

Supporting information for:

[NH₂(C₂H₄)₂O]MX₅: a new family of morpholinium nonlinear materials among halogenoantimonate(III) and halogenobismuthate(III) compounds. Structural characterization, dielectric and piezoelectric properties.

Magdalena Owczarek,^a Przemysław Szklarz,^a Ryszard Jakubas,^{*a} and Andrzej Miniewicz^b

^aFaculty of Chemistry, University of Wrocław, F. Joliot Curie 14, 50-383 Wrocław, Poland

^bInstitute of Physical and Theoretical Chemistry, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

Table S1. Selected bond lengths (Å) and angles (deg) for [MX₅]²⁻ moieties at 100 K.

| MCA | | | |
|-----------------------|-----------|-----------------------------|-----------|
| Sb-Cl(1) | 2.4091(7) | Cl(1)-Sb-Cl(5) | 83.99(3) |
| Sb-Cl(2) | 2.8888(8) | Cl(4)-Sb-Cl(5) | 90.81(2) |
| Sb-Cl(3) | 2.5058(7) | Cl(3)-Sb-Cl(5) | 171.77(2) |
| Sb-Cl(4) | 2.4408(7) | Cl(1)-Sb-Cl(2) | 84.03(2) |
| Sb-Cl(5) | 2.8380(8) | Cl(4)-Sb-Cl(2) | 173.73(2) |
| Cl(1)-Sb-Cl(4) | 93.66(2) | Cl(3)-Sb-Cl(2) | 84.74(2) |
| Cl(1)-Sb-Cl(3) | 87.79(3) | Cl(5)-Sb-Cl(2) | 94.73(2) |
| Cl(4)-Sb-Cl(3) | 89.35(2) | | |
| MBA | | | |
| Sb-Br(1) | 2.5823(5) | Br(1)-Sb-Br(2) | 84.62(2) |
| Sb-Br(2) | 3.0180(6) | Br(4)-Sb-Br(2) | 174.85(6) |
| Sb-Br(3) | 2.6509(5) | Br(3)-Sb-Br(2) | 85.64(2) |
| Sb-Br(4) | 2.6109(5) | Br(1)-Sb-Br(5) | 84.65(2) |
| Sb-Br(5) | 3.0489(7) | Br(4)-Sb-Br(5) | 92.67(2) |
| Br(1)-Sb-Br(4) | 94.29(2) | Br(3)-Sb-Br(5) | 173.79(6) |
| Br(1)-Sb-Br(3) | 89.34(2) | Br(2)-Sb-Br(5) | 92.23(2) |
| Br(4)-Sb-Br(3) | 89.33(2) | | |
| MBB | | | |
| Bi-Br(1) | 2.6853(6) | Br(3)-Bi-Br(2) | 85.74(2) |
| Bi-Br(2) | 3.0041(7) | Br(1)-Bi-Br(5) | 84.20(2) |
| Bi-Br(3) | 2.7192(6) | Br(4)-Bi-Br(5) | 93.95(2) |
| Bi-Br(4) | 2.7093(6) | Br(3)-Bi-Br(5) | 173.44(2) |
| Bi-Br(5) | 3.1124(8) | Br(2)-Bi-Br(5) | 91.61(2) |
| Bi-Br(5) ¹ | 3.1843(7) | Br(1)-Bi-Br(5) ¹ | 175.91(2) |
| Br(5)-Bi ² | 3.1844(7) | Br(4)-Bi-Br(5) ¹ | 88.84(2) |
| Br(1)-Bi-Br(4) | 95.22(2) | Br(3)-Bi-Br(5) ¹ | 91.01(2) |
| Br(1)-Bi-Br(3) | 89.57(2) | Br(2)-Bi-Br(5) ¹ | 91.42(2) |
| Br(4)-Bi-Br(3) | 88.65(2) | Br(5)-Bi-Br(5) ¹ | 95.05(2) |
| Br(1)-Bi-Br(2) | 84.58(2) | Bi-Br(5)-Bi ² | 171.51(2) |
| Br(4)-Bi-Br(2) | 174.39(2) | | |

| MCB | | | |
|-----------------------------|------------|------------------------------|-----------|
| Bi-Cl(1) | 2.5557(9) | Cl(3)-Bi-Cl(5) ³ | 174.83(2) |
| Bi-Cl(2) | 2.5928(9) | Cl(1)-Bi-Cl(4) | 83.96(3) |
| Bi-Cl(3) | 2.6570(2) | Cl(2)-Bi-Cl(4) | 170.74(2) |
| Bi-Cl(4) | 2.7973(9) | Cl(3)-Bi-Cl(4) | 87.51(2) |
| Bi-Cl(5) | 2.9600(9) | Cl(5) ³ -Bi-Cl(4) | 89.19(3) |
| Bi-Cl(5) ³ | 2.7866(10) | Cl(1)-Bi-Cl(5) | 168.74(2) |
| Cl(5)-Bi ⁴ | 2.7866(10) | Cl(2)-Bi-Cl(5) | 85.63(3) |
| Cl(1)-Bi-Cl(2) | 87.68(3) | Cl(3)-Bi-Cl(5) | 93.63(3) |
| Cl(1)-Bi-Cl(3) | 95.35(3) | Cl(5) ³ -Bi-Cl(5) | 83.26(3) |
| Cl(2)-Bi-Cl(3) | 89.31(2) | Cl(4)-Bi-Cl(5) | 103.24(3) |
| Cl(1)-Bi-Cl(5) ³ | 88.26(3) | Bi ⁴ -Cl(5)-Bi | 170.25(3) |
| Cl(2)-Bi-Cl(5) ³ | 94.55(3) | | |

