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The crystal structure of 3,3'-[1,4-phenylenebis(methylene)]bis(1-ethenyl-1*H*-imidazol-3-ium) dichloride – dichloromethane – water (1/1/1), C₁₉H₂₄Cl₄N₄O₁

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Abstract

C₁₉H₂₄Cl₄N₄O₁, triclinic, $P\bar{1}$ (no. 2), $a = 8.5930(4)$ Å, $b = 12.0814(5)$ Å, $c = 12.2430(5)$ Å, $\alpha = 69.805(2)^\circ$, $\beta = 75.2820(10)^\circ$, $\gamma = 86.733(2)^\circ$, $V = 1153.07(9)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0411$, $wR_{\text{ref}}(F^2) = 0.1053$, $T = 296$ K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.12 × 0.10 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.53 mm ⁻¹
Diffraction, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.3°, 98%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	11,517, 5737, 0.036
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4737
$N(\text{param})_{\text{refined}}$:	291
Programs:	Bruker [1], Olex2 [2, 3]

Source of material

About 8.5 g of vinyl imidazole and 5 g of α,α -Dichloro-*p*-xylene were dissolved in 30 mL of DMSO. Then, the mixture was stirred at 50 °C for 24 h under nitrogen atmosphere. After the reaction was completed, the crude product was washed with ether for several times, and then filtered and dried in vacuum at room temperature to constant weight. The final colorless crystals were obtained by slowly evaporating the solution of the title compound at room temperature.

Experimental details

All the H atoms on the benzene rings were placed geometrically and included with fixed U_{iso} parameters.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Cl1	0.97060 (5)	−0.25898 (4)	0.12781 (4)	0.03941 (12)
Cl2	0.50058 (4)	−0.23901 (3)	0.43371 (3)	0.03151 (10)
Cl3A ^a	0.3697 (8)	0.3632 (2)	0.0889 (5)	0.0973 (13)
Cl3B ^b	0.4272 (4)	0.3379 (5)	0.0575 (3)	0.0767 (10)
Cl4A ^b	0.1332 (3)	0.2234 (6)	0.22311 (19)	0.0824 (10)
Cl4B ^a	0.1476 (3)	0.1619 (5)	0.2064 (3)	0.0858 (13)
C19	0.2855 (3)	0.2352 (2)	0.0845 (2)	0.0585 (5)
H19A ^b	0.334704	0.159534	0.091698	0.070*
H19B ^b	0.235082	0.256389	0.017862	0.070*
H19C ^a	0.237698	0.257800	0.016443	0.070*
H19D ^a	0.371714	0.182430	0.070633	0.070*
O1	0.68048 (16)	−0.42479 (12)	0.32114 (15)	0.0505 (4)
H1A	0.619093	−0.382545	0.355709	0.076*
H1B	0.745280	−0.375520	0.262148	0.076*
N1	0.70313 (16)	0.08316 (12)	0.18770 (11)	0.0297 (3)
N2	0.69578 (18)	0.24761 (13)	0.21964 (13)	0.0362 (3)
C1	0.3657 (2)	−0.07543 (15)	0.05513 (14)	0.0345 (4)
H1	0.275706	−0.126266	0.092243	0.041*
C2	0.4838 (2)	−0.08022 (14)	0.11491 (14)	0.0349 (4)
H2	0.472536	−0.134124	0.192244	0.042*
C3	0.6189 (2)	−0.00525 (13)	0.06044 (13)	0.0293 (3)
C4	0.7429 (2)	−0.00531 (15)	0.12783 (16)	0.0357 (4)
H4A	0.744816	−0.082873	0.187228	0.043*
H4B	0.848726	0.013116	0.072507	0.043*
C5	0.5816 (2)	0.07082 (17)	0.28992 (14)	0.0384 (4)
H5	0.515330	0.004282	0.336127	0.046*
C6	0.5777 (2)	0.17362 (17)	0.30959 (15)	0.0419 (4)
H6	0.508069	0.191633	0.372461	0.050*
C7	0.76951 (19)	0.19010 (15)	0.14643 (15)	0.0324 (3)
H7	0.853296	0.220253	0.078061	0.039*
C8	0.7289 (3)	0.36615 (18)	0.2077 (2)	0.0503 (5)
H8	0.676987	0.393225	0.269655	0.060*
C9	0.8251 (5)	0.4362 (3)	0.1172 (3)	0.0855 (10)
H9A	0.854 (4)	0.511 (3)	0.115 (3)	0.105 (11)*
H9B	0.875 (4)	0.424 (3)	0.040 (3)	0.093 (10)*
N3	0.16449 (15)	0.43687 (11)	0.39404 (12)	0.0296 (3)
N4	−0.00547 (15)	0.29811 (11)	0.51798 (12)	0.0276 (3)
C10	−0.11256 (19)	−0.03180 (14)	0.45203 (15)	0.0315 (3)
H10	−0.188520	−0.053076	0.419985	0.038*
C11	−0.14664 (19)	0.05456 (13)	0.50454 (14)	0.0315 (3)
H11	−0.245111	0.091061	0.507283	0.038*
C12	−0.03437 (18)	0.08688 (13)	0.55312 (13)	0.0278 (3)
C13	−0.0702 (2)	0.18327 (13)	0.60786 (14)	0.0324 (3)
H13A	−0.185692	0.187065	0.637262	0.039*
H13B	−0.022283	0.165158	0.675481	0.039*
C14	−0.08828 (19)	0.37833 (14)	0.44444 (14)	0.0312 (3)
H14	−0.197048	0.373253	0.447691	0.037*
C15	0.01741 (19)	0.46533 (14)	0.36707 (15)	0.0319 (3)
H15	−0.004362	0.531778	0.307053	0.038*
C16	0.14719 (19)	0.33517 (13)	0.48595 (14)	0.0301 (3)
H16	0.228148	0.296868	0.521437	0.036*
C17	0.3128 (2)	0.50344 (15)	0.33711 (17)	0.0389 (4)
H17	0.399823	0.479423	0.371019	0.047*
C18	0.3324 (3)	0.5957 (2)	0.2405 (2)	0.0550 (5)
H18A	0.254 (3)	0.622 (2)	0.198 (2)	0.066 (7)*

