Morpholinium chloroindate(III) complex: rare acentric structural arrangement leading to piezoelectric properties

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SUPPORTING INFORMATION

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1. Experimental section

All starting materials were used as received: morpholine (≥99%, Sigma Aldrich), $InCl_3$ (≥99%, Sigma Aldrich), $InBr_3$ (99%, Sigma Aldrich), (hydrochloric acid (37%, Sigma Aldrich), hydrobromic acid (48%, Sigma Aldrich). Simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed using a Setaram SETSYS 16/18 instrument in the temperature range 300–750 K with a ramp rate of 2 K min^{-1}. The scans were performed under flowing nitrogen (flow rate: 1 dm^3 h^{-1}). Perkin Elmer 8500 Differential Scanning Calorimeter (DSC), calibrated using *n*-heptane and indium, was used to analyze thermal stability of the compound. Hermetically sealed Al pans with the polycrystalline material were prepared in a controlled-atmosphere N_2 glovebox. The frequency dependence of complex electric permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$, was measured between 120 and 300 K with an Agilent 4980A Precision LCR Meter in the frequency range 10 kHz to 1 MHz. A silver conductive paste was applied onto the opposite large faces of a crystal. The dimensions of the sample were approximately 3 × 4 × 0.6 mm^3. The overall error in electric permittivity measurements was less than 5%.

2. Differential Scanning Calorimetry

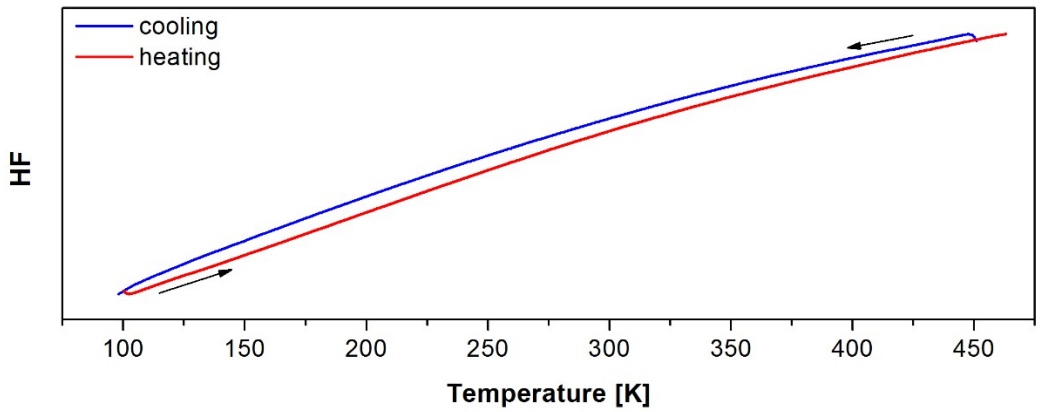

Figure S1. DSC curves for **$[C_4H_{10}NO][InCl_5(C_4H_{10}NO)]$** for cooling (blue) and heating (red) runs.

3. Single-crystal X-ray diffraction

a) Crystal structure of $[C_4H_{10}NO][InCl_5(C_4H_{10}NO)]$

X-ray diffraction measurements of **$[C_4H_{10}NO][InCl_5(C_4H_{10}NO)]$** crystal were performed on an Xcalibur diffractometer equipped with Mo Kα X-ray microsource and a CCD area detector. Data collection, cell refinement, and data reduction were carried out with the Xcalibur PX software, CrysAlis PRO. The structures were solved with the ShelXS structure solution program using direct

methods and refined with the ShelXL[1] with anisotropic thermal parameters for non-H atoms. All H atoms were treated as riding and placed in geometrically optimized positions. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC 1557930. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif website.

Table S1. Crystal data, data collection and structure refinement parameters of **$[C_4H_{10}NO]^+[InCl_5(C_4H_{10}NO)]^-$**.

Empirical formula	$[C_4H_{10}NO]^+[InCl_5C_4H_{10}NO]^-$
Formula weight (g mol^{-1})	468.33
Temperature (K)	100
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	$Cmc2_1$
a (Å)	32.227(9)
b (Å)	14.685(6)
c (Å)	14.001(6)
V (Å^3)	6626(4)
Z	16
D_{calc} (Mg m^{-3})	1.878
μ (mm^{-1})	2.228
F(000)	3712
Crystal size (mm^3)	0.26 × 0.23 × 0.11
θ range (º)	2.8–28.7
Ranges of h, k, l	$-41 \le h \le 39$ $-19 \le k \le 19$ $-18 \le l \le 17$
Absorption correction	Analytical
Refl. collected/unique	23654/7360
R_{int}	0.025
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7360/1/337
Goodness-of-fit on F^2	0.985
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0194$ $wR_2 = 0.0426$
R indices (all data)	$R_1 = 0.0216$ $wR_2 = 0.0430$
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.91/–0.47
Flack parameter	0.028(11)
CCDC number	1557930

Table S2. Geometric parameters of the **$[InCl_5(C_4H_{10}NO)]^-$** octahedral unit.

