Multiparameter high-throughput and *in situ* X-ray
diffraction study of six new bismuth
sulfonatocarboxylates – discovery, phase
transformation and reaction trends

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ABSTRACT: Employing high-throughput methods the system Bi^{3+} / 4,8-Disulfonyl-2,6-naphthalenedicarboxylic acid (H_4DSNDC) / H_2O / additive (HNO_3 or NaOH) was systematically investigated under hydrothermal reaction conditions. The influence of the molar ratio of starting materials, pH as well as reaction temperature and time were investigated in more than 500 reactions. The product formation is highly sensitive towards small changes of the synthesis parameters but six new bismuth sulfonatocarboxylates were reproducibly obtained starting from clear solutions of the reactants. All compounds were structurally characterized from single crystal X-ray diffraction data. Fully deprotonated linker ions are found in $[\text{Bi}_6\text{O}_6(\text{OH})_2(\text{H}_2\text{O})_4(\text{DSNDC})]$ (**1**), $[\text{Bi}_2(\text{OH})_2(\text{DSNDC})]$ (**2**), $[\text{Bi}_8\text{O}_7(\text{OH})_2(\text{H}_2\text{O})_2(\text{DSNDC})_2]$ (**3**) and $[\text{Bi}_7\text{O}_5(\text{OH})_3(\text{H}_2\text{O})_4(\text{DSNDC})_2] \cdot 4\text{H}_2\text{O}$ (**4**), while the presence of larger amounts of acid or short reaction times lead to compounds with non-coordinating $-\text{COOH}$ groups, $[\text{Bi}_2(\text{OH})_2(\text{H}_2\text{O})_2(\text{DSNDC})(\text{H}_2\text{DSNDC})]$ (**5**) and $[\text{Bi}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_{12}(\text{H}_2\text{DSNDC})_3] \cdot x\text{H}_2\text{O}$ (**6**), respectively. The inorganic-building units (IBUs) in all six structures differ substantially from each other; the IBUs found in **2** ($\{\text{Bi}_2(\text{OH})_2\}$), **5** (BiO_8 polyhedron) and **6** ($\{\text{Bi}_6\text{O}_4(\text{OH})_4\}$ cluster) have been reported in literature, while new IBUs are observed for **1** (chains of composition $\{\text{Bi}_3\text{O}_3(\text{OH})\}_\infty$), **3** ($\{\text{Bi}_{16}\text{O}_{14}(\text{OH})_4\}$ cluster) and **4** ($\{\text{Bi}_7\text{O}_5(\text{OH})_3\}$ cluster). Systematic variation of reaction temperature and time indicated their distinct influence on product formation. Hence *in situ* powder X-ray diffraction (PXRD) measurements at DESY, Hamburg, employing synchrotron radiation were carried out. In all studied *in situ* reactions compound **6** is first observed and subsequently transformed to **1**, **2**, **4** and **5**, depending on the reaction time and temperature as well as concentration of the starting materials.

Introduction

Coordination polymers (CPs) are compounds with repeating coordination entities extending in 1, 2, or 3 dimensions.¹ These compounds are composed of inorganic building units (IBUs) interconnected by a ligand. While certain metal ions such as Cu^{2+} and Zr^{4+} tend to form distinct and very stable IBUs, i.e. paddle wheel units and hexanuclear clusters, respectively,² others exhibit a larger structural variability often due to the different possible coordination numbers.

Complexes containing Bi^{3+} ions have been shown to exhibit various Bi-O coordination environments. A survey of bismuth carboxylates,^{3–10} sulfonates^{11–19} and sulfonatocarboxylates^{20,21,22} demonstrated that IBUs in the crystal structures range from mononuclear complexes to Bi-O clusters with up to 38 bismuth ions to infinite Bi-O chains and even Bi-O layers. While the Bi-O clusters and dinuclear IBUs are mostly formed through reactions at room temperature or hydrolysis at moderate temperatures, respectively, the Bi-O chains were mostly obtained employing hydrothermal synthesis. A large diversity of reaction methods have been employed to study these compounds, e.g. slow solvent evaporation²³ or diffusion of solvent, hydrolysis,²⁴ solvothermal and ionothermal⁵ reactions and solid state metathesis²⁵ using reaction temperatures between -28 and 180 °C and reaction times of a few minutes up to several days. Unfortunately, only very few systematic multiparameter studies on the product formation have been reported today, hence Bi CPs seem to be perfectly suited for these investigations. Ideally, the linker of the studied system should contain both carboxylic and sulfonic acid groups and be rigid and large enough to segregate the IBUs. Hence, we choose 4,8-disulfonyl-2,6-naphthalenedicarboxylic acid (H_4DSNDC) as linker molecule for this systematic investigation.

