## Supplementary Information

# Dichlorine-containing chlorobismuthate(III) supramolecular hybrid: structure and experimental studies of stability

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### Synthetic procedures

All reagents were obtained from commercial sources and used without additional purification. **Caution:** All experiments with dichlorine require obligatory use of fume hood and presence of adequate exhaust ventilation, as well as eye (goggles) and skin (gloves) protection.

### Synthesis of 1

93.2 mg (0.2 mmol) of $Bi_2O_3$ and 44 mg (0.4 mmol) of $Me_4NCl$ were dissolved in 4 ml of concentrated HCl and heated to 60°C. At this temperature, excess of dichlorine was bubbled through the solution for 5 min. Solution was filtered and $Cl_2$ was bubbled for another 5 min. Then the vial was closed and slowly cooled to 5°C. Within one day, there form transparent crystals of **1**. Yield: 69%. For $C_{12}H_{36}Bi_2Cl_{11}N_3$ calcd, %: C, 14.05; H, 3.54; N, 4.10; found, %: C, 14.06; H, 3.58; N, 4.11.

### X-ray Diffractometry

Crystallographic data and refinement details for **1** are given in Table S1. The diffraction data were collected on a Bruker D8 Venture diffractometer with a CMOS PHOTON III detector and IμS 3.0 source (Mo Kα radiation, λ = 0.71073 Å) at 150 K. The ϕ- and ω-scan techniques were employed. Absorption correction was applied by SADABS (Bruker Apex3 software suite: Apex3, SADABS-2016/2 and SAINT, version 2018.7-2; Bruker AXS Inc.: Madison, WI, 2017.). Structures were solved by SHELXT[1] and refined by full-matrix least-squares treatment against $|F|^2$ in anisotropic approximation with SHELX 2014/7[2] in ShelXle program.[3] H-atoms were refined in the geometrically calculated positions. The crystallographic data have been deposed in the Cambridge Crystallographic Data Centre under the deposition codes CCDC 2141780.

[1] G.M. Sheldrick, Acta Crystallogr. Sect. A Found. Adv. 71 (2015) 3–8.

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

[3] C.B. Hübschle, G.M. Sheldrick, B. Dittrich, J. Appl. Crystallogr. 44 (2011) 1281–1284.

**Table S1.** Details of XRD experiment for **1**

| | **1** |
|---|---|
| Chemical formula | $C_{12}H_{36}Bi_2Cl_{11}N_3$ |
| $M_r$ | 1030.35 |
| Crystal system, space group | Hexagonal, $P6_3/mmc$ |
| Temperature (K) | 150 |
| $a$, $c$ (Å) | 9.1792 (3), 21.9776 (10) |
| $V$ (Å$^3$) | 1603.69 (13) |
| $Z$ | 2 |
| Radiation type | Mo $K$a |
| μ (mm$^{-1}$) | 11.88 |
| Crystal size (mm) | 0.12 × 0.10 × 0.04 |
| Diffractometer | Bruker D8 Venture diffractometer |
| Absorption correction | Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10 |
| $T_{min}$, $T_{max}$ | 0.524, 0.746 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 16530, 621, 615 |
| $R_{int}$ | 0.110 |
| θ values (°) | $\theta_{max}$ = 25.7, $\theta_{min}$ = 2.6 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.609 |
| Range of $h$, $k$, $l$ | -11 ≤ $h$ ≤ 11, -11 ≤ $k$ ≤ 11, -26 ≤ $l$ ≤ 26 |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.061, 0.141, 1.45 |
| No. of reflections, parameters, restraints | 621, 50, 94 |
| H-atom treatment | H-atom parameters constrained |
| Weighting scheme | $w = 1/[\sigma^2(F_o^2) + 50.5902P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $D\rho_{max}$, $D\rho_{min}$ (e Å$^{-3}$) | 1.76, -2.46 |

Computer programs: *APEX3* (Bruker-AXS, 2016), *SAINT* (Bruker-AXS, 2016), *SHELXT* 2014/5 (Sheldrick, 2014), *SHELXL2017*/1 (Sheldrick, 2017).