Symmetry transformations used to generate equivalent atoms:
 1: x+1/2,-y+1/2,-z+1 2: x-1/2,-y+1/2,-z+1
 3: x-1/2,-y+1/2,-z+1 4: x+1/2,-y+1/2,-z+1

Table S2. Hydrogen bonds for $[\text{NH}_2(\text{C}_2\text{H}_4)_2\text{O}]_2\text{MX}_5$ at 100 K.

| D - H...A | d(D - H) | d(H...A) | d(D...A) | <(DHA) |
|---------------------------------|----------|----------|----------|--------|
| MCA | | | | |
| N(1)-H(1C)...O(1) ¹ | 0.92 | 2.51 | 3.182(2) | 131 |
| N(1)-H(1C)...Cl(2) | 0.92 | 2.67 | 3.336(2) | 130 |
| N(1)-H(1D)...Cl(5) ² | 0.92 | 2.40 | 3.291(2) | 162 |
| N(2)-H(2C)...Cl(2) ³ | 0.92 | 2.65 | 3.386(2) | 137 |
| N(2)-H(2C)...Cl(3) ³ | 0.92 | 2.67 | 3.396(2) | 136 |
| N(2)-H(2D)...Cl(2) ⁴ | 0.92 | 2.34 | 3.172(2) | 151 |
| MBA | | | | |
| N(1)-H(1C)...O(1) ³ | 0.92 | 2.64 | 3.310(2) | 130 |
| N(1)-H(1C)...Br(2) | 0.92 | 2.73 | 3.414(2) | 132 |
| N(1)-H(1D)...Br(5) ⁵ | 0.92 | 2.57 | 3.452(2) | 161 |
| N(2)-H(2C)...Br(2) ¹ | 0.92 | 2.82 | 3.543(2) | 136 |
| N(2)-H(2C)...Br(3) ¹ | 0.92 | 2.80 | 3.522(2) | 137 |
| N(2)-H(2D)...Br(2) ⁶ | 0.92 | 2.52 | 3.321(2) | 145 |
| MBB | | | | |
| N(1)-H(1C)...O(1) ⁷ | 0.92 | 2.53 | 3.231(4) | 133 |
| N(1)-H(1C)...Br(2) | 0.92 | 2.77 | 3.416(3) | 128 |
| N(1)-H(1D)...Br(5) ² | 0.92 | 2.62 | 3.499(3) | 160 |
| N(2)-H(2C)...Br(2) ⁸ | 0.92 | 2.92 | 3.627(3) | 134 |
| N(2)-H(2C)...Br(3) ⁸ | 0.92 | 2.72 | 3.456(3) | 137 |
| N(2)-H(2D)...Br(2) ⁶ | 0.92 | 2.51 | 3.318(3) | 147 |
| MCB | | | | |
| N(1)-H(1C)...O(1) ³ | 0.92 | 2.64 | 3.260(3) | 126 |
| N(1)-H(1C)...Cl(1) ² | 0.92 | 2.75 | 3.413(3) | 130 |
| N(1)-H(1C)...Cl(3) ⁹ | 0.92 | 2.78 | 3.399(3) | 126 |
| N(1)-H(1D)...O(2) ⁹ | 0.92 | 2.03 | 2.862(3) | 150 |

| | | | | |
|----------------------------------|------|------|----------|-----|
| N(1)-H(1D)...Cl(2) ⁹ | 0.92 | 2.99 | 3.621(3) | 127 |
| N(2)-H(2C)...Cl(3) ¹⁰ | 0.92 | 2.46 | 3.281(3) | 149 |
| N(2)-H(2C)...Cl(1) ⁶ | 0.92 | 2.88 | 3.450(3) | 121 |
| N(2)-H(2D)...Cl(4) ⁶ | 0.92 | 2.31 | 3.221(3) | 169 |

Symmetry transformations used to generate equivalent atoms:

- 1: $-x+1, y+1/2, -z+3/2$ 2: $x+1/2, -y+1/2, -z+1$ 3: $-x+1, y-1/2, -z+1/2$
4: $-x+1/2, -y+1, z-1/2$ 5: $x+1/2, -y+3/2, -z+1$ 6: $-x+1/2, -y+1, z+1/2$
7: $-x+1, y+1/2, -z+1/2$ 8: $-x+1, y-1/2, -z+3/2$ 9: $x-1/2, -y+1/2, -z+1$
10: $-x+3/2, -y+1, z+1/2$

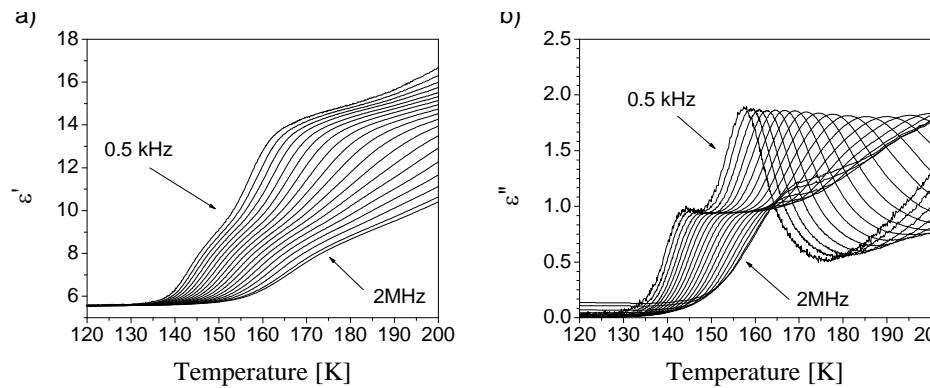


Figure S1. Temperature dependence of the real (a) and imaginary (b) parts of the complex electric permittivity obtained on cooling for MBB crystal.

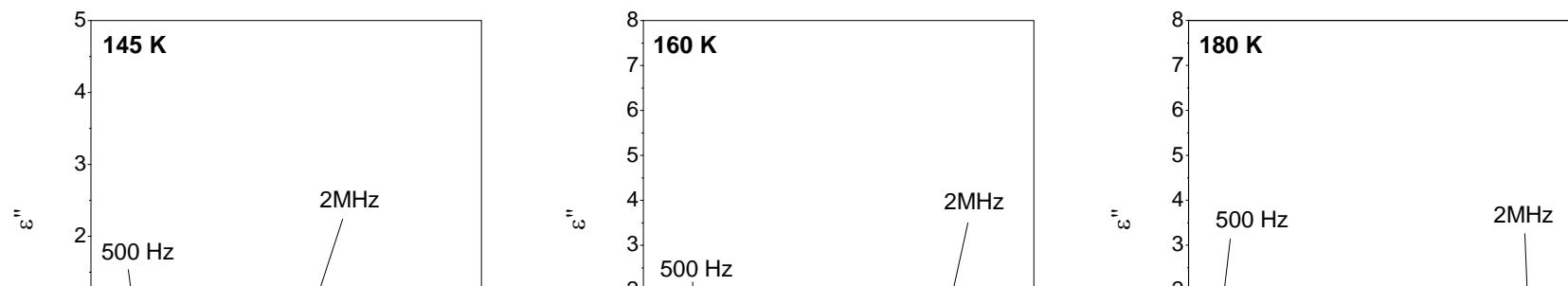


Figure S2. Cole-Cole plots of ϵ'' vs ϵ' at selected temperatures obtained for MBB crystal.

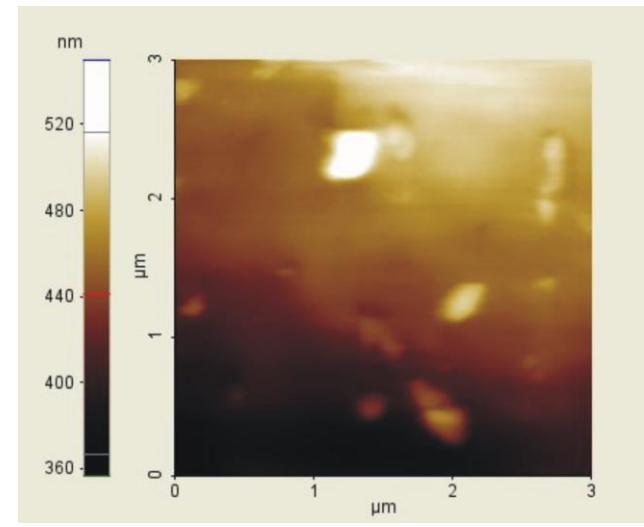
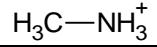
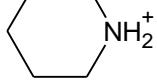
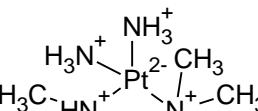
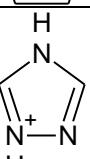
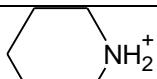
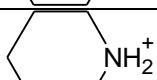
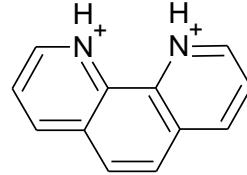
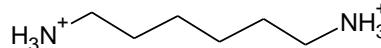
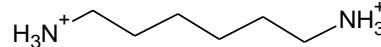
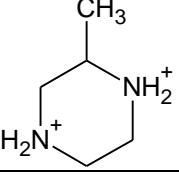
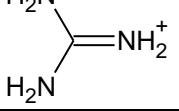


Figure S3. Topography image of MCB crystal.