High-throughput (HT) methods are a very efficient tool for such systematic investigation of complex chemical systems. They have been employed for example to study the temperature

dependent formation of seven structurally differing cobalt succinates,²⁶ to understand the formation of Fe containing metal organic frameworks (MOFs)²⁷ or in the discovery and synthesis optimization of MOFs and CPs.^{28–30} The combination of HT methods with *in situ* crystallization studies are of even greater interest since in addition to establishing optimized synthesis conditions, the formation process with the occurrence of possible crystalline intermediates can be established.^{31,32}

Herein we report the systematic investigations of the chemical system $\text{Bi}^{3+} / \text{H}_4\text{DSNDC} / \text{H}_2\text{O} / \text{HNO}_3$ or NaOH under hydrothermal reaction conditions employing HT methods for the discovery and synthesis optimization of the title compounds and for establishing their fields of formation as well as reaction trends. To get further insight into this complex reaction system, *in situ* powder X-ray diffraction studies were carried out using synchrotron radiation (beamline P08 and P09, PETRA III, Deutsches Elektronen-Synchrotron (DESY)).

Experimental

H_4DSNDC (4,8-disulfonyl-2,6-naphthalenedicarboxylic acid) was synthesized according to a literature procedure.³³ The other chemicals are commercially available and were used without further purification. $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was purchased from Alfa Aesar. It was dissolved in 2 M nitric acid to afford a Bi^{3+} solution of 2 mol/L. The linker H_4DSNDC was dissolved in H_2O resulting in a 0.25 mol/L solution. The systematic investigations of the chemical system $\text{Bi}^{3+} / \text{H}_4\text{DSNDC} / \text{H}_2\text{O} / \text{HNO}_3$ or NaOH were carried out employing our 24-high-throughput reactor system using 2 ml Teflon reactors.^{27,34,35} All reactants were deployed as solutions, which were dispensed employing a Zinsser Analytical Dosing Robot *Lissy*. The use of clear solutions is very important since solid starting materials resulted in poor reproducibility. The molar ratio Bi^{3+} to H_4DSNDC

was varied from 6 : 1 to 1 : 6 (a value of 1 corresponds to 0.025 mmol of reactant) and addition of up to 0.25 mmol NaOH or HNO₃ was tested. The amount of additional water was calculated to attain a final reaction volume of 1 ml. Reaction temperatures and times were varied from 120 to 180 °C and 8 min to 48 h. For the shortest reaction time (8 min) only glass vials (DURAN culture tubes D50 GL 14m.KAP, SCHOTT 261351155) were used. In these reactions, the amount of all reactants and solvents was doubled, keeping the molar ratios of all starting materials constant. In these reactions the solutions were dispensed manually. The glass vessels were sealed and inserted into a preheated aluminum block placed on a conventional heating plate (Figure S1)

After filtration and washing with water the products were identified via high-throughput powder X-ray diffraction (PXRD) measurements using a STOE HT diffractometer (Cu-K α radiation) in transmission geometry equipped with a xy-stage and a MYTHEN1K detector. High resolution PXRD patterns were measured on a STOE Stadi P diffractometer (Cu-K α 1-radiation) equipped with a MYTHEN1K detector. The crystal structures were determined from single-crystal XRD data. These XRD measurements were performed on a Stoe IPDS diffractometer equipped with an image-plate detector using Mo-K α radiation (λ = 71.073 pm). The crystal structures were solved by Direct Methods employing the program SHELXT-2014 and refined using the program SHELXL-2014.^{36,37} Numerical absorption correction was carried out by using the programs XShape and XRed.³⁸ IR-spectra were recorded on an ALPHA-P FTIR spectrometer from Bruker. Elemental analyses were carried out employing an Eurovektor EA. The Connolly surface was calculated using the program suite Materials Studio.³⁹ *In situ* PXRD patterns were measured at beamlines P08 and P09 PETRA III at HASYLAB, DESY, Hamburg (λ = 49.59 pm, 25 keV). For these investigations the SynRAC set-up was used which combines capabilities like rapid, high-precision temperature adjustment and liquid dosing with a remote-controlled operation, while

closely mimicking laboratory conditions. A detailed description of the set-up can be found in references.^{40–42}

CCDC entries 1837217–1837222 for compounds **1** – **6** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis

The reaction conditions that led to the formation of single crystals of the six title compounds and details for the *in situ* PXRD measurements are summarized in the following paragraphs and Table 1.

