

1 Electronic Supplementary Information (ESI)

1.1 Crystal structure

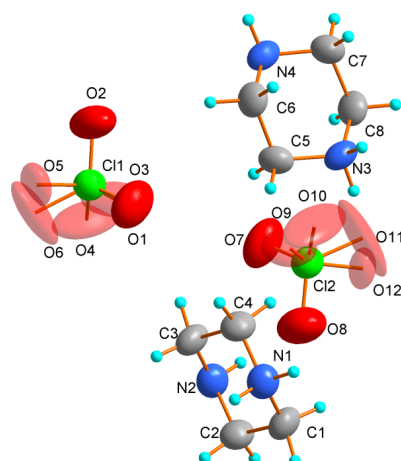


Fig. S2 Asymmetric unit of phase III, $T=413$ K, $P\bar{1}$ space group. Disordered atoms are made transparent. Site occupancy factor for O5, O6, O9, O10, O11 and O12 is equal to 0.5.

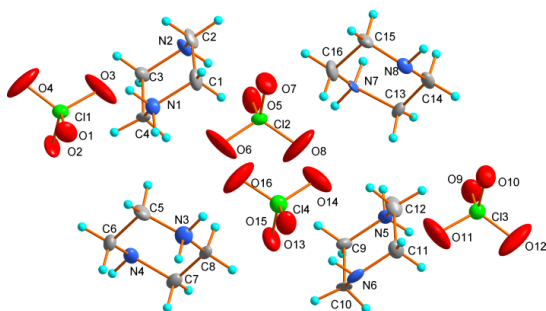


Fig. S1 Asymmetric unit in phase V, $T=200$ K, $P1$ space group. Disordered hydrogen atoms are made transparent.

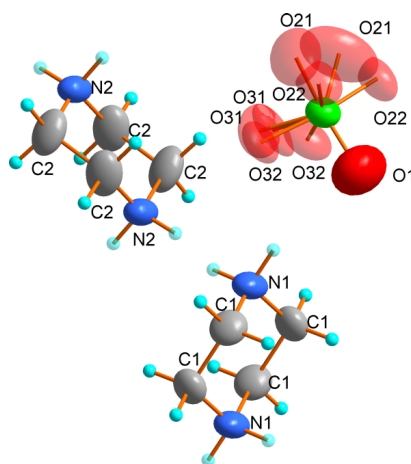


Fig. S3 Nonequivalent molecules in Phase II, the atoms from the asymmetric unit are labeled. Site occupancy factor for O22 and O21 is equal to 0.5 whereas for O31 and O32 is equal to 0.25.

Table S1 Selected geometric parameters (Å) at 200 K–Phase IV, (a) 426 K, at 413 K–Phase III and at 426 K–Phase II. Independent ClO₄⁻ groups and piperazinium counter-ions are numbered.