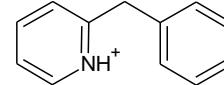
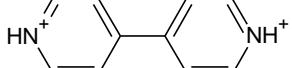
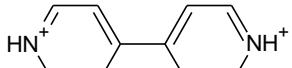
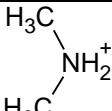
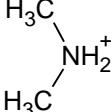
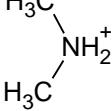
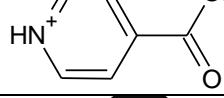
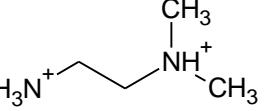
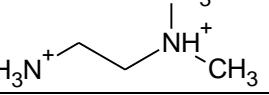
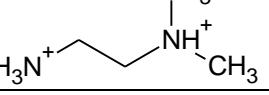
Results of the Cambridge Structural Database (CSD) survey.

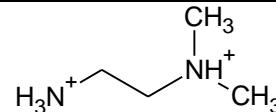
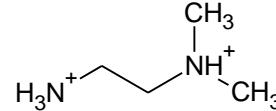
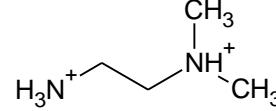
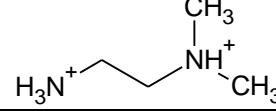
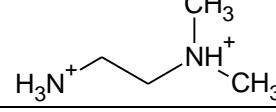
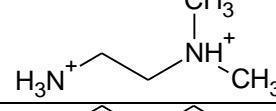
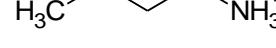
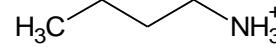
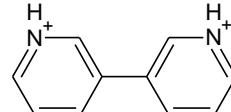
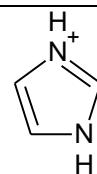
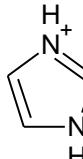
Table S3. Structures of halogenoantimonates(III) and halogenobismuthates(III) containing $[MX_5]^{2-}$ units retrieved from the CSD. Entries marked with a bolded font were used for the structural analysis of the R_2MX_5 (R – cation, M = Bi, Sb, X = Cl, Br) composition.

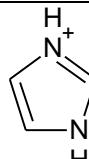
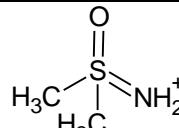
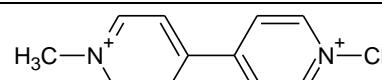
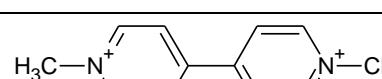
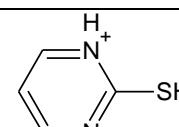
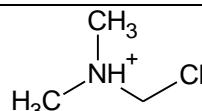
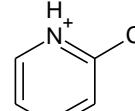
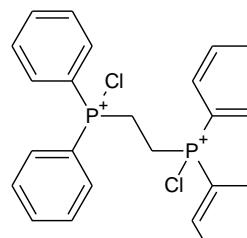
| Refcode | Empirical formula | Cation | Space group | Anionic structure type |
|---------|---|-------------------|--------------|------------------------|
| ACIKED | $(C_5H_{16}N_2)BiCl_5$ | H_3N^+ NH_3^+ | $P2_12_12_1$ | <i>cis</i> mode chain |
| AFEVEM | $(C_2H_4N_3)_2SbCl_5 \cdot (C_2H_4N_3)Cl$ | | $P2_12_12_1$ | <i>cis</i> mode chain |