Table 1: Reaction conditions that led to single crystals of the title compounds. The molar ratio of $\text{Bi}^{3+} : \text{H}_4\text{DSNDC} : \text{HNO}_3$, with the value of 1 equivalent being 0.025 mmol and 0.05 mmol for reaction in the HT reactor and the glass vials, respectively, the volume of the starting material solutions and the reaction temperature and time are given .

	Molar ratio $\text{Bi}^{3+} : \text{H}_4\text{DSNDC} : \text{HNO}_3$	Method	H_2O [μL]	HNO_3 [μL]	H_4DSN D [μL]	Bi^{3+} [μL]	Temperature [$^{\circ}\text{C}$] / time
1	1 : 1 : 5	HT	825	62.5	100	12.5	180 / 48 h
2	5 : 5 : 5	HT	375	62.5	500	62.5	180 / 48 h
3	0.25 : 0.75 : 3	HT	457.2	37.5	25	9.4	180 / 13 h
4	1 : 2 : 12	vial	1200	300	400	50	150 / 40 min
5	4 : 4 : 10	vial	1150	250	400	200	150 / 8 min
6	4 : 2 : 12	vial	1200	300	400	100	150 / 8 min

[Bi₆O₆(OH)₂(H₂O)₂(DSNDC)]·2H₂O (1): Single crystals of compound **1** were obtained using the molar ratio Bi³⁺: linker: HNO₃ = 1: 1: 5. A Teflon insert of a steel autoclave was filled with 825 μL H₂O, 62.5 μL nitric acid (2 mol/L, 0.125 mmol), 100 μL of the H₄DSNDC solution (0.025 mmol) and 12.5 μL bismuth nitrate solution (0.025 mmol) and sealed. The autoclave was heated at 180°C for 48 h in an oven and cooled to room temperature within 12 h. The reaction product was filtered off and washed with water. The orange brown crystals were identified by PXRD and characterized by single crystal XRD. Elemental analysis; (Bi₆S₂O₂₂C₁₂H₁₄), calc. (found): C 7.9 (8.1), H 0.8 (0.8), S 3.5 (3.7), IR: $\tilde{\nu}$ = 3556 (w), 1664 (w), 1540 (s), 1395 (s), 1350 (s), 1173 (s), 1038 (s), 813 (m), 776 (m), 636 (s), 522 (br), 456 (br) cm⁻¹.

[Bi₂(OH)₂(DSNDC)] (2): Single crystals of compound **2** were obtained using the molar ratio Bi³⁺: linker: HNO₃ = 1: 1: 1. A Teflon insert of a steel autoclave was filled with 375 μL H₂O, 62.5 μL nitric acid (2 mol/L, 0.125 mmol), 500 μL of the H₄DSNDC solution (0.125 mmol) and 62.5 μL bismuth nitrate solution (0.125 mmol) and sealed. The autoclave was heated at 180°C for 48 h in an oven and cooled to room temperature within 12 h. The reaction product was filtered off and washed with water. The yellow brown crystals were identified by PXRD and characterized by single crystal XRD. All samples contained small amounts of inorganic impurities which is reflected in the results of the elemental analysis. Elemental analysis; (Bi₂S₂O₁₂C₁₂H₆), calc. (found): C 17.5 (13.9), H 0.7 (0.5), S 7.8 (7.1), the deviations are due to the inorganic impurities. IR: $\tilde{\nu}$ = 1537 (m), 1388 (m), 1350 (m), 1161 (s), 1024 (s), 817 (m), 785 (m), 602 (m), 527 (s), 442 (s) cm⁻¹.