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H18B	0.438 (3)	0.633 (2)	0.207 (2)	0.064 (7)*

^aOccupancy: 0.552 (9), ^bOccupancy: 0.448 (9).

Comment

The diverse applications of polymerized ionic liquids (PILs), in polymer electrolytes, electrochemical devices, smart materials, catalyst support the construction of porous polymers, and antibacterial materials, require different PIL structures and properties [4]. The design and synthesis of PIL relies on the direct continuous chain growth polymerization of ionic liquid (IL) monomers [5]. Here, a novel vinylimidazolium-based IL was synthesized, which can be used as a cross-linking agent as well as a functional monomer for the preparation of adsorbents.

Single-crystal X-ray diffraction reveals that the title compound crystallizes in the triclinic space group *P* $\bar{1}$ and each asymmetric unit contains two crystallographically independent halves of 3,3'-(1,4-phenylenebis(methylene)) bis(1-vinyl-1*H*-imidazol-3-ium) cations located on inversion centers, two chloride anions as the counterions, one dichloromethane (DCM) and one water molecule (see the left part of the Figure). The DCM molecules are found to be disordered over two positions with the occupancies of 0.552(9):0.448(9). The C–C and C–N bond lengths in the organic cations are all in the expected ranges [6–8]. The organic cations in the crystal structure use their conformational flexibility by a rotation about the C3–C4–N1 and C12–C13–N4 single bonds, respectively and the corresponding dihedral angles between the imidazole rings and the phenyl rings are 75.8(3) and 78.6(2)°, respectively, which are comparable to some analogs of the organic cations [9, 10]. The imidazole rings in the same organic cation are perfectly parallel (forced by the space group symmetry and the position of the cation) and located on the opposite sides of the benzene rings, which resulted in the formation of the lightning shape of the organic cations. Furthermore, the vinyl groups (C8–C9, C17–C18) are nearly coplanar with the imidazole rings.

Organic cations, chloride anions, and water molecules are connected by C–H···Cl, O–H···Cl and C–H···O hydrogen bonds. Chloride anions all accept at least three hydrogen atoms and the oxygen atom from the water molecule accepts at least two hydrogen atoms from the organic cations. All Cl···H and O···H distances are obviously shorter than the typical van der Waals distances and similar hydrogen bonds have been observed in some reported crystals [11–13]. These hydrogen bonds joined these components together to generate a three-

dimensional (3D) framework and the voids in this framework are further filled with the DCM molecules via the C–H $\cdots\pi$ and Cl $\cdots\pi$ interactions between the DCM molecules and organic cations (see the right part of the Figure). The distances between the hydrogen atoms of DCM molecules and the centroids of the benzene rings are shorter than 2.75 Å, while the distances between the Cl atoms of DCM and the centroids of the benzene or imidazole rings are in the range of 3.386(4)–3.793(6) Å.

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References

1. BRUKER. SAINT, APEX2 and SADABS; Bruker AXS Inc.: Madison, Wisconsin, USA, 2009.
2. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, 42, 339–341.
3. Bourhis L. J., Dolomanov O. V., Gildea R. J., Howard J. A. K., Puschmann H. The anatomy of a comprehensive constrained, restrained refinement program for the modern computing environment-Olex2 dissected. *Acta Crystallogr.* 2015, A71, 59–75.
4. Qian W., Texter J., Yan F. Frontiers in poly(ionic liquid)s: syntheses and applications. *Chem. Soc. Rev.* 2017, 46, 1124–1159.
5. Park J. B., Isik M., Park H. J., Jung I. H., Mecerreyes D. Polystyrene-block-Poly(ionic liquid) copolymers as work function modifiers in inverted organic photovoltaic cells. *ACS Appl. Mater. Interfaces* 2018, 10, 4887–4894.
6. Suresh P., Samanta A., Sathyanarayana A., Prabusankar G. Synthesis and characterization of vinylimidazolium salts: solution state study to realize the influence of different anions. *J. Mol. Struct.* 2012, 1024, 170–175.
7. Fei Z. f., Bobbink F. D., Păunescu E., Scopelliti R., Dyson P. J. Influence of elemental iodine on imidazolium-based ionic liquids: solution and solid-state effects. *Inorg. Chem.* 2015, 54, 10504–10512.
8. Moers E. G., Behm H., Smits J. M. M., Beurskens P. T. Crystal and molecular structure of 1-vinyl-3-methylimidazolium iodide, $C_6H_9N_2I$. *J. Chem. Crystallogr.* 1995, 25, 601–603.
9. Vaddamanu M., Karupnaswamy R., Srinivas K., Prabusankar G. Facile access to diselenide containing macrocyclic ring from diselone. *ChemistrySelect* 2016, 1, 4668–4671.
10. Steiner T. C–H–O Hydrogen bonding in crystals. *Crystallogr. Rev.* 1996, 6, 1–57.
11. Aktaş A., Celepci D. B., Gök Y. Synthesis, crystal structures, spectral FT-IR, NMR and UV–Vis investigations and Hirshfeld surface analysis of two new 2-hydroxyethyl-substituted *N*-heterocyclic carbene precursors. *J. Chin. Chem. Soc.* 2019, 66, 1389–1396.
12. Khan T., Mishra N., Mhatre D. S., Datta A. Crystal structure and UV spectra of a 1,2-disubstituted benzimidazolium chloride. *Acta Crystallogr.* 2017, E73, 1143–1147.
13. Ahmad J., Abdul Halim S. N., How F. N.-F. Crystal structure of benzyltriphenylphosphonium chloride monohydrate. *Acta Crystallogr.* 2015, E71, o410–o411.