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Guanidinium chloride–18-crown-6 (2/1)

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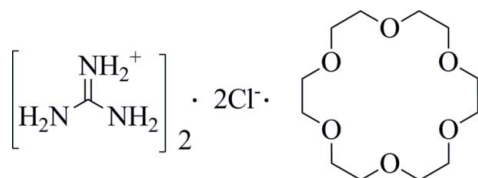
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.008$ Å; R factor = 0.074; wR factor = 0.220; data-to-parameter ratio = 21.5.

In the crystal of the title compound, $2\text{CH}_6\text{N}_3^+ \cdot 2\text{Cl}^- \cdot \text{C}_{12}\text{H}_{24}\text{O}_6$, the 18-crown-6 molecule is located across an inversion center. The guanidinium cation links to the 18-crown-6 molecule and chloride anion via $\text{N}-\text{H} \cdots \text{O}$ and $\text{N}-\text{H} \cdots \text{Cl}$ hydrogen bonds.

Related literature

For applications of crown ethers, see: Clark *et al.* (1998). For ferroelectric metal-organic 18-crown-6 clathrates, see: Fu *et al.* (2009, 2011); Ye *et al.* (2006); Zhang *et al.* (2008, 2010).



Experimental

Crystal data

 $2\text{CH}_6\text{N}_3^+ \cdot 2\text{Cl}^- \cdot \text{C}_{12}\text{H}_{24}\text{O}_6$ $M_r = 453.37$ Monoclinic, $P2_1/n$ $a = 8.9685$ (18) Å $b = 9.7305$ (19) Å $c = 13.995$ (3) Å $\beta = 102.14$ (3)° $V = 1194.0$ (4) Å³ $Z = 2$ Mo $K\alpha$ radiation $\mu = 0.31$ mm⁻¹ $T = 293$ K $0.20 \times 0.20 \times 0.20$ mm

Data collection

Rigaku SCXmini diffractometer

Absorption correction: multi-scan

(CrystalClear; Rigaku, 2005)

 $T_{\min} = 0.939$, $T_{\max} = 0.940$

12074 measured reflections

2732 independent reflections

1154 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.130$

2 standard reflections every 150 reflections

intensity decay: ?

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.074$ $wR(F^2) = 0.220$ $S = 1.01$

2732 reflections

127 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.35$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.23$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N1}-\text{H1A} \cdots \text{O1}$	0.86	2.19	2.976 (5)	152
$\text{N1}-\text{H1B} \cdots \text{Cl1}$	0.86	2.49	3.294 (4)	155
$\text{N2}-\text{H2A} \cdots \text{O1}$	0.86	2.36	3.102 (5)	145
$\text{N3}-\text{H3A} \cdots \text{Cl1}^{\dagger}$	0.86	2.42	3.228 (4)	158

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The author is grateful to the starter fund of Southeast University for the purchase of the diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5505).

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supplementary materials

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Guanidinium chloride–18-crown-6 (2/1)**Bin Wei****Comment**

Recent years, crown ethers have attracted much attention because of their wide application in catalysis, solvent extraction, isotopeseparation, bionics, host–guest chemistry and supramolecular chemistry (Clark *et al.*, 1998). Several 18-crown-6 clathrates were discovered to be dielectric-ferroelectric materials (Fu *et al.*, 2011), hence we design the title compound to find new hydrogen bonding type dielectric materials. Dielectric-ferroelectric materials, comprising organic ligands, metal-organic coordination compounds and organic-inorganic hybrids almost show dielectric constant of temperature-dependent (Fu *et al.*, 2009; Zhang *et al.*, 2010; Zhang *et al.*, 2008; Ye *et al.*, 2006). Unfortunately, the dielectric constant of the title compound as a function of temperature indicates that the permittivity is basically temperature-independent, below the melting point (395K–396K) of the compound, we have found that title compound has no dielectric discontinuity from 80 K to 405 K. Herein we describe the crystal structure of this compound.

At room temperature (25°C), the single-crystal X-ray diffraction reveals that the structure gets crystallization in the monoclinic system, space group P 2₁/n and the asymmetric unit of the title compound consists of a guanidinium cation, a chloride anion and a 18-crown-6 molecule (Fig. 1). The three –NH₂⁺ groups of guanidinium interact with O atoms of one crown ether molecule and Cl anions through two N—H···O and two N—H···Cl hydrogen bonds (Table 1), composing a three-dimensional crystal structure (Fig. 2).

Experimental

The hydrochloric acid (0.36 g, 10 mmol) and guanidinium carbonate (0.9 g, 5 mmol) were dissolved in 30 ml water, and the solution was combined with methanol solution of 18-crown-6 (10 mmol). The mixture solution was stirred for 30 min to react fully. Blocky single crystals were obtained by slow evaporation of the filtrate after two weeks (yield 63%).