[Bi₈O₇(OH)₂(H₂O)(DSNDC)₂]·H₂O (3): Single crystals of compound **3** were obtained using the molar ratio Bi³⁺: linker: HNO₃ = 5: 9: 10. A Teflon insert of a steel autoclave was filled with 657.2 μL H₂O, 62.5 μL nitric acid (2 mol/L, 0.125 mmol), 250 μL of the H₄DSNDC solution

(0.1125 mmol) and 31.3 μL bismuth nitrate solution (0.0625 mmol) and sealed. The autoclave was heated at 180°C for 13 h in an oven and cooled to room temperature within 3 h. The reaction product was filtered off and washed with water. The yellow crystals were identified by PXRD and characterized by single crystal XRD. Elemental analysis; ($\text{Bi}_8\text{S}_4\text{O}_{31}\text{C}_{24}\text{H}_{14}$), calc. (found): C 11.1 (11.4), H 0.5 (0.5), S 4.9 (5.4), IR: $\tilde{\nu}$ = 1689 (w), 1353 (br), 1190 (s), 1144 (br), 1026 (s), 805 (w), 769 (w), 737 (w), 605 (m), 518 (m), 406 (m) cm^{-1} .

[Bi₇O₅(OH)₃(H₂O)₂(DSNDC)₂]·6H₂O (4): Single crystals of compound **4** were obtained using the molar ratio Bi³⁺: linker: HNO₃ = 1: 2: 6. A glass vial was filled with 1200 μL H₂O, 300 μL nitric acid (2 mol/L, 0.6 mmol), 400 μL of the H₄DSNDC solution (0.1 mmol) and 50 μL bismuth nitrate solution (0.05 mmol) and sealed. The autoclave was inserted into a heated aluminum block at 150°C for 40 min. After cooling to room temperature, the reaction product was filtered off and washed with water. The yellow brown crystals were identified by PXRD and characterized by single crystal XRD. Elemental analysis; ($\text{Bi}_7\text{S}_4\text{O}_{36}\text{C}_{24}\text{H}_{27}$), calc. (found): C 11.6 (12.0), H 1.1 (0.7), S 5.2 (5.2), IR: $\tilde{\nu}$ = 3558 (w), 1691 (w), 1563 (m), 1387 (m), 1349 (m), 1219 (s), 1196 (s), 1144 (s), 1020 (s), 1002 (s), 785 (m), 632 (m), 514 (br), 439(m) cm^{-1} .

[Bi₂(OH)₂(DSNDC)(H₂DSNDC)]·2H₂O (5): Single crystals of compound **5** were obtained using the molar ratio Bi³⁺: linker: HNO₃ = 1: 1: 4. A glass vial was filled with 1675 μL H₂O, 100 μL nitric acid (2 mol/L, 0.2 mmol), 200 μL of the H₄DSNDC solution (0.05 mmol) and 25 μL bismuth nitrate solution (0.05 mmol) and sealed. The autoclave was inserted into a heated aluminum block at 150°C for 8 min. After cooling to room temperature, the reaction product was filtered off and washed with water. The light-yellow crystals were identified by PXRD and characterized by single crystal XRD. Elemental analysis; ($\text{Bi}_2\text{S}_4\text{O}_{24}\text{C}_{24}\text{H}_{16}$), calc. (found): C 23.4 (22.8), H 1.3 (1.2), S 10.4 (10.3), IR: $\tilde{\nu}$ = 3634 (w), 3563 (w), 2660 (w), 2551 (w), 1687 (s), 1606

(m), 1523 (m), 1431 (s), 1366 (m), 1294 (m), 1195 (s), 1141 (s), 1112 (s), 1053 (s), 1020 (s), 934 (br), 825 (s), 741 (m), 605 (m), 480 (m) cm^{-1} .

[Bi₆O₄(OH)₄(H₂O)₁₂(H₄DSNDC)₃] $\cdot$ xH₂O (6): Single crystals of compound **6** were obtained using the molar ratio Bi³⁺: linker: HNO₃ = 2: 1: 6. A glass vial was filled with 1200 μL H₂O, 300 μL nitric acid (2 mol/L, 0.6 mmol), 400 μL of the H₄DSNDC solution (0.1 mmol) and 100 μL bismuth nitrate solution (0.2 mmol) and sealed. The autoclave was inserted into a heated aluminum block at 150°C for 8 min. After cooling to room temperature, the reaction product was filtered off and washed with water. The orange crystals were identified by PXRD and characterized by single crystal XRD. Elemental analysis; (Bi₆S₆O₅₀C₃₆H₄₆, X = 0), calc. (found): C 15.9 (14.8), H 1.7 (1.3), S 7.1 (6.6), the deviations are probably due to the presence of the voids that can contain different amounts of included solvent molecules. IR: $\tilde{\nu}$ = 3364 (w), 2636 (w), 2541 (w), 1689 (m), 1421 (m), 1284 (m), 1163 (br), 1110 (w), 1033 (s), 920 (s), 769 (w), 633 (w), 517(br) cm^{-1} .