| | | | | |
|---------|--|---|--------------|-----------------------|
| BOYWIV | $(\text{CH}_6\text{N})_2\text{SbCl}_5 \cdot (\text{CH}_6\text{N})\text{Cl}$ |  | $P2_1/c$ | <i>cis</i> mode chain |
| CAJXIV | $(\text{C}_5\text{H}_{12}\text{N})_2\text{BiCl}_5$ |  | $Pna2_1$ | <i>cis</i> mode chain |
| ENPTCB | $(\text{C}_5\text{H}_{20}\text{N}_4\text{Pt})\text{SbCl}_5$ |  | $P2_12_12_1$ | <i>cis</i> mode chain |
| LURXEB | $(\text{C}_2\text{H}_4\text{N}_3)_2\text{SbCl}_5$ |  | $P2_1/n$ | <i>cis</i> mode chain |
| PIPBSSB | $(\text{C}_5\text{H}_{12}\text{N})_2\text{SbBr}_5$ |  | $P2_12_12_1$ | <i>cis</i> mode chain |
| PIPRBI | $(\text{C}_5\text{H}_{12}\text{N})_2\text{BiBr}_5$ |  | $P2_12_12_1$ | <i>cis</i> mode chain |
| PURLIX | $(\text{C}_{12}\text{H}_{10}\text{N}_2)\text{BiCl}_5 \cdot 2\text{H}_2\text{O}$ |  | $P2/c$ | <i>cis</i> mode chain |
| SOWPAV | $(\text{C}_6\text{H}_{18}\text{N}_2)\text{BiCl}_5$ |  | $P2_1/n$ | <i>cis</i> mode chain |
| SOWQEA | $(\text{C}_6\text{H}_{18}\text{N}_2)\text{SbBr}_5$ |  | $Pn2_1a$ | <i>cis</i> mode chain |
| SUXTUB | $(\text{C}_5\text{H}_{14}\text{N}_2)\text{BiCl}_5$ |  | $P2_12_12_1$ | <i>cis</i> mode chain |
| YOYWOY | $(\text{CH}_6\text{N}_3)_2\text{SbCl}_5 \cdot 2(\text{CH}_6\text{N}_3)\text{Cl}$ |  | $P2_1/c$ | <i>cis</i> mode chain |

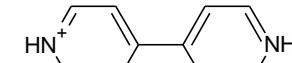
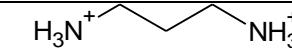
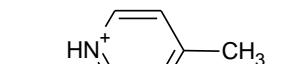
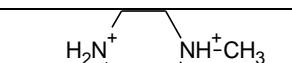
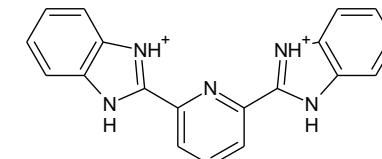
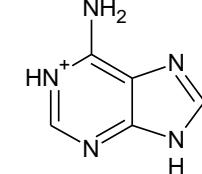
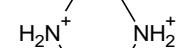
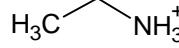
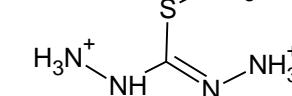
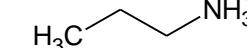
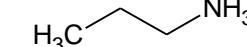
| | | | | |
|----------|--|--|--------------|--------------------------------|
| ZETGIO | $(C_5H_7N_5)SbCl_5 \cdot H_2O$ | | $P2_1/c$ | <i>cis</i> mode chain |
| GIWVUE | $(C_5H_{14}N)_2SbBr_5$ | | $Pna2_1$ | deformed <i>cis</i> mode chain |
| GIWVUE01 | $(C_5H_{14}N)_2SbBr_5$ | | $P2_12_12_1$ | deformed <i>cis</i> mode chain |
| IWIJAZ | $(C_2H_8N)_2SbBr_5$ | | $Pbca$ | deformed <i>cis</i> mode chain |
| IWIJAZ01 | $(C_2H_8N)_2SbBr_5$ | | $Cmca$ | deformed <i>cis</i> mode chain |
| PERNAC02 | $(C_4H_{12}N)_2SbCl_5$ | | $Pccn$ | deformed <i>cis</i> mode chain |
| RUJVOI | $(C_6H_8N)_2SbBr_5$ | | $Pbca$ | deformed <i>cis</i> mode chain |
| SOYBAK | $(C_{17}H_{20}N_3O_3F)SbCl_5 \cdot H_2O$ | | $P2_1/c$ | deformed <i>cis</i> mode chain |
| ANILAC10 | $(C_6H_8N)_2SbCl_5$ | | $P2_1/c$ | <i>pseudo-cis</i> mode chain |
| AWOXUF | $(C_{12}H_{18}N)_2SbCl_5 \cdot 2H_2O$ | | $Cmc2_1$ | <i>pseudo-cis</i> mode chain |
| BPCLSB01 | $(C_{12}H_{18}N)_2SbCl_5$ | | $C2/c$ | <i>pseudo-cis</i> mode chain |
| DILBUW | $(C_2H_7O)_2SbCl_5$ | | $Pnma$ | <i>pseudo-cis</i> mode chain |