200 K, P1				413 K, P1			
1		2		1		2	
Cl1—O4	1.413 (7)	Cl3—O12	1.407 (8)	Cl1—O6	1.416 (3)	Cl2—O11	1.3989 (15)
Cl1—O1	1.430 (6)	Cl3—O11	1.384 (7)	Cl1—O4	1.397 (2)	Cl2—O10	1.397 (2)
Cl1—O3	1.456 (7)	Cl3—O9	1.415 (7)	Cl1—O3	1.398 (2)	Cl2—O7	1.4051 (17)
Cl1—O2	1.441 (6)	Cl3—O10	1.444 (7)	Cl1—O1	1.4036 (17)	Cl2—O8	1.422 (3)
3		4		Cl1—O2	1.4080 (17)	Cl2—O9	1.382 (7)
Cl2—O6	1.399 (7)	Cl4—O16	1.427 (7)	Cl1—O5	1.400 (2)	Cl2—O12	1.401 (2)
Cl2—O8	1.412 (7)	Cl4—O13	1.425 (6)	3		4	
Cl2—O5	1.416 (6)	Cl4—O14	1.446 (7)	N1—C1	1.464 (4)	N3—C8	1.476 (4)
Cl2—O7	1.432 (7)	Cl4—O15	1.420 (7)	N1—C4	1.470 (4)	N3—C5	1.490 (4)
5		6		N2—C3	1.428 (4)	N4—C6	1.451 (4)
N1—C4	1.4718 (13)	N5—C9	1.4730 (13)	N2—C2	1.440 (4)	N4—C7	1.467 (4)
N1—C1	1.4732 (13)	N5—C12	1.4718 (13)	C1—C2	1.514 (4)	C5—C6	1.503 (4)
N2—C2	1.4703 (13)	N6—C11	1.475 (9)	C3—C4	1.515 (4)	C7—C8	1.505 (4)
N2—C3	1.472 (9)	N6—C10	1.457 (6)	426 K, C ₂ /m			
C1—C2	1.5004 (13)	C9—C10	1.545 (6)	1		2	
C3—C4	1.504 (10)	C11—C12	1.529 (10)	Cl1—O21	1.397 (2)	N1—C1	1.447 (5)
7		8		Cl1—O31	1.400 (3)	N1—C1 ⁱ	1.447 (5)
N3—C5	1.4718 (13)	N7—C16	1.4716 (13)	Cl1—O22	1.398 (2)	C1—C1 ⁱⁱ	1.484 (8)
N3—C8	1.4720 (13)	N7—C13	1.4724 (13)	Cl1—O1	1.401 (3)	N2—C2	1.426 (6)
N4—C6	1.4704 (13)	N8—C15	1.472 (6)	Cl1—O32	1.400 (2)	N2—C2 ⁱ	1.426 (6)
N4—C7	1.4703 (13)	N8—C14	1.467 (6)			C2—C2 ⁱⁱⁱ	1.498 (10)
C5—C6	1.528 (6)	C13—C14	1.5003 (13)	Symmetry codes: (i) x, -y+1, z;			
C7—C8	1.4999 (13)	C15—C16	1.526 (6)	(ii) -x, y, -z+1; (iii) -x+1, y, -z+2			

Table S2 Selected hydrogen-bond parameters at 200 K, 413 K and 426 K

200 K, P1					413 K, P-1				
D—H...A	D—H (Å)	H...A (Å)	D...A (Å)	D—H...A (°)	D—H...A	D—H (Å)	H...A (Å)	D...A (Å)	D—H...A (°)
N1—H1A...N4i	0.89	1.99	2.858 (7)	165.6	N1—H1A...N4i	0.9	2.05	2.922 (4)	163.7
N1—H1B...O2i	0.89	2.05	2.917 (9)	164.9	N1—H1B...O2i	0.9	2.08	2.961 (4)	166.5
N2—H2A...O7	0.89	2.20	3.053 (10)	161.3	N1—H1B...O3i	0.9	2.55	3.254 (10)	135.8
N3—H3C...N2iii	0.89	2.02	2.905 (9)	173.7	N2—H2A...O8	0.9	2.26	3.145 (5)	168.9
N3—H3D...O15	0.89	2.36	2.938 (9)	122.4	N2—H2B...N3ii	0.9	2.04	2.899 (4)	159.1
N3—H3D...O16	0.89	2.45	3.258 (9)	151.6	N3—H3C...N2iii	0.9	2.01	2.899 (4)	171.5
N4—H4D...O10v	0.89	2.44	3.064 (9)	127.6	N3—H3D...O8iv	0.9	2.31	3.005 (4)	133.6
N5—H5C...N8ii	0.89	2.02	2.901 (9)	170.6	N3—H3D...O12iv	0.9	2.33	3.135 (9)	149.3
N5—H5D...O10ii	0.89	2.05	2.907 (9)	161.3	N4—H4C...O2v	0.9	2.44	3.152 (4)	135.9
N6—H6C...O15	0.89	2.20	3.078 (9)	168.9	N4—H4C...O5v	0.9	2.50	3.341 (11)	154.8
N7—H7C...N6iv	0.89	1.96	2.839 (8)	170.1	N4—H4D...N1vi	0.9	2.06	2.922 (4)	159
N7—H7D...O7	0.89	2.39	2.978 (8)	123.4	Symmetry code(s): (i) x, y-1, z; (ii) x-1, y, z; (iii) x+1, y, z;				
N7—H7D...O14	0.89	2.46	3.015 (10)	120.4	(iv) -x+1, -y+1, -z+1; (v) -x+1, -y+2, -z+2; (vi) x, y+1, z.				
N8—H8D...O2vi	0.89	2.46	3.074 (9)	126.9	426 K, C ₂ /m				
N8—H8D...O4vi	0.89	2.59	3.457 (11)	163.8	N2—H3A...N1	0.9	2.00	2.899 (9)	176.9
Symmetry code(s): (i) x, y+1, z; (ii) x-1, y, z; (iii) x, y-1, z-1;					N1—H1B...N2	0.9	2.02	2.899 (9)	165.9
(iv) x, y-1, z; (v) x+1, y, z; (vi) x, y+1, z+1.									