***In situ* reactions:** Five *in situ* PXRD measurements (R1 to R5) were carried out to study the formation and transformation of the title compounds. Four different molar ratios of starting materials between 2:2 and 4:4 and three reaction temperatures (120, 150 and 180 °C) were chosen to study the temporal evolution of the phases. A summary of the reactions carried out is given in Table 2. A detailed description is presented in the SI. In general, the chemicals were added in the following order: H₂O, HNO₃/NaOH, H₄DSNDC, Bi³⁺. For all reactions clear aqueous solutions of the starting materials in the predefined concentrations were employed. The reaction mixtures were homogenized by shaking and subsequently the vials were inserted into the SynRAC set up with active stirring. The PXRD measurements and heating were started remote controlled. In the reaction R5 (Table 2) the reaction conditions were changed after 20 min, employing the remote-controlled dosing of the SynRAC setup.

Table 2: Overview of the *in situ* investigations carried out to study the formation and transformation of the title compounds. The molar ratios (1 eq = 0.05 mmol), volume of solvents and solutions as well as reaction time and temperature are given.

	Molar ratio Bi ³⁺ : H ₄ DSNDC : HNO ₃ / NaOH	H ₂ O [μL]	HNO ₃ [μL]	H ₄ DSND [μL]	Bi ³⁺ [μL]	T [°C]
R1	2 : 2 : 0	1550	0	400	50	120
R2	2 : 2 : 0	1550	0	400	50	150
R3	2 : 4 : 5	1025	125	800	50	180
R4	4 : 4 : 5	975	125	800	100	180
R5 ^a	4 : 4 : 0	1100	0	800	100	120

^a addition of 500 μL NaOH after 20 min, changing the ratio to 3 : 3 : 20

Results and discussion

The systematic HT investigation of the chemical systems Bi³⁺ / H₄DSNDC / H₂O / HNO₃ or NaOH resulted in most cases in crystalline products. Among these are the known inorganic phases α-Bi₂O₃ and [Bi₆O₆(NO₃)₄(OH)₂] · 2H₂O, recrystallized linker and six new coordination polymers which were structurally characterized from single crystal XRD data (Table 3).

Table 3 Results of the crystal structure refinement of the six title compounds [Bi₆O₆(OH)₂(H₂O)₄(DSNDC)] (1), [Bi₂(OH)₂(DSNDC)] (2), [Bi₈O₇(OH)₂(H₂O)₂(DSNDC)₂] (3) and [Bi₇O₅(OH)₃(H₂O)₄(DSNDC)₂] $\cdot$ 4H₂O (4), [Bi₂(OH)₂(H₂O)₂(DSNDC)(H₂DSNDC)] (5) and [Bi₆O₄(OH)₄(H₂O)₁₂(H₂DSNDC)₃] $\cdot$ xH₂O (6).

Compound	1	2	3	4	5	6
Formula	Bi ₃ SO ₁₁ C ₆ H ₁₃	BiSO ₆ C ₆ H ₃	Bi ₈ S ₄ O ₃₁ C ₂₄ H ₁₄	Bi ₇ S ₄ O ₃₅ C ₂₄ H ₁₉	BiS ₂ O ₁₃ C ₁₂ H ₁₁	Bi ₃ S ₃ O ₂₅ C ₁₈ H ₈
Space group	<i>Pbcn</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> , Å	15.780(3)	5.6233(3)	11.827(2)	10.601(2)	5.6597(11)	11.046(2)
<i>b</i> , Å	14.700(3)	7.4471(5)	12.391(3)	19.453(4)	7.5223(15)	11.763(2)
<i>c</i> , Å	11.224(2)	10.4371(6)	14.841(3)	10.954(2)	19.891(4)	15.092(3)
α , β , γ , °	90, 90, 90	104.508(5), 100.005(5), 106.289(5)	76.93(3), 79.19(3), 70.51(3)	90, 108.74(3), 90	89.08(3), 88.69(3), 73.81(3)	77.75(3), 76.38(3), 65.71(3)
<i>V</i> , Å ³	2603.6(9)	391.90(4)	1982.3(8)	2139.2(8)	813.0(3)	1722.3(8)
<i>Z</i>	8	2	2	2	2	2
no. of reflns	25242	25242	25060	24974	25242	25242
no. of indep reflns	2439	5177	14957	17100	7542	12471
<i>R</i> _{int}	0.0983	0.0421	0.0825	0.0588	0.0315	0.0479
GoF	1.044	0.936	0.94	1.164	0.905	1.028
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0265, 0.0608	0.0339, 0.0869	0.0516, 0.1293	0.0299, 0.0692	0.0309, 0.0837	0.0536, 0.1336
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0279, 0.0616	0.0363, 0.0886	0.062, 0.1361	0.0342, 0.0709	0.0344, 0.0859	0.0787, 0.1505

