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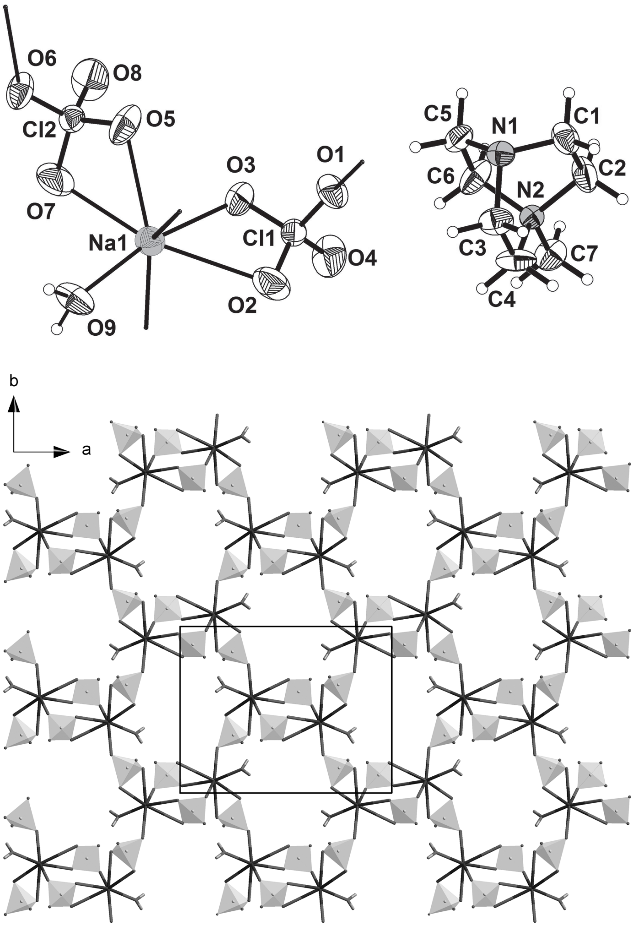
Crystal structure of 1-methyl-1,4-diazabicyclo[2.2.2]octan-1-ium poly[aqua-bis(μ_2-perchlorato-κ^3*O*,*O′*:*O″*)sodium], $C_7H_{17}Cl_2N_2NaO_9$



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Abstract

$C_7H_{17}Cl_2N_2NaO_9$, orthorhombic, *Pbca* (no. 61), $a = 13.907(3)$ Å, $b = 10.927(2)$ Å, $c = 19.194(4)$ Å, $V = 2916.8(10)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0472$, $wR_{ref}(F^2) = 0.1129$, $T = 298$ K.

CCDC no.: 1448801

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	$0.2 \times 0.2 \times 0.2$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	5.2 cm^{-1}
Diffractometer, scan mode:	Bruker P4, ω scans
$2\theta_{max}$, completeness:	55°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	28451, 3337, 0.058
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2635
$N(param)_{refined}$:	198
Programs:	SHELX [1], Bruker programs [2]

The asymmetric unit of the title crystal structure is shown in upper part of the figure; the anionic polymeric substructure is shown in the lower part of the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of materials

1-Methyl-1,4-diazabicyclo[2.2.2]octane iodide, was synthesized by the reaction of 1,4-diazabicyclo[2.2.2]octane (2.8 g, 0.025 mol) and methyl iodide (2.86 g, 0.020 mol) in 100 mL of chloroform. **Safety Note:** The reaction is a strongly exothermic, which may result in a potential explosion. Thus the methyl iodide chloroform solution must be added very slowly. With stirring, a white precipitates formed at once. Then the mixture was stirred for 24 h at room temperature, and then the solids were filtered off and washed with 10 mL chloroform. 1-Methyl-1,4-diazabicyclo[2.2.2]octane iodide was dissolved in 20 mL ethanol and the solution of $NaClO_4{\cdot}H_2O$ in ethanol was subsequently added with stirring, while a white precipitate formed. The suspension was filtered, and the resulting solid was washed with ethanol and dried over P_4O_{10} at room temperature. Colorless crystals were obtained from a solution of 1 g in 25 mL methanol by slow evaporation after 2 weeks, with a yield of 75%.

Experimental details

The hydrogen atoms were placed on calculated positions (AFIX 23 and 137) with the help of the SHELX program [1].