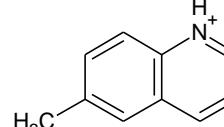
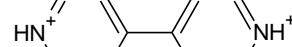
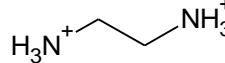
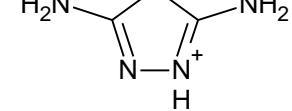
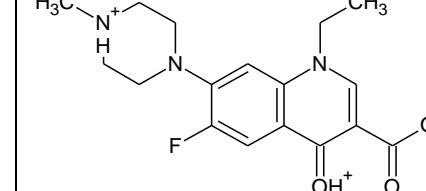
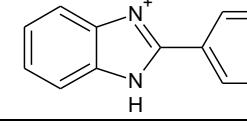
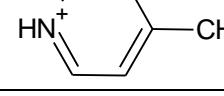
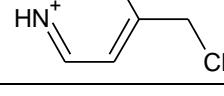
| | | | | |
|----------|-----------------------------------|---|--|---------------------------------------|
| LUHVOZ | $(C_{12}H_{12}N)_2SbCl_5$ |  | <i>P</i> -1 | <i>pseudo-cis</i> mode chain |
| PYCLSB01 | $(C_{10}H_{10}N_2)_2SbCl_5$ |  | <i>Pbc2</i> ₁ | <i>pseudo-cis</i> mode chain |
| PYCLSB02 | $(C_{10}H_{10}N_2)_2SbCl_5$ |  | <i>Pbcm</i> | <i>pseudo-cis</i> mode chain |
| SAWJOP | $(C_2H_8N)_2SbCl_5$ |  | <i>Pnma</i> | <i>pseudo-cis</i> mode chain |
| SAWJOP01 | $(C_2H_8N)_2SbCl_5$ |  | <i>Pnma</i> | <i>pseudo-cis</i> mode chain |
| SAWJOP02 | $(C_2H_8N)_2SbCl_5$ |  | <i>Pnma</i> | <i>pseudo-cis</i> mode chain |
| YOTBOZ | $(C_6H_6NO_2)_2SbCl_5 \cdot H_2O$ |  | <i>P2</i> ₁ /c | <i>pseudo-cis</i> mode chain |
| YOTCIU | $(C_4H_{10}NO)_2SbCl_5$ |  | <i>P2</i> ₁ <i>2</i> ₁ <i>2</i> ₁ | <i>pseudo-cis</i> mode chain |
| MENTIJ | $(C_4H_{14}N_2)_2SbCl_5$ |  | <i>P2</i> ₁ /n | deformed <i>pseudo-cis</i> mode chain |
| MENTIJ01 | $(C_4H_{14}N_2)_2SbCl_5$ |  | <i>P2</i> ₁ /n | deformed <i>pseudo-cis</i> mode chain |
| MENTIJ02 | $(C_4H_{14}N_2)_2SbCl_5$ |  | <i>P2</i> ₁ /n | deformed <i>pseudo-cis</i> mode chain |

| | | | | |
|----------|---------------------------|---|----------------|---------------------------------------|
| MENTIJ03 | $(C_4H_{14}N_2)SbCl_5$ |  | $P\bar{2}_1/n$ | deformed <i>pseudo-cis</i> mode chain |
| REYFUW | $(C_4H_{14}N_2)SbCl_5$ |  | $P\bar{2}_1/c$ | deformed <i>pseudo-cis</i> mode chain |
| REYFUW01 | $(C_4H_{14}N_2)SbCl_5$ |  | $P\bar{2}_1/c$ | deformed <i>pseudo-cis</i> mode chain |
| REYFUW02 | $(C_4H_{14}N_2)SbCl_5$ |  | $P\bar{2}_1/c$ | deformed <i>pseudo-cis</i> mode chain |
| REYFUW03 | $(C_4H_{14}N_2)SbCl_5$ |  | $P\bar{2}_1/c$ | deformed <i>pseudo-cis</i> mode chain |
| REYFUW04 | $(C_4H_{14}N_2)SbCl_5$ |  | $P\bar{2}_1/c$ | deformed <i>pseudo-cis</i> mode chain |
| PERNAC | $(C_4H_{12}N)_2SbCl_5$ |  | $Pccn$ | deformed <i>pseudo-cis</i> mode chain |
| PERNAC01 | $(C_4H_{12}N)_2SbCl_5$ |  | $Ibam$ | disordered <i>cis</i> mode chain |
| MADGUU | $(C_{10}H_{10}N_2)SbCl_5$ |  | $P\bar{2}_1/c$ | atypical <i>cis</i> mode chain |
| QAFHUB | $(C_3H_5N_2)_2SbCl_5$ |  | $Pbcn$ | atypical <i>cis</i> mode chain |
| [1] | $(C_3H_5N_2)_2SbCl_5$ |  | $Pna\bar{2}_1$ | atypical <i>cis</i> mode chain |