High-throughput investigations

The influence of reaction parameters e.g. the starting materials concentration, molar ratio of metal to linker to additive, as well as reaction temperature and time on the product formation was investigated employing our 24-high-throughput reactor system using 2 ml Teflon reactors^{34,35} and glass vials (5 mL). The later are also suitable for *in situ* studies.^{40–42} The concentrations of Bi³⁺ and H₄DSNDC in the reaction mixture were varied from 0.025 mol/L to 0.15 mol/L, the molar

metal to linker ratio from 1:6 to 6:1 and the addition of HNO_3 or NaOH from 0 to 0.4 mol/L or 0.25 mol/L respectively, leading to pH values between 0 and 14. The temperature dependence was studied between 120 and 180 °C and reaction times between a few minutes and several days were investigated. All six new crystalline compounds could be synthesized employing the high-throughput reactor system with Teflon reaction vessels, at 180 °C for 48 h. Phase identification was carried out by PXRD. The results of the systematic study are shown in Figure 1.

Figure 1. Investigated parameter space and results using a reaction temperature of 180 °C and a reaction time of 48 h. The value of 1 eq. corresponds to 0.025 mmol. The color of the upper half of the circles represents the main component and the lower half the side products. High concentrations of metal, linker or additive result in the formation of inorganic byproducts ($\alpha\text{-Bi}_2\text{O}_3$ and $[\text{Bi}_6(\text{NO}_3)_4(\text{OH})_2\text{O}_6]$). The cross section at 5 eq. of HNO_3 is shown on the right in more detail. All six new compounds are observed in this cross section of the parameter space. A detailed view of the cross sections at the other NaOH/HNO_3 values are shown in the SI Figure S33.

It is apparent that at ten eq. of either NaOH or HNO₃ inorganic products (α -Bi₂O₃ and [Bi₆(NO₃)₄(OH)₂O₆]) are more common (Figure 1), hence no higher concentrations of the additives were investigated. The same trend is observed when large amounts of metal and linker are employed. At first glance it is clearly seen that two reaction products dominate the crystallization diagram, i.e. **1** and **2**. Compound **1** is formed at low concentrations, i.e. one equivalent, of metal and/or linker, for example at Bi³⁺ : H₄DSNDC : HNO₃ = 4 : 1 : 10 and 1 : 4 : 0. The addition of 5 eq. NaOH leads also predominantly to the formation of **1**. Compound **2** is formed at high concentrations of starting materials, especially at low concentrations of NaOH or HNO₃. All six phases are observed when five eq. of HNO₃ are employed (Figure 1, right). Hence subsequent experiments were carried out using this part of the parameter space.

The influence of the reaction time on the product formation was also studied using molar ratios metal : H₄DSNDC : HNO₃ of 1-4 : 1-4 : 5 (Figure 2) and decreasing the reaction time from 48 to 12 h. At this shorter reaction time, five of the six compounds were obtained, but the exact location in the parameter fields differs, which demonstrates the strong influence of the reaction time on the product formation. The most obvious change is the formation of compound **2** at linker concentrations of 3 and 4 eq. instead of 5 and 6 eq.. Compound **5** is only observed as a byproduct when 4 eq. of linker and metal are employed. This indicates the faster product formation of compound **2** compared to **5** and a lower stability of **2** at longer reaction times. Hence, **2** dissolves to form compounds **4** or **5** at longer reaction times. For compounds **1** and **3** no time depending product formation is observed. Both seem to form at reaction times under 12 h and show no further transformation at longer reaction times up to 48 h.

Figure 2. Excerpt of the results of the HT investigation using a reaction temperature of 180 °C and a reaction time of 48 h (left) and 12 h (right) and five eq. of HNO₃. The value of 1 eq. corresponds to 0.025 mmol. The color of the upper half of the circles represents the main component and the lower half the side products. On the left side compounds **1** and **3-6** are seen, while on the right side compound **1** and **2** are dominant.