In1—Cl2	2.4771(9) Å	O1—In1—Cl3	88.13(7)°
In1—Cl2^i	2.4771(9) Å	Cl5—In2—Cl8	91.48(4)°
In1—Cl1	2.4591(13) Å	Cl7—In2—Cl5	170.08(3)°
In1—Cl3	2.4819(9) Å	Cl7—In2—Cl8	89.10(4)°

In1—Cl3^{i}	2.4819(9) Å	Cl7—In2—Cl6	88.89(4)°
In1—O1	2.351(3) Å	Cl6—In2—Cl5	88.88(4)°
In2—Cl5	2.4838(9) Å	Cl6—In2—Cl8	170.33(3)°
In2—Cl8	2.4863(9) Å	Cl4—In2—Cl5	93.23(3)°
In2—Cl7	2.4752(9) Å	Cl4—In2—Cl8	93.53(3)°
In2—Cl6	2.4796(9) Å	Cl4—In2—Cl7	96.61(4)°
In2—Cl4	2.4532(11) Å	Cl4—In2—Cl6	96.09(4)°
In2—O2	2.404(3) Å	O2—In2—Cl5	84.73(6)°
In3—Cl10^{ii}	2.4796(9) Å	O2—In2—Cl8	83.87(6)°
In3—Cl10	2.4796(9) Å	O2—In2—Cl7	85.49(6)°
In3—Cl9	2.4461(14) Å	O2—In2—Cl6	86.54(6)°
In3—Cl11^{ii}	2.4943(9) Å	O2—In2—Cl4	176.65(7)°
In3—Cl11	2.4943(9) Å	Cl10—In3—Cl10^{ii}	91.35(4)°
In3—O3	2.323(3) Å	Cl10^{ii}—In3—Cl11^{ii}	170.96(3)°
Cl2^{i}—In1—Cl2	91.93(4)°	Cl10—In3—Cl11	170.96(3)°
Cl2—In1—Cl3^{i}	88.73(3)°	Cl10^{ii}—In3—Cl11	88.76(3)°
Cl2^{i}—In1—Cl3	88.73(3)°	Cl10—In3—Cl11^{ii}	88.76(3)°
Cl2^{i}—In1—Cl3^{i}	170.25(3)°	Cl9—In3—Cl10^{ii}	94.81(4)°
Cl2—In1—Cl3	170.25(3)°	Cl9—In3—Cl10	94.81(4)°
Cl1—In1—Cl2	94.60(4)°	Cl9—In3—Cl11^{ii}	94.19(4)°
Cl1—In1—Cl2^{i}	94.60(4)°	Cl9—In3—Cl11	94.19(4)°
Cl1—In1—Cl3^{i}	95.04(4)°	Cl11^{ii}—In3—Cl11	89.71(4)°
Cl1—In1—Cl3	95.04(4)°	O3—In3—Cl10	83.94(6)°
Cl3^{i}—In1—Cl3	88.99(4)°	O3—In3—Cl10^{ii}	83.94(6)°
O1—In1—Cl2^{i}	82.33(6)°	O3—In3—Cl9	178.21(9)°
O1—In1—Cl2	82.33(6)°	O3—In3—Cl11^{ii}	87.08(6)°
O1—In1—Cl1	175.55(9)°	O3—In3—Cl11	87.08(6)°
O1—In1—Cl3^{i}	88.13(7)°		
Symmetry codes: −*x*, *y*, *z*; (*ii*) −*x*, *y*, *z*			

Table S3. Hydrogen bonds parameters (Å, °) of **[$C_4H_{10}NO$]$^+$[$InCl_5(C_4H_{10}NO)$]$^-$**.

