

Reversible dynamic isomerism change in the solid state, from Bi_4I_{16} clusters to BiI_4 1D chains in L-cystine based hybrids: templating effect of cations in iodobismuthate network formation†

Wenhua Bi and Nicolas Mercier*

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The dehydration of a iodobismuthate hybrid built up from Bi_4I_{16} clusters and protonated L-cystine molecules involves an unprecedented reversible dynamic structural change in the solid state leading to 1D BiI_4 chains and 1D helical molecular chains, highlighting the templating effect of cations in the formation of iodobismuthate network.

Studies on solid-state reactions in ionic salts, pure organic compounds, and coordination polymers, especially single-crystal-to-single-crystal transformations, have been greatly accelerated during the past decade, due to not only the improvement of diffraction facility, but also their particular advantages.¹ While in most cases these transformations only correspond to a conformational change of organic molecules or inorganic networks, which can be induced by the departure of guest molecules, it is comparatively rare that the structure is totally rearranged during phase transfer accompanied by the loss of solvent. This leads to define a unique category of organic–inorganic hybrids showing the so-called “dynamic structural changes”.² In the field of halogenometalate hybrids, a few of them exhibit such transformations.³ In particular, Brammer and co-workers demonstrated that the elimination of HCl molecules from a salt constructed by isolated CuCl_4^{2-} entities leads to a $\text{CuCl}_2(3\text{-Clpy})_2$ based coordination polymer (py = pyridine), and that transformation was reversible.^{3a}

Halogenometalate hybrid materials of Bi(III) and Pb(II) are of high interest due to the potential combination of properties of the two moieties within one compound. For instance, they can be processed into thin films by room-temperature techniques; while interesting electrical (semiconducting, high mobilities) properties can be expected from them.⁴ To date, more than sixty iodo-bismuthate complexes have been reported. The inorganic frameworks are either discrete clusters ranging from $(\text{BiI}_6^{3-})^5$ to $(\text{Bi}_8\text{I}_{30}^{6-})^6$ or 1D infinite chains, commonly $[\text{BiI}_4^-]_n^7$ and $[\text{BiI}_5^{2-}]_n^8$ while only one hybrid of iodobismuthate with 2D extended anionic network, namely $[\text{Bi}_{2/3}\text{I}_4^{2-}]_n^9$ has been described. As well known, it is still a great challenge to control the structures or the dimensionalities of metal halide anionic frameworks. The structures vary

depending on the experimental conditions, such as solvent, ratio of reagents, temperature, as well as the features of counterions, such as size, charge density and conformation. Even though there is no obvious rule, the trend is that non-bulky ligands with higher charge density such as primary ammonium groups will favour the formation of anions with high I/M ratios.

In the course of our investigations on halogenometalate compounds based on dications containing a disulfide group, which give rise to interesting NLO switch materials due to the conformational change of disulfide in the solid state,¹⁰ L-cystine was selected, which possesses two chiral carbon atoms besides the disulfide bridge. Herein, we report an unprecedented reversible solid-state reaction driven by dehydration/rehydration, which implies an isomerism transformation between Bi_4I_{16} clusters and 1D BiI_4 chains, accompanied by changes of the H-bond network and conformations of disulfides in the structures.

Reaction of BiI_3 (99%, Acros) and L-cystine (99%, Aldrich) and concentrated HI (57%, Aldrich) in the molar ratio of 2 : 1 : 8.94 in CH_3CN gives a few deep red prism crystals of compound **1**, namely $[\text{L-cystineH}_2\text{-(BiI}_4)_2]_n$, in a high viscosity solution. After this mixture of crystals and sticky solution was allowed to stand in the air for 3 weeks at room temperature, light red crystals of compound **2**, namely $(\text{L-cystineH}_2)_2\text{-(BiI}_{16})\cdot 6\text{H}_2\text{O}$, were obtained (XRD pattern 3, Fig. 1) in good yield (2.251 g, 65%). The departure of all of the six water molecules in **2** was followed by TGA and DSC