Reactions in glass vials

Since the reaction time plays an important role on the product formation, we were interested to study even shorter reaction times. This is not possible using the HT reactor set up since heating of the reactor to the target temperature takes at least 1h. Therefore, the reaction vessel was changed from multiclaves with 2 ml Teflon inserts to glass vials with a maximum volume of 5 ml. To keep concentrations and molar ratios constant the twofold amount of solvent and starting materials was employed to further investigate the influence of reaction time and temperature on the product formation (Figure 3). Except for compound **3**, all title compounds were obtained in glass vials at 180 °C for 48 h, although at different regions of the parameter space (Figure 2A and Figure 3A).

This fact is probably due to differences in heating rates or reactor surfaces. In the reactions using the glass vials compound **4** and **6** were found at lower Bi^{3+} concentrations and compound **5** was found only at a metal to linker ratio of 4:3 instead of 2-4:4. Compound **1** is only formed at low metal concentrations.

In the following reactions, the reaction time was shortened to 8 min and reaction temperature was decreased to 150 and finally to 120 °C. The results of these reactions are shown in Figure 3 B-D. At 180°C and a reaction time of 8 min compound **6** is dominantly observed. In addition, an unknown product of low crystallinity was detected. Compound **1** and **4** are formed at low metal concentrations and one eq. of linker. Decreasing the reaction temperature and keeping the reaction time at 8 min results almost exclusively in the formation of compounds **6**, while in some cases also compound **1** was obtained. Since temperature and especially reaction time is an important factor in the product formation *in situ* crystallization studies were carried out.

Figure 3. Investigated parameter space and results of the investigation in the glass vials using molar ratios of $\text{Bi}^{3+} : \text{H}_4\text{DSNDC} : \text{HNO}_3 = 1\text{-}4 : 1\text{-}4 : 5$. Reaction times and temperatures of 180 °C and 48 h (A) and 8 min (B), 150 °C and 8 min (C) and 120 °C and 8 min (D) were used. At short reaction times compound 6 dominates. All reaction mixtures contain five eq. of HNO_3 . The value of 1 eq. corresponds to 0.05 mmol. The color of the upper half of the circles represents the main component and the lower half the side products.

***In situ* investigations**

In situ crystallization studies using synchrotron radiation are an important tool to follow the formation and transformation of crystalline products.⁴³ In addition to qualitative investigations the data can also be employed to extract kinetic parameters. In the current study we were only interested in the formation and transformation of the title compounds since extraction of kinetic parameters would have demanded much more beam time (availability of limited beam time). *In situ* investigations were carried out at PETRA III, DESY, using the SynRAC setup and the same glass vials as in the preliminary described *ex situ* studies. This reactor system offers the advantages of precise and remote-controlled heating and injection of up to two solvents or solutions or one solid.⁴⁰⁻⁴² A summary of the reaction parameters for the *in situ* study is given in Table 1. Reactions were carried out at 120, 150 and 180 °C using the following reaction compositions: metal to H_4DSNDC to $\text{HNO}_3 = 2\text{:}2\text{:}0$, $2\text{:}4\text{:}5$, $4\text{:}4\text{:}5$ and $4\text{:}4\text{:}0$. In the last reaction 20 equivalents of NaOH were injected after $t = 20$ min. To quantify the amount of crystallized product in the reaction mixture the area of one reflection or each phase was determined.

Using the compositions metal to H₄DSNDC to HNO₃ = 2:2:0 two reactions were carried out at 120 and 150 °C, respectively. The reaction temperature was reached within 2 min after the heating is started and the results of these *in situ* measurements are shown in Figure 4. At both reaction temperatures compound **6** is formed as the first crystalline phase upon heating and subsequently compound **4** crystallizes (after 10 and 3 min, respectively). Within the investigated reaction time (52 min) compound **6** is not fully transformed into compound **4** at 120 °C even though the investigation showed, that the transformation is still occurring after 52 min. Full transformation is detected at 150 °C already after 6 minutes. Comparison of the *in situ* PXRD data and simulated PXRD patterns are given in Figures S34-S38 to support the assignment of the different crystalline products.

Figure 4. Results of the *in situ* PXRD measurements using molar ratios of $\text{Bi}^{3+} : \text{H}_4\text{DSNDC} : \text{HNO}_3 = 2 : 2 : 0$ and reaction temperatures of 120 (top) and 150 °C (bottom). Left: three-dimensional plots of the PXRD measurements; right: diagrams showing the temperature within the SynRAC cell and evolution of the compounds, determined by integration of one characteristic reflection per compound and normalization. Top: At $t = 0$ heating to 120 °C was started and compound **6** (green) is formed instantly. After ten minutes additional peaks corresponding to compound **4** (purple) appear. Bottom: At $t = 0$ heating to 150 °C started and after 2 min compound **6** crystallizes. After three minutes it disappears and compound **4** appears.