D—H···*A*	*D*—H	*H*···*A*	*D*···*A*	*D*—H···*A*
anion-anion hydrogen bonds				
N1—H1*C*···Cl11^{iii}	0.99	2.58	3.373(4)	137
N1—H1*C*···Cl11^{iv}	0.99	2.58	3.373(4)	137
N1—H1*D*···Cl10^{v}	0.99	2.61	3.394(3)	136
N1—H1*D*···Cl10^{vi}	0.99	2.61	3.394(3)	136
N3—H3*A*···Cl2^{v}	0.99	2.57	3.323(3)	133
N3—H3*A*···Cl2^{vii}	0.99	2.57	3.323(3)	133
N3—H3*B*···Cl3^{viii}	0.99	2.55	3.345(4)	137
N3—H3*B*···Cl3^{iv}	0.99	2.55	3.345(4)	137
N2—H2*C*···Cl5^{v}	0.99	2.57	3.357(3)	136
N2—H2*C*···Cl8^{v}	0.99	2.57	3.345(3)	135
N2—H2*D*···Cl7^{iv}	0.99	2.51	3.295(3)	136
N2—H2*D*···Cl6^{iv}	0.99	2.51	3.291(3)	136

anion-cation hydrogen bonds				
N5—H5*C*···Cl2^{i}	0.99	2.52	3.336(3)	139
N5—H5*C*···Cl3	0.99	2.63	3.411(3)	136
N5—H5*D*···Cl5	0.99	2.62	3.399(3)	136
N5—H5*D*···Cl6	0.99	2.51	3.297(3)	136
N4—H4*C*···Cl8	0.99	2.49	3.313(3)	140
N4—H4*C*···Cl7	0.99	2.63	3.384(3)	134
N4—H4*D*···Cl10^{ii}	0.99	2.63	3.397(3)	135
N4—H4*D*···Cl11	0.99	2.57	3.392(3)	141

Symmetry codes: (*i*) −*x*+1, *y*, *z*; (*ii*) −*x*, *y*, *z*; (*iii*) *x*+1/2, −*y*+3/2, *z*−1/2; (*iv*) −*x*+1/2, −*y*+3/2, *z*−1/2; (*v*) −*x*+1/2, *y*+1/2, *z*; (*vi*) *x*+1/2, *y*+1/2, *z*; (*vii*) *x*−1/2, *y*+1/2, *z*; (*viii*) *x*−1/2, −*y*+3/2, *z*−1/2.