Refinement

H atoms were placed in geometrically idealized positions with C—H = 0.97 and N—H = 0.86 Å, and refined in riding mode with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{N}, \text{C})$.

Computing details

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear* (Rigaku, 2005); data reduction: *CrystalClear* (Rigaku, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

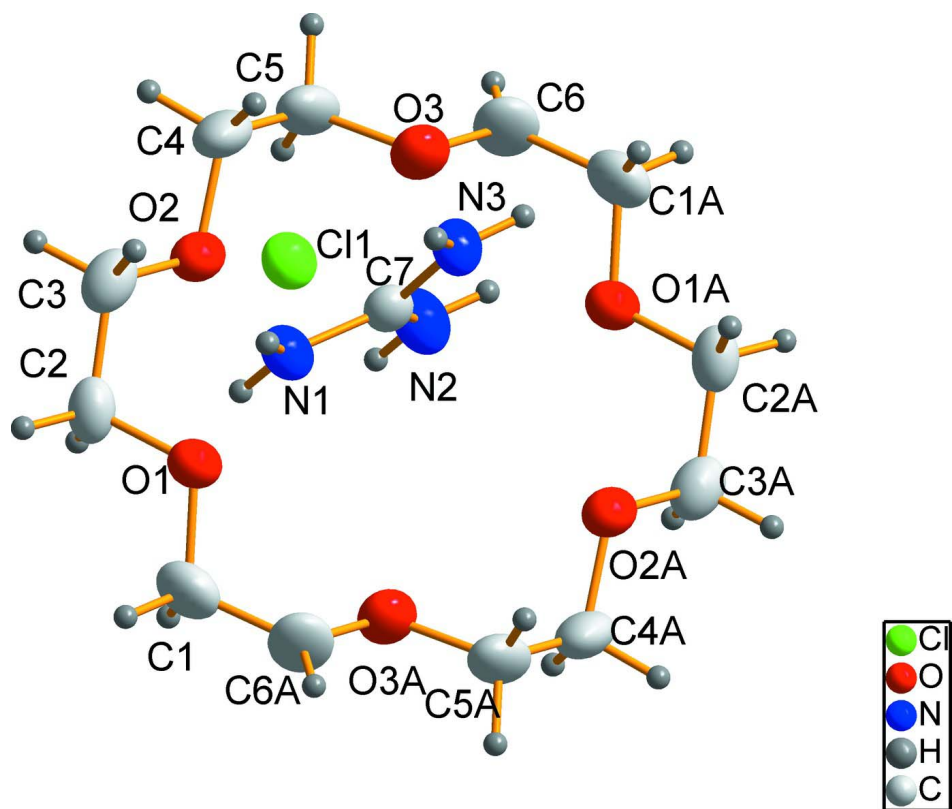
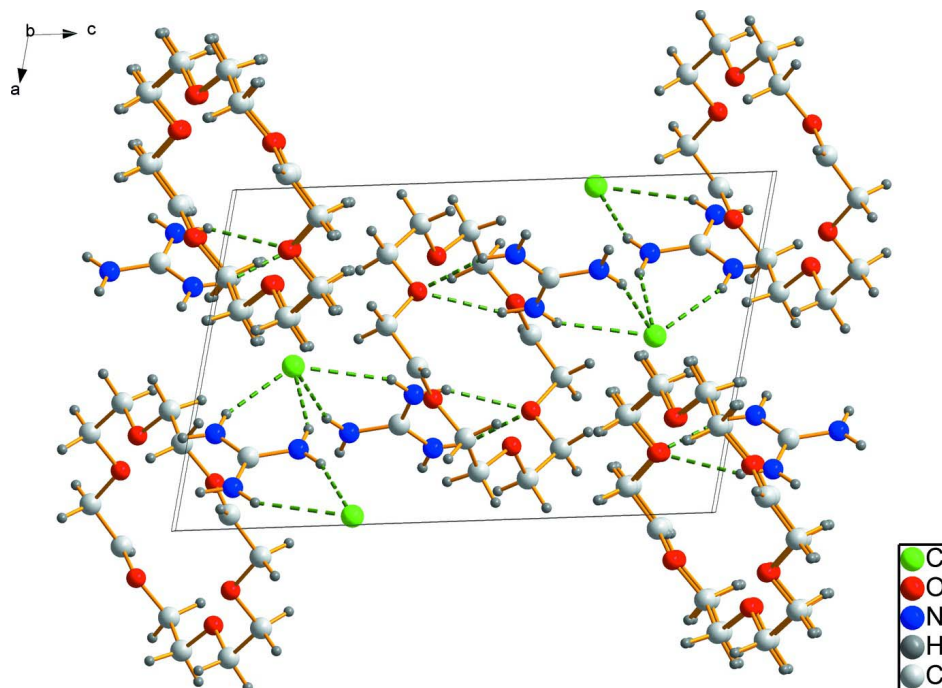


Figure 1

The molecular structure of the title compound, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

**Figure 2**

A view of the packing of the title compound, stacking along the *b* axis. Dashed lines indicate hydrogen bonds.