The influence of the amount of metal on the product formation was studied at a reaction temperature of 180 °C using molar ratios of Bi^{3+} to H_4DSNDC to $\text{HNO}_3 = 2: 4: 5$ and $4: 4: 5$. The results are presented in Figure 5. Before heating is started, compound **6** is observed for the lower metal concentration and upon heating to 180 °C compound **6** is observed in both experiments. The final reaction temperature is reached after ~ 4 min. Even before reaching the reaction temperature of 180 °C the peaks of compound **6** decrease in intensity and signals for compound **1** and **5** are observed, for ratios of 2: 4: 5 and 4: 4: 5, respectively. While at the higher metal content the crystallization of **5** is finished after about 10 min, for the reaction using a lower metal content a second transformation from compound **1** to **2** takes place after ca. 20 min. This confirms our result, that compound **6** is formed rapidly but is not stable at longer reaction times at high temperatures and that the metal content has a strong influence on the product formation. This observation also explains the results shown in Figure 3. Compound **2** is not observed even at high concentrations due to the short reaction times employed.

Figure 5. Results of the *in situ* PXRD measurements using Bi³⁺ : H₄DSNDC : HNO₃ = 2: 4: 5 (topo) and 4: 4: 5 (bottom) and a reaction temperature of 180 °C. Left: thee-dimensional plots of the PXRD measurements; right: diagrams showing the temperature in the SynRAC cell and evolution of the compounds, determined by integration of one characteristic reflection per compound and normalization. Top: At t = 0 min heating to 180°C started and compound **6** (green) crystallizes further. After four min it disappears and compound **1** (blue) crystallizes, which dissolves

after 30 min to form compound **2** (orange). Bottom: At $t = 0$ min heating to 180°C started and compound **6** is formed. After three min it disappears and compound **5** (yellow) crystallizes.

To study the influence of the addition of a base on the product formation a final reaction was set up using a molar ratio of Bi^{3+} to $\text{H}_4\text{DSNDC} = 4 : 4$ and adding 20 eq of NaOH ($T = 120^{\circ}\text{C}$ after 20 min). At room temperature compound **6** is already observed and upon heating the peak intensity increases (Figure 6). Upon addition of 500 μL of 2 M NaOH after 20 min via a syringe pump an almost spontaneous transformation to compound **1** is observed. The fast transformation makes a dissolution-recrystallization process probable.

Figure 6. Results of *in situ* PXRD measurements of two reactions with 4 eq. of metal and linker.

Left: three-dimensional plot of the PXRD measurements; right: diagram showing the temperature in the SynRAC cell and evolution of the compounds, determined by integration of one characteristic reflection per compound and normalization. At $t = 0$ min heating to 120°C started and the already present compound **6** (green) crystalizes further. After 20 min NaOH is added and it disappears and compound **1** (blue) crystalizes.

The results of the *in situ* measurements are summarized in Figure 7 and confirm the trends extracted from the *ex situ* studies. Compound **6** is formed rapidly even at low temperatures and dissolves over time, faster at temperatures above 120 °C. At higher concentrations compound **6** is formed faster and dissolves again, while compounds **1**, **4** and **5** form, depending on the concentrations of the starting materials. Compound **2** is the last to be formed at high temperatures of 180 °C. The reversibility of the reactions was demonstrated by addition of NaOH during the *in situ* PXRD study. The pH change leads to the transformation of **6** to **1**, as expected from *ex situ* experiments and the reaction conditions.

R5	4:4	6						
R4	4:4 HNO ₃	6				5		
R5*	3:3 NaOH			1				
R3	2:4 HNO ₃	0	6			1	2	
R1	2:2	0	6	6+4	4			
R2								
		RT	120°C	Time	150°C	Time	180°C	Time

Figure 7. Schematic summary of the results of the *in situ* investigations. The 0 stands for no crystalline product. The colored squares show which compound is formed at the concentration in

that row and the reaction temperature and time of the column. Every arrow represents one observed phase transition in the *in situ* investigation.

Crystal Structures

All six title compounds were structurally characterized by single-crystal XRD. Since