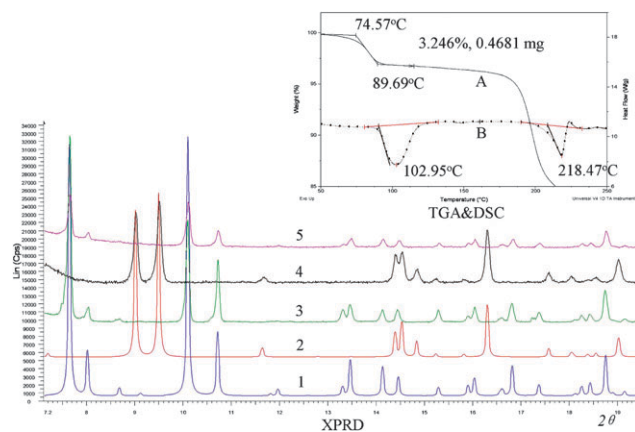


Fig. 1 Theoretical (trace 1 (**2**)), trace 2 (**1**) and experimental (trace 3 (**2**)), trace 4 (**1**, from dehydration of **2**), trace 5 (**2**, rehydration of **1**) X-ray powder patterns, and part of the TGA (A) and DSC (B) curves of **2**.

Chimie Ingénierie Moléculaire d'Angers UMR-CNRS 6200, 2 Bd Lavoisier, 49045 Angers, France.

E-mail: nicolas.mercier@univ-angers.fr; Fax: +33 (2) 41 73 54 05; Tel: +33 (2) 41 73 50 83

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experiments (Fig. 1. inset): **2** has a weight loss of 3.25% at 90 °C under an N₂ atmosphere, which accords well with the theoretical percentage of six H₂O (calc.: 3.12%). As indicated by the XRPD patterns, the dehydrated phase of **2** (trace 4, Fig. 1, sample heated at 120 °C for 1 h) corresponds to **1**, in good accordance with the same L-cystine : Bi : I ratio in both compounds, and the reversibility of this transformation has also been proved (trace 5, Fig. 1: XRPD of a sample of **1** placed in water vapour for 5 days). Finally, **1** can be prepared in good yield from a two-step reaction: first in solution (yield 65%); then in the solid state (yield 100%).

Since there are two chiral carbon atoms in the molecule of L-cystine, both structures are refined in the enantiomorphic space group *P*2₁.[‡] General views of structural layout are plotted in Fig. 2 (**1**) and Fig. 3 (**2**). In **1**, there are two crystallographic independent Bi(III) in the asymmetric unit, which are coordinated by six I⁻ to form two slightly distorted octahedra. The bond distances of Bi–I range from 3.356(1) to 2.850(1) Å (Bi1–I1 and Bi1–I4, see also Fig. S3, ESI[†]), and the bond angles between adjacent Bi–I bonds deviate from 90° by <10° (I1–Bi1–I6 = 80.10°), which are comparable with those in reported structures.^{7,8} Moreover, the BiI₆³⁻ octahedra are connected up *via* edge-shared mode extending along the 2₁ axis to form an infinite chain of anion (Fig. 2(B)).⁷ The charges of the anion chains are balanced by the spiral dication of L-cystineH₂²⁺, which are linked through H-bonding between two carboxylic groups, making up the well known supra-molecular centrosymmetric dimer-type synthon¹¹ (Fig. 4, O1–(H)··O4 = 2.65(1) Å, O3–(H)··O2 = 2.64(1) Å) already observed in halogenometalate hybrids.¹² The resulting 1D chains of cations and those of anions are packed tightly in alternating mode to form a 3D network (Fig. 2(A)).

The structure of **2** is built up from the well known Bi₄I₁₆⁴⁻ clusters. The bond lengths are in the range 2.855(1)–3.448(1) Å, which are comparable to values in literature.¹³ The anionic entities are charge balanced by two independent L-cystineH₂²⁺ cations, while six water molecules are also trapped in the structure, four of them interacting strongly with OH parts of carboxylic groups (*d*(O(H)··O(water)) in the range of 2.71(1)–2.75(1) Å, Fig. 3(B)). Every two adjacent L-cystine dication pairs form coupled pairs which are surrounded by four Bi₄I₁₆⁴⁻ clusters, and the dication pairs are linked into supra-molecular double chains along the *a* axis by water molecules (Fig. 3(A)).

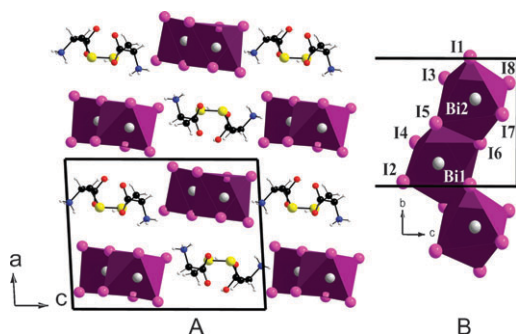


Fig. 2 The structure of **1**: view along *b* axis (A) and Bi₄I₁₆ edge-shared octahedra network (B).