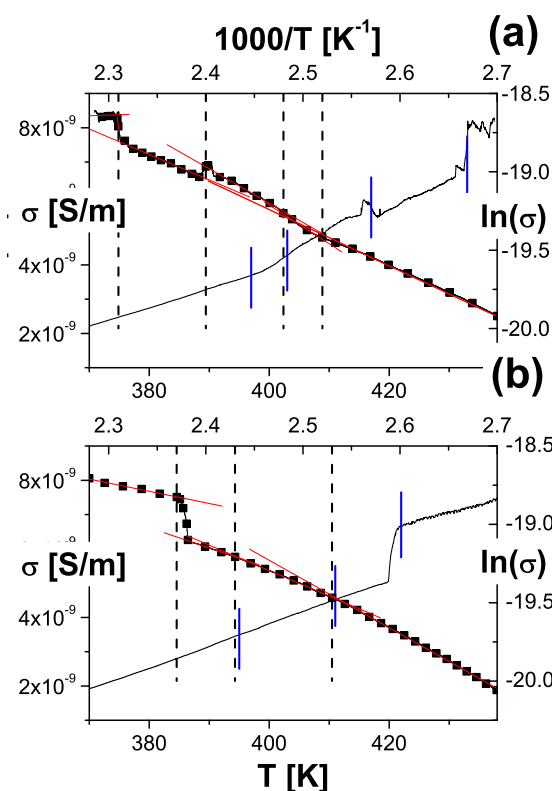


Fig. S4 Direct current conductivity vs. temperature and $\ln(\sigma_{DC})$ vs. reciprocal temperature on heating (a) and cooling (b). The thin line is the electrical conductivity, short blue lines stand for PTs. The point–line data are $\ln(\sigma_{DC})$, the long dotted lines stand for PTs in reciprocal temperature scale. The red lines are the fit of $\ln(\sigma_{DC})$.

1.2 DC conductivity measurements

The measurements of electrical conductivity were carried out on the sample along $[1 \bar{1} 0]$ direction in order to examine the possible proton conductivity in hydrogen bonds N—H...N. The results are presented in figure S4. The reciprocal temperature dependence of $\ln \sigma_{DC}$ in each phase followed the Arrhenius formula:

$$\sigma_{DC} = A_0 \cdot \exp\left(\frac{E_a}{RT}\right), \quad (1)$$

where σ_{DC} , A_0 , E_a and R stand for conductivity at direct current, preexponential factor, activation energy and the gas constant, respectively. The following table presents the obtained values of activation energy.

	E_a [kJ/mol]
phase I	10.5
phase II	17.4
phase III	21.9
phase V	29.0

All the values are in the range 10–30 kJ/mol and diminish with increasing temperature. Such a values were encountered for some ionic conductors such as $0.5 \text{ Ag}_2\text{S}—0.5 \text{ Ge}_2\text{S}^1$, $[\text{C}(\text{NH}_2)_3]_2\text{SbCl}_5 \cdot x[\text{C}(\text{NH}_2)_3]\text{Cl}^2$, $\alpha\text{-TMAOH}^3$, $\text{Ag}_2\text{HfS}_3^4$ or $\text{H}_3\text{Mo}_{12}\text{PO}_{40} \cdot 29\text{H}_2\text{O}$ and $\text{H}_3\text{W}_{12}\text{PO}_{40} \cdot 29\text{H}_2\text{O}^5$. However, the values of DC conductivity of the title crystal are distinctly lower than conductivity of compounds mentioned above. In spite of this the mechanism of conductivity seems to be the same, i.e. proton transfer along hydrogen bond. The rise of conductivity with temperature point at changes of dynamical state of proton in hydrogen bond. The abrupt change of DC conductivity at $\text{II} \leftrightarrow \text{I}$ PT, however, may be related to additional contribution of other types of ions to conductivity process. It might be due to the high disorder in crystal structure in phase I suggested by the X-ray and DSC measurements.

References

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