**Powder X-ray diffractometry**

XRD analysis of polycrystals was performed on Shimadzu XRD-7000 diffractometer (CuK-alpha radiation, Ni – filter, linear One Sight detector, 5 – 50° 2θ range, 0.0143° 2θ step, 2s per step). A polycrystalline sample was slightly ground with hexane in an agate mortar, and the resulting suspension was deposited on the polished side of a standard quartz sample holder, and a

smooth thin layer being formed after drying. Plotting of PXRD patterns and data treatment was performed using X'Pert Plus software.

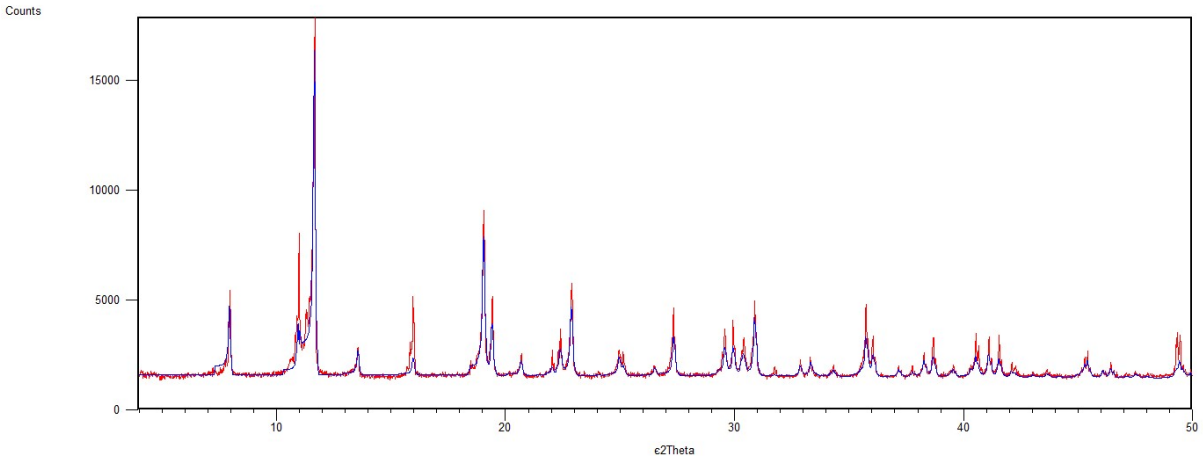


**Figure S1.** Theoretical (blue) and experimental (red) PXRD patterns for **1**

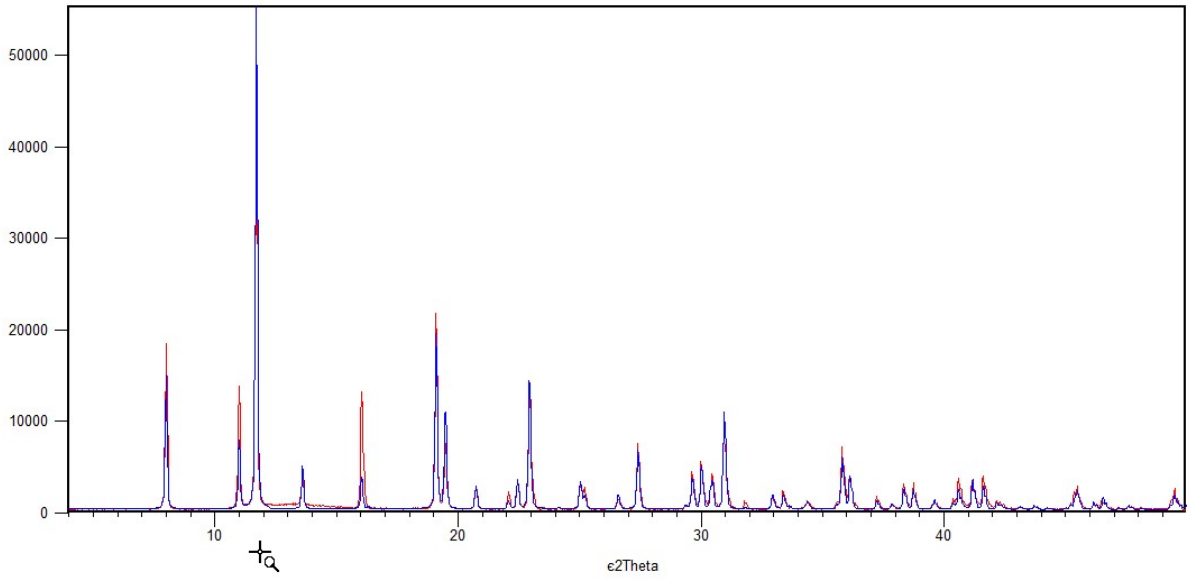


**Figure S2.** Experimental PXRD pattern (red) of the sample of **1** after TGA thermostatic experiment (140°C, ≈40 min) compared to theoretical pattern of **1** (blue)

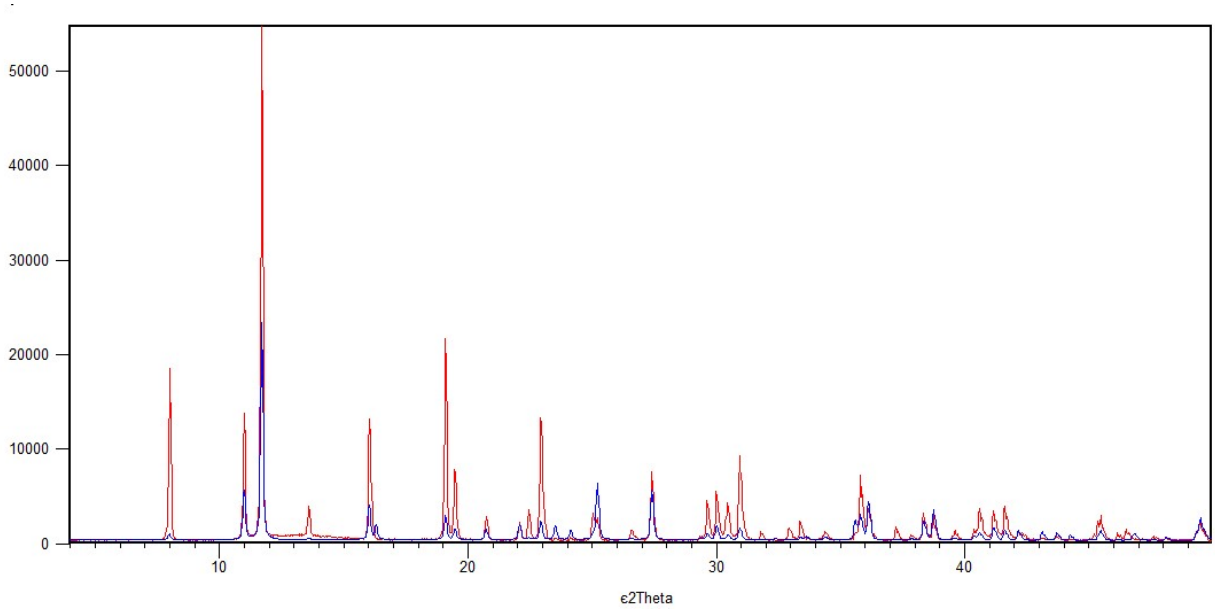


**Figure S3.** Experimental PXRD pattern (red) of the sample of **1** after TGA thermostatic experiment (140°C, ≈40 min) compared to theoretical pattern of $TMA_3[Bi_2Cl_9]$ (blue)

**Raman spectroscopy**

Raman spectra were collected using a LabRAM HR Evolution (Horiba) spectrometer with the excitation by the 633 nm line of the He-Ne laser. The spectra at room temperatures were obtained in the backscattering geometry with a Raman microscope. The laser beam was focused to a diameter of 2 micrometers using a LMPlan FL 50x/0.50 Olympus objective. The spectral resolution was 0.7 $cm^{-1}$. The laser power on the sample surface was about 0.03 mW.

**Thermogravimetric analyses (TGA)** were carried out on a TG 209 F1 Iris thermobalance (NETZSCH, Germany). The measurements were made in a helium flow in the temperature range of 30–450°C using the heating rate of 10°C $min^{-1}$ the gas flow rate of 60 mL $min^{-1}$ and open Al crucibles.