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.0076(2)	0.4950(3)	0.10930(17)	0.0493(7)
H1A	−0.0294	0.4838	0.0669	0.059*
H1B	−0.0077	0.5751	0.1281	0.059*
C2	−0.0204(2)	0.3969(3)	0.16200(19)	0.0558(8)
H2A	−0.0441	0.4351	0.2042	0.067*
H2B	−0.0712	0.3461	0.1430	0.067*
C3	0.1327(2)	0.3692(2)	0.06316(14)	0.0471(7)
H3A	0.2011	0.3642	0.0537	0.057*
H3B	0.0987	0.3595	0.0194	0.057*
C4	0.1040(3)	0.2667(3)	0.11264(15)	0.0574(9)
H4A	0.0555	0.2156	0.0909	0.069*
H4B	0.1595	0.2160	0.1229	0.069*
C5	0.1643(2)	0.5035(2)	0.15773(14)	0.0438(7)
H5A	0.1490	0.5820	0.1785	0.053*
H5B	0.2326	0.5022	0.1476	0.053*
C6	0.1404(2)	0.4013(3)	0.20940(16)	0.0545(8)
H6A	0.1978	0.3543	0.2197	0.065*
H6B	0.1168	0.4363	0.2526	0.065*
C7	0.0387(2)	0.2200(3)	0.22776(15)	0.0478(7)
H7A	−0.0106	0.1701	0.2073	0.072*
H7B	0.0152	0.2552	0.2703	0.072*
H7C	0.0941	0.1706	0.2374	0.072*
Cl1	0.43911(4)	0.39159(5)	0.08792(3)	0.03395(17)
Cl2	0.74815(4)	0.65128(5)	0.14705(3)	0.03434(17)
H9A	0.8320(16)	0.393(2)	−0.0246(12)	0.041*
H9B	0.8229(17)	0.2957(18)	0.0163(14)	0.041*
N1	0.11021(16)	0.48907(19)	0.09296(11)	0.0355(5)
N2	0.06545(14)	0.31983(18)	0.17837(10)	0.0294(4)
Na1	0.66160(7)	0.42592(10)	0.05911(6)	0.0422(3)
O1	0.37664(15)	0.4766(2)	0.05404(11)	0.0556(6)
O2	0.48755(18)	0.3184(2)	0.03730(13)	0.0709(7)
O3	0.51097(15)	0.4566(2)	0.12622(12)	0.0607(6)
O4	0.38464(17)	0.3165(2)	0.13335(14)	0.0742(7)
O5	0.67432(17)	0.6467(2)	0.09479(12)	0.0668(7)
O6	0.82413(14)	0.7295(2)	0.12514(12)	0.0559(6)
O7	0.78299(19)	0.5314(2)	0.15887(17)	0.0868(9)
O8	0.70694(18)	0.6975(3)	0.20912(13)	0.0781(8)
O9	0.79176(17)	0.3566(2)	0.00121(13)	0.0614(6)

Comment

1,4-Diazabicyclo[2.2.2]octane (dabco) [3, 4] and its organic-inorganic salts [5] show reversible phase transition and switchable dielectric transition, offering a way to design these functional material. In the course of studies of dabco derivatives, we synthesized the title compound and determined its crystal structure.

The Na(1) atom is seven-coordinated to seven oxygen atoms from four perchlorate anions and one coordinated water molecule. The bond lengths of Na–O are in the range of 2.25–3.05 Å. Among them, the bond lengths of Na–O (ClO_4) = 2.48–3.05 Å and Na–O (water) = 2.256 Å, reflect the differences of the two types of Na–O coordination bonds. The ClO_4 anions as bidentate ligands provide three coordination sites to link adjacent sodium atom, yielding an infinite 2D host anionic framework in the *ab* plane. The anionic host framework and the guest cations are connected through hydrogen bonds forming 2D network along *c* axis. 1-Methyl-DABCO cations form H-bonding interactions (O9···-N1# = 2.823(3) Å, #: x, 1/2 − y, 1/2 + z) with the water molecules from the adjacent anionic layers. The water molecule coordinating the Na atom, also forms an intramolecular hydrogen bond (O9···-O5# = 2.952(3) Å, #: 1/2 − x, −1/2 + y, z) with an oxygen atom from a perchlorate anion from a neighboring unit. These weak hydrogen bond in the solid state impose the 1-methyl-DABCO cations to appear perfectly ordered.

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