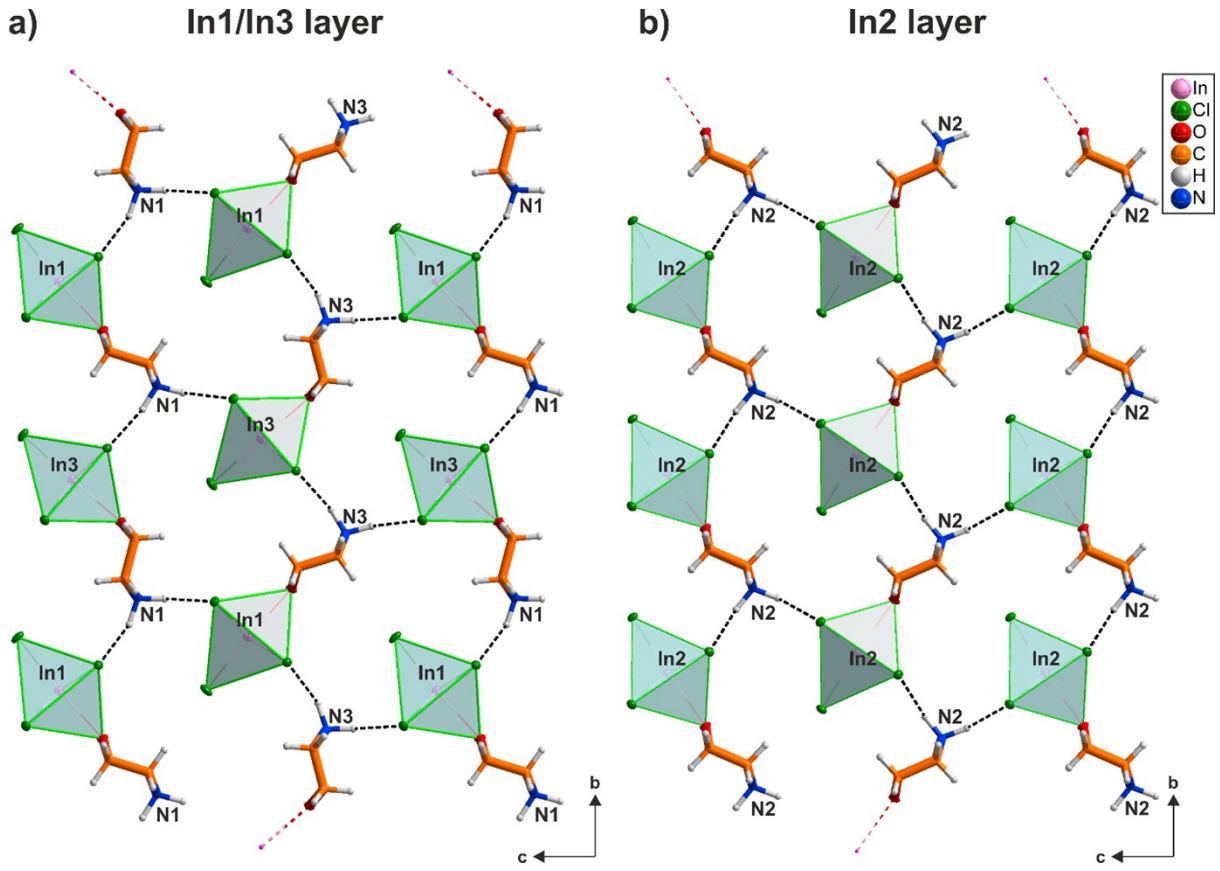

Figure S2. The projection of In1/In3 layer (a) and In2 layer (b) along the *a*-axis. Black dashed lines represents N—H···Cl hydrogen bonds.

b) Crystal structure of $[C_4H_{10}NO]_2[InBr_5(H_2O)]\cdot H_2O$

Single crystal X-ray diffraction data for **$[C_4H_{10}NO]_2[InBr_5(H_2O)]\cdot H_2O$** was collected at 100 K on Agilent Technologies Xcalibur Ruby κ-axis four circle diffractometers equipped with an Oxford Cryosystem cooler using graphite monochromated MoKα radiation. The structure was solved by direct method with SHELXS-

2014 program[1] and refined by the full-matrix least-squares methods on all F^2 data using SHELXL-2014 program[2]. Data collection was made using CrysAlis CCD, reduction was executed on CrysAlisPro. In and Br atoms were refined anisotropically. H atoms attached to O and N atoms were found in a difference Fourier map. Water H atoms were refined with O─H, H···H distance restrained to 0.8400(2), 1.3800(2) Å, respectively. H atoms isotropic temperature factors were assumed as 1.2 times U_{eq}(N) and 1.5 times U_{eq}(O). Then water H atoms and N-bound H atoms were constrained to ride on their parent atoms (AFIX 3 instruction in SHELXL-2014). H atoms attached to C were treated as riding model and their isotropic temperature factors were assumed as 1.2 timed U_{eq}. The crystal data together with experimental and refinements details are given in Table S4.

The data shown below have not been deposited in the Cambridge Crystallographic Data Centre and should be treated as preliminary. **$[C_4H_{10}NO]_2[InBr_5(H_2O)]\cdot H_2O$** gives twinned crystals which constitute a challenge for the single-crystal X-ray data collection.

Table S4. Crystal data, data collection and structure refinement parameters of **$[C_4H_{10}NO]_2[InBr_5(H_2O)]\cdot H_2O$**.

Empirical formula	$[C_4H_{10}NO]_2[InBr_5(H_2O)]\cdot H_2O$
Formula weight (g mol^{-1})	726.66
Temperature (K)	100
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	31.017(4)
b (Å)	8.234(2)
c (Å)	15.769(5)
β (°)	103.75(2)
V (Å^3)	3911.9(17)
Z	8
D_{calc} (Mg m^{-3})	2.468
μ (mm^{-1})	11.43
F(000)	2736
Crystal size (mm^3)	0.22 × 0.13 × 0.05
θ range (º)	2.7–30.8
Ranges of h, k, l	$-37 \le h \le 37$ $-9 \le k \le 9$ $-19 \le l \le 18$
Absorption correction	Analytical
Refl. collected/unique	29244/7272
R_{int}	0.055
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7272/12/221

Goodness-of-fit on F^2	1.32
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1320$ $wR_2 = 0.3596$
R indices (all data)	$R_1 = 0.1350$ $wR_2 = 0.3605$
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	6.03/–3.62

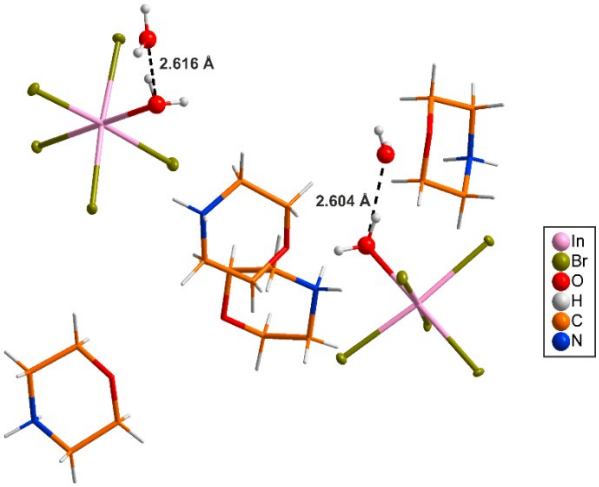

Figure S3. Asymmetric part of the unit cell of **$[C_4H_{10}NO]_2[InBr_5(H_2O)]\cdot H_2O$**.