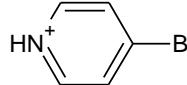
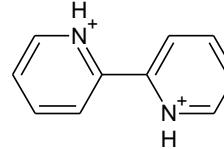
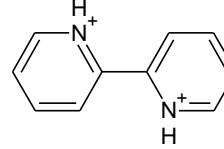
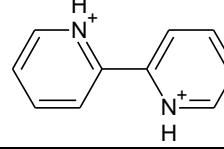
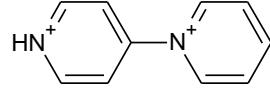
| | | | | |
|--------|---------------------------------|---|-------------------|---------------------------------------|
| [1] | $(C_3H_5N_2)_2SbCl_5$ |  | <i>Pbcn</i> | atypical <i>cis</i> mode chain |
| REGYIL | $(C_2H_8NOS)_2SbCl_5$ |  | <i>C2/c</i> | atypical <i>cis</i> mode chain |
| [2] | $(C_{12}H_{14}N_2)BiBr_5$ |  | <i>P2_1/c</i> | <i>trans</i> mode chain |
| [2] | $(C_{12}H_{14}N_2)BiBr_5$ |  | <i>P2_1</i> | <i>trans</i> mode chain |
| FORYUH | $(C_4H_5N_2S)_2SbBr_5$ |  | <i>P2_1/n</i> | disordered <i>trans</i> mode chain |
| BOMQUP | $(C_4H_{12}N)_2SbCl_5$ |  | <i>P2_12_12_1</i> | <i>pseudo-trans</i> mode chain |
| CLPYSB | $(C_5H_5NCl)_2SbBr_5$ |  | <i>Pa</i> | <i>pseudo-trans</i> mode chain |
| LUWZIM | $(C_{26}H_{24}Cl_2P_2)_2SbCl_5$ |  | <i>P -I</i> | isolated, interaction with cation |

| | | | | |
|-----------------|---|--|---------------|--|
| TEDVED | $(C_8H_{20}N)_2SbCl_5$ | | P4/mnc | isolated |
| TEDVED01 | $(C_8H_{20}N)_2SbCl_5$ | | Pcnn | isolated |
| TEZSIA | $(C_7H_{23}N_5ClCr)SbCl_5$ | | Pbca | isolated, interaction with cation |
| TEZSOG | $(C_{11}H_{31}N_5ClCr)SbCl_5 \cdot H_3O^+Cl^- \cdot H_2O$ | | Cc | isolated |
| DAKWIW | $(C_6H_8N)_2SbCl_5 \cdot (C_6H_8N)Cl \cdot H_2O$ | | P-1 | isolated, close to $M_2X_{10}^{4-}$ unit |
| DAKWIW01 | $(C_6H_8N)_2SbCl_5 \cdot (C_6H_8N)Cl \cdot H_2O$ | | P-1 | isolated, close to $M_2X_{10}^{4-}$ unit |
| FOTTUE | $(C_{12}H_{11}N_3)SbCl_5 \cdot H_2O$ | | P21/c | isolated, close to $M_2X_{10}^{4-}$ unit |

| | | | | |
|-----------------|--|---|-------------------------|--|
| PYCLSB | (C ₁₀ H ₁₀ N ₂)SbCl ₅ |  | P-1 | isolated, close to M ₂ X ₁₀ ⁴⁻ unit |
| VAVRIT | (C ₃ H ₁₂ N ₂)SbCl ₅ |  | P2₁/c | isolated, close to M ₂ X ₁₀ ⁴⁻ unit |
| VIKCUO | (C ₆ H ₈ N) ₂ SbCl ₅ |  | P-1 | isolated, close to M ₂ X ₁₀ ⁴⁻ unit |
| XISDOT | (C ₅ H ₁₄ N ₂)SbCl ₅ · H ₂ O |  | P2₁/c | isolated, close to M ₂ X ₁₀ ⁴⁻ unit |
| YIVLIZ | (C ₁₉ H ₁₅ N ₅)SbCl ₅ |  | P-1 | isolated, close to M ₂ X ₁₀ ⁴⁻ unit |
| ZETGOU | (C ₅ H ₆ N ₅) ₂ SbCl ₅ · H ₂ O |  | P-1 | isolated, close to M ₂ X ₁₀ ⁴⁻ unit |
| <hr/> | | | | |
| CASPES | (C ₄ H ₁₂ N ₂) ₂ Bi ₂ Cl ₁₀ · 3H ₂ O |  | C2/c | M ₂ X ₁₀ ⁴⁻ unit |
| COJXAA | (C ₂ H ₈ N) ₄ Sb ₂ Cl ₁₀ · 2(C ₂ H ₈ N)Cl |  | P-1 | M ₂ X ₁₀ ⁴⁻ unit |
| COJXAA01 | (C ₂ H ₈ N) ₄ Sb ₂ Cl ₁₀ · 2(C ₂ H ₈ N)Cl |  | P-1 | M ₂ X ₁₀ ⁴⁻ unit |
| CUMPAB | (C ₂ H ₁₀ N ₄ S) ₂ Bi ₂ Cl ₁₀ · 4H ₂ O |  | P-1 | M ₂ X ₁₀ ⁴⁻ unit |
| DEWKUM | (C ₃ H ₈ N) ₄ Sb ₂ Cl ₁₀ · 2(C ₃ H ₈ N)Cl |  | P-1 | M ₂ X ₁₀ ⁴⁻ unit |
| DEWKUM01 | (C ₃ H ₈ N) ₄ Sb ₂ Cl ₁₀ · 2(C ₃ H ₈ N)Cl |  | P-1 | M ₂ X ₁₀ ⁴⁻ unit |