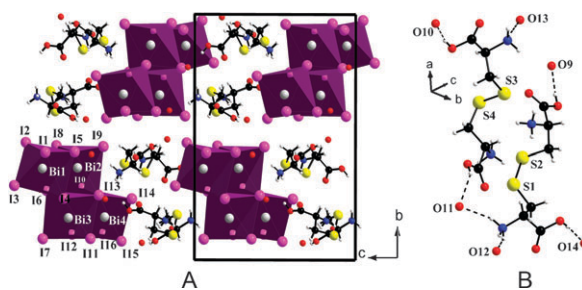


Fig. 3 The structure of **2** viewed along *a* axis (A) and the H bonding among *M* helical L-cystine and H₂O molecules (B) (H atoms of H₂O not located).

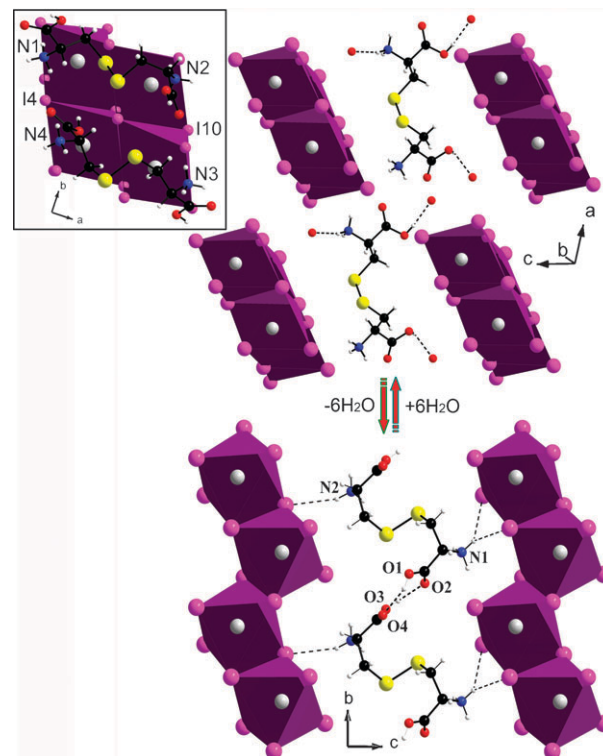


Fig. 4 The solid-state transformation driven by dehydration/hydration. Inset: part of **2** viewed along *c* showing the templating effect of cations.

After the loss of water molecules, **2** is then transformed into **1**, which was a big surprise considering the completely different frameworks in **1** and **2**. Furthermore, after being exposed in the air for a few days, **1** can be transformed back into **2** (see Fig. 1). This process belongs to the third category of solid-state reaction, namely reactions between solid and vapor,^{1a} and can be related to the dynamic structural change described by Kitagawa for a unique category of organic–inorganic compounds.^{2a} Indeed, the process includes a iodobismuthate isomerism transformation, changes in H-bond networks, and also a conformational change of disulfides. Such kind of molecular movement in the solid state has been already described for other disulfide-based compounds.¹⁰ While the organic dication is in *P* helical conformation with a torsion angle of 80.80° in **1**, both of the independent dication pairs adopt *M* conformation with torsion angles of –78.31 and –85.16°, respectively. After the departure of H₂O, all of the *M* helical