4. Cambridge Structural Database (CSD) survey

a) Six-membered aliphatic heterocyclic amines coordinating to a metal center

A Cambridge Structural Database survey was carried out on the CSD version 5.38 (November 2016). To find as many crystal structures with the shown below structural motifs (Figure S2), only a '3D coordinates determined' general filter was used.

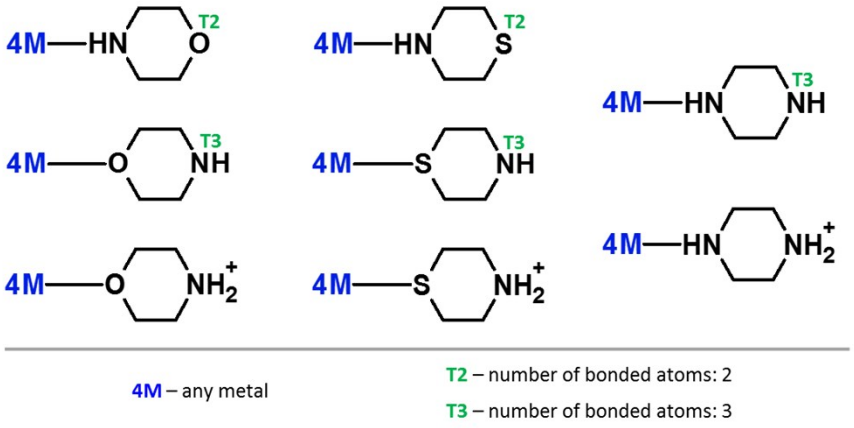

Figure S4. Structural motifs along with element filters used for the CSD survey.

b) Histograms of donor-acceptor distance in O—H···O hydrogen bond

A Cambridge Structural Database survey of a donor-acceptor distance in O—H···O hydrogen bonds with the OHO angle in a range between 150° and 180° has been performed for three structural motifs shown in Figure S4. General filters that has been used are shown below.

GENERAL FILTERS	
✓ 3D coordinates	✓ No errors
✓ *R* factor ≤ 0.05	✓ Not polymeric
✓ Not disordered	✓ Only organic

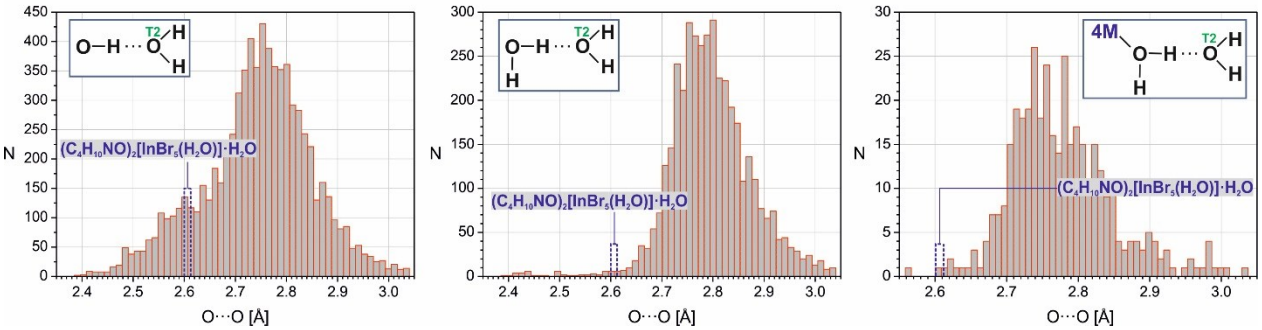

Figure S5. Distribution of O···O distance in crystal structures deposited in CSD for three structural motifs. O···O distances found in **$[C_4H_{10}NO]_2[InBr_5(H_2O)]\cdot H_2O$** are marked with blue lines. **4M** – any metal; **T2** – number of bonded atoms: 2.

5. References

[1] Sheldrick, G. M.; *Acta Crystallogr. Sect. A Found. Crystallogr.* 2007, **64**, 112–122.

[2] Sheldrick, G. M.; *Acta Crystallogr. Sect. C Struct. Chem.* 2015, **71**, 3–8.