| | | | | |
|-----------------|---|---|-----------------|-----------------------|
| IBENAF | $(C_{10}H_{10}N)_4Sb_2Cl_{10}$ |  | <i>C2/m</i> | $M_2X_{10}^{4-}$ unit |
| IDOKIW | $(C_{10}H_{10}N_2)_2Bi_2Br_{10}$ |  | P-1 | $M_2X_{10}^{4-}$ unit |
| JIVZAP | $(C_2H_{10}N_2)_2Bi_2Cl_{10} \cdot 4H_2O$ |  | <i>P2_1/n</i> | $M_2X_{10}^{4-}$ unit |
| JUFKEA | $(C_2H_5N_4S)_4Bi_2Br_{10}$ |  | P-1 | $M_2X_{10}^{4-}$ unit |
| MODBIR | $(C_{17}H_{22}N_3O_3F)_2Bi_2Cl_{10} \cdot 2(C_{17}H_{22}N_3O_3F)Cl \cdot 8H_2O$ |  | <i>C2/m</i> | $M_2X_{10}^{4-}$ unit |
| POWREZ | $(C_{12}H_{11}N_3)_2Bi_2Cl_{10} \cdot 2H_2O$ |  | <i>P2_1/c</i> | $M_2X_{10}^{4-}$ unit |
| QEESOX | $(C_{12}H_{18}N)_4Bi_2Cl_{10} \cdot 2H_2O$ |  | <i>P2_1/c</i> | $M_2X_{10}^{4-}$ unit |
| QQQGRV01 | $(C_6H_8N)_4Sb_2Br_{10}$ |  | P-1 | $M_2X_{10}^{4-}$ unit |
| RAGPAR | $(C_7H_{10}N)_4Sb_2Cl_{10}$ |  | P4_12_12 | $M_2X_{10}^{4-}$ unit |

| | | | | |
|---------------|--|--|---------------|-----------------------|
| RIHLAV | $(C_{12}H_{18}N_4OS)_2Sb_2Cl_{10}$ | | P-1 | $M_2X_{10}^{4-}$ unit |
| RIZBEH | $(C_9H_8N)_4Bi_2Cl_{10}$ | | P-1 | $M_2X_{10}^{4-}$ unit |
| RIZBIL | $(C_9H_8N)_4Bi_2Cl_{10} \cdot 2H_2O$ | | <i>Cmca</i> | $M_2X_{10}^{4-}$ unit |
| SIWZUU | $(C_9H_8NO)_4Bi_2Cl_{10} \cdot (C_9H_8NO)_2(BiCl_5H_2O) \cdot 6H_2O$ | | <i>C2/c</i> | $M_2X_{10}^{4-}$ unit |
| VIZFAM | $(C_3H_5N_2)_4Bi_2Br_{10} \cdot 2H_2O$ | | <i>C2/m</i> | $M_2X_{10}^{4-}$ unit |
| WAVZUP | $(C_5H_{14}N_2)_2Bi_2Cl_{10} \cdot 2H_2O$ | | <i>P2_1/n</i> | $M_2X_{10}^{4-}$ unit |
| XANKAZ | $(C_{16}H_{19}N_3O_3F)_4Bi_2Cl_{10} \cdot 8H_2O$ | | <i>C2/m</i> | $M_2X_{10}^{4-}$ unit |
| XERLIP | $(C_{10}H_{10}N_2)_2Bi_2Cl_{10}$ | | P-1 | $M_2X_{10}^{4-}$ unit |
| ZIKFUU | $(C_2H_8N)_4Bi_2Cl_{10}$ | | <i>P2_1/c</i> | $M_2X_{10}^{4-}$ unit |

| | | | | |
|-----------------|----------------------------------|---|-------------------------|-----------------------|
| PUQSAW | $(C_5H_5NBr)_4Sb_2Br_{10}$ |  | P-1 | $M_2X_{10}^{4-}$ unit |
| PURLOD | $(C_{10}H_{10}N_2)_4Bi_4Cl_{20}$ |  | P2₁/c | $M_4X_{20}^{8-}$ unit |
| PURLOD01 | $(C_{10}H_{10}N_2)_4Bi_4Cl_{20}$ |  | P2₁/c | $M_4X_{20}^{8-}$ unit |
| CEFNIK | $(C_{10}H_{10}N_2)_4Sb_4Cl_{20}$ |  | P2₁/c | $M_4X_{20}^{8-}$ unit |
| MADHAB | $(C_{10}H_{10}N_2)_4Sb_4Cl_{20}$ |  | P2₁/c | $M_4X_{20}^{8-}$ unit |

[1] A. Piecha, A. Białońska, R. Jakubas, J. Mater. Chem. 22 (2012) 333

[2] W. Bi, N. Leblanc, N. Mercier, P. Auban-Senzier and C. Pasquier , Chem. Mater. 2009, 21, 4099–4101