dications are then adjusted into the same *P* conformation and are arranged into H-bonded spiral chains along the *b* axis in **1**. Owing to the existence of chiral carbon atoms, it is impossible to have the mirror image of the chiral chain, that is to say an enantiomeric chain constructed from D-cystine molecules, in the structure. However, is it possible to obtain crystals with pure *M*-helical or even racemic (*M* and *P*) crystals? After checking the model molecule of L-cystine, we can imagine another kind of helical chain, but this hypothetical chain would imply structural changes such as different unit cell parameters. However, in our case, the XRPD pattern of **1** fitting perfectly with its theoretical pattern calculated from the single-crystal X-ray diffraction, we assume that only one kind of crystal is present in which the chiral conformation of disulfides is *M* in the sample of **1**. The most impressive phenomenon during this reversible solid-state reaction process concerns the inorganic network, which was changed from a Bi₄I₁₆ cluster into its isomer (BiI₄)_{*n*} chain. Certainly, consecutive clusters along the *a* axis in **2** can provide two chains running along *b* in **1** (Fig. 4). Looking at general views (Fig. 2 and 3), one can also conceptually go from **2** to **1** by shifts along *c* of blocks containing molecules and half clusters of **2** leading to the layout of **1**. However, it is not easy to figure out the exact way of how to rearrange all of the atoms during the phase transformation. Nevertheless, we may also speculate that electron-rich sulfur atoms can temporary coordinate with unsaturated Bi centers during the process of disassembly of Bi₄I₁₆⁴⁻ clusters into BiI₄⁻ chains. No direct proof, however, is available. Anyway, the suitable flexibility of organic moieties as underlined by conformational change can help the reorganisation of networks.

The reversible transformation between clusters and chains highlights the templating effect of cations in the formation of a given iodobismuthate network during a crystallization process. Thus, the supermolecular chains template a 1D zigzag inorganic network in **1**, and it is interesting to note that the period of L-cystine dication chains (for instance between two consecutive N1 atoms) is equal to the length of the Bi₂I₈ subunit along (010) as well as the length of the *b* axis (Fig. 4). While in **2**, pairs of dications template the clusters with about the same size: when viewing along *c* axis, it is easy to appreciate that the area of coupled pair is comparable to the size of Bi₄I₁₆⁴⁻ cluster (N1...N2 = 7.06 Å, N3...N4 = 7.18 Å, I4...I10 = 7.71 Å, Fig. 4, inset). Further, guest water molecules are free to separate blocks of ion pairs. Once removing the water molecules, the structure is unstable due to anionic repulsion between consecutive clusters, and the inorganic framework rearrangement into 1D chains also helped by the molecular reorganisation into H-bonded 1D chains. Owing to the absence of a symmetry centre in their structure, both **1** and **2** exhibit SHG (second harmonic generation) properties. However, the 532 nm signals (excitation at 1064 nm) are weak as the crystals are deep red. However, it is worth noting that the signal in **1** is much higher than it in **2**, which can be

explained by the orientation of the polar axis along 1D networks in **1**.

In conclusion, two novel hybrids based on iodobismuthate and L-cystine dications have been prepared and structurally characterized. The reversible solid-state reactions between them involve a dynamic change in the structure, in particular an unprecedented isomerism transformation, from Bi₄I₁₆ clusters to 1D (BiI₄)_{*n*} chains. This phenomenon also highlights the templating effect of cations in the formation of iodobismuthate networks. Finally, the removal of guest water molecules trapped in the structure by H-bond donor or acceptor molecules could also lead to novel iodobismuthate networks.

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Notes and references

† *Crystal data for 1*: C₆H₁₄O₄N₂S₂Bi₂I₈, *M* = 1675.47, monoclinic, space group *P*2₁, *a* = 12.317(3), *b* = 7.763(2), *c* = 15.223(3) Å, β = 93.07(3)°, *V* = 1453.6(6) Å³, *Z* = 2, crystal size: 0.26 × 0.08 × 0.06 mm; *T* = 296(2) K. *Crystal data for 2*: C₁₂H₄₀Bi₄I₁₆N₄O₁₄S₄, *M* = 3459.08, monoclinic, space group *P*2₁, *a* = 11.280(2), *b* = 20.396(4), *c* = 14.375(3) Å, β = 101.79(3)°, *V* = 3237.4(11) Å³, *Z* = 2, crystal size: 0.16 × 0.08 × 0.02 mm; *T* = 296(2) K. The refinements of positions and anisotropic thermal motion parameters of the non-H atoms, converge to *R*_(F) = 0.044 (8773 reflections (48 600 collected (*R*_{int} = 0.044)), 222 parameters), *wR*2(*F*²) = 0.082 (all data), GOF on *F*² = 1.068, Δ*ρ*_{max} = 1.46 e Å⁻³ for **1**; and to *R*_(F) = 0.038 (15 908 reflections (93 175 collected (*R*_{int} = 0.055)), 496 parameters), *wR*2(*F*²) = 0.054 (all data), GOF on *F*² = 1.059, Δ*ρ*_{max} = 1.34 e Å⁻³ for **2**.

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