 (5) | 132 |

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