Guanidinium chloride–18-crown-6 (2/1)

Crystal data

$2\text{CH}_6\text{N}_3^+ \cdot 2\text{Cl}^- \cdot \text{C}_{12}\text{H}_{22}\text{O}_6$

$M_r = 453.37$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2_1n$

$a = 8.9685\ (18)\ \text{\AA}$

$b = 9.7305\ (19)\ \text{\AA}$

$c = 13.995\ (3)\ \text{\AA}$

$\beta = 102.14\ (3)^\circ$

$V = 1194.0\ (4)\ \text{\AA}^3$

$Z = 2$

$F(000) = 484$

$D_x = 1.261\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3638 reflections

$\theta = 3.0\text{--}27.5^\circ$

$\mu = 0.31\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, colorless

$0.20 \times 0.20 \times 0.20\ \text{mm}$

Data collection

Rigaku SCXmini

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan

(*CrystalClear*; Rigaku, 2005)

$T_{\min} = 0.939$, $T_{\max} = 0.940$

12074 measured reflections

2732 independent reflections

1154 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.130$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.0^\circ$

$h = -11 \rightarrow 11$

$k = -12 \rightarrow 12$

$l = -18 \rightarrow 18$

2 standard reflections every 150 reflections

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.074$
 $wR(F^2) = 0.220$
 $S = 1.01$
 2732 reflections
 127 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0875P)^2 + 0.3032P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.35 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.23 \text{ e } \text{Å}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.02647 (14)	-0.02938 (12)	0.66801 (8)	0.0671 (5)
O1	0.3181 (3)	0.2939 (3)	0.3760 (2)	0.0642 (9)
O2	0.2159 (3)	0.5624 (3)	0.3980 (2)	0.0708 (10)
O3	0.3634 (4)	0.7298 (3)	0.5591 (3)	0.0813 (11)
N1	0.2175 (4)	0.1712 (4)	0.5467 (3)	0.0644 (11)
H1A	0.2267	0.1837	0.4874	0.077*
H1B	0.1607	0.1059	0.5603	0.077*
N3	0.2713 (4)	0.2314 (4)	0.7073 (3)	0.0660 (11)
H3A	0.3162	0.2840	0.7540	0.079*
H3B	0.2139	0.1655	0.7192	0.079*
C7	0.2905 (5)	0.2520 (4)	0.6168 (3)	0.0552 (11)
N2	0.3776 (5)	0.3520 (4)	0.5987 (3)	0.0798 (13)
H2A	0.3884	0.3664	0.5399	0.096*
H2B	0.4241	0.4034	0.6456	0.096*
C3	0.1188 (6)	0.4537 (6)	0.3581 (4)	0.0781 (15)
H3C	0.0303	0.4894	0.3129	0.094*
H3D	0.0842	0.4046	0.4097	0.094*
C5	0.2433 (7)	0.7737 (6)	0.4850 (4)	0.0949 (19)
H5A	0.2832	0.8123	0.4316	0.114*
H5B	0.1853	0.8444	0.5098	0.114*
C2	0.2036 (6)	0.3607 (5)	0.3069 (3)	0.0715 (14)
H2C	0.1349	0.2933	0.2703	0.086*
H2D	0.2497	0.4123	0.2613	0.086*
C6	0.4578 (7)	0.8402 (6)	0.5976 (4)	0.0956 (19)
H6	0.4410	0.9319	0.5799	0.115*
C4	0.1448 (6)	0.6568 (7)	0.4502 (4)	0.0962 (19)

H4A	0.1177	0.6107	0.5056	0.115*
H4B	0.0515	0.6898	0.4082	0.115*
C1	0.4143 (7)	0.2120 (6)	0.3307 (4)	0.0898 (17)
H1C	0.4518	0.2667	0.2827	0.108*
H1D	0.3564	0.1357	0.2969	0.108*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0803 (9)	0.0601 (7)	0.0605 (8)	-0.0002 (7)	0.0141 (6)	0.0060 (6)
O1	0.068 (2)	0.064 (2)	0.0615 (19)	0.0040 (17)	0.0179 (17)	-0.0044 (16)
O2	0.0586 (19)	0.085 (3)	0.070 (2)	0.0093 (18)	0.0169 (17)	-0.0028 (18)
O3	0.083 (2)	0.068 (2)	0.089 (3)	0.022 (2)	0.006 (2)	-0.0035 (19)
N1	0.078 (3)	0.059 (2)	0.056 (2)	-0.004 (2)	0.014 (2)	-0.003 (2)
N3	0.065 (3)	0.078 (3)	0.055 (2)	-0.007 (2)	0.010 (2)	-0.001 (2)
C7	0.055 (3)	0.049 (3)	0.059 (3)	0.009 (2)	0.008 (2)	0.002 (2)
N2	0.095 (3)	0.075 (3)	0.070 (3)	-0.023 (3)	0.018 (2)	-0.004 (2)
C3	0.061 (3)	0.091 (4)	0.079 (4)	-0.002 (3)	0.009 (3)	0.020 (3)
C5	0.105 (5)	0.091 (5)	0.085 (4)	0.051 (4)	0.011 (4)	-0.005 (3)
C2	0.067 (3)	0.075 (4)	0.064 (3)	-0.016 (3)	-0.004 (3)	0.006 (3)
C6	0.115 (5)	0.050 (3)	0.113 (5)	0.028 (3)	0.003 (4)	-0.011 (3)
C4	0.067 (4)	0.141 (6)	0.082 (4)	0.039 (4)	0.017 (3)	-0.011 (4)
C1	0.102 (4)	0.078 (4)	0.091 (4)	-0.010 (3)	0.024 (4)	-0.034 (3)

Geometric parameters (\AA , $^\circ$)

O1—C2	1.412 (5)	C3—C2	1.462 (7)
O1—C1	1.418 (6)	C3—H3C	0.9700
O2—C4	1.408 (6)	C3—H3D	0.9700
O2—C3	1.409 (6)	C5—C4	1.459 (8)
O3—C5	1.395 (6)	C5—H5A	0.9700
O3—C6	1.403 (6)	C5—H5B	0.9700
N1—C7	1.319 (5)	C2—H2C	0.9700
N1—H1A	0.8600	C2—H2D	0.9700
N1—H1B	0.8600	C6—C1 ⁱ	1.448 (7)
N3—C7	1.329 (5)	C6—H6	0.9300
N3—H3A	0.8600	C4—H4A	0.9700
N3—H3B	0.8600	C4—H4B	0.9700
C7—N2	1.305 (5)	C1—C6 ⁱ	1.448 (7)
N2—H2A	0.8600	C1—H1C	0.9700
N2—H2B	0.8600	C1—H1D	0.9700
C2—O1—C1	112.1 (4)	O3—C5—H5B	109.8
C4—O2—C3	112.7 (4)	C4—C5—H5B	109.8
C5—O3—C6	111.1 (4)	H5A—C5—H5B	108.3
C7—N1—H1A	120.0	O1—C2—C3	109.2 (4)
C7—N1—H1B	120.0	O1—C2—H2C	109.8
H1A—N1—H1B	120.0	C3—C2—H2C	109.8
C7—N3—H3A	120.0	O1—C2—H2D	109.8
C7—N3—H3B	120.0	C3—C2—H2D	109.8

H3A—N3—H3B	120.0	H2C—C2—H2D	108.3
N2—C7—N1	121.6 (4)	O3—C6—C1 ⁱ	108.9 (5)
N2—C7—N3	120.0 (4)	O3—C6—H6	125.6
N1—C7—N3	118.4 (4)	C1 ⁱ —C6—H6	125.6
C7—N2—H2A	120.0	O2—C4—C5	111.9 (5)
C7—N2—H2B	120.0	O2—C4—H4A	109.2
H2A—N2—H2B	120.0	C5—C4—H4A	109.2
O2—C3—C2	108.5 (4)	O2—C4—H4B	109.2
O2—C3—H3C	110.0	C5—C4—H4B	109.2
C2—C3—H3C	110.0	H4A—C4—H4B	107.9
O2—C3—H3D	110.0	O1—C1—C6 ⁱ	110.8 (4)
C2—C3—H3D	110.0	O1—C1—H1C	109.5
H3C—C3—H3D	108.4	C6 ⁱ —C1—H1C	109.5
O3—C5—C4	109.2 (5)	O1—C1—H1D	109.5
O3—C5—H5A	109.8	C6 ⁱ —C1—H1D	109.5
C4—C5—H5A	109.8	H1C—C1—H1D	108.1

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N1—H1A...O1	0.86	2.19	2.976 (5)	152
N1—H1B...C11	0.86	2.49	3.294 (4)	155
N2—H2A...O1	0.86	2.36	3.102 (5)	145
N3—H3A...C11 ⁱⁱ	0.86	2.42	3.228 (4)	158

Symmetry code: (ii) $-x+1/2, y+1/2, -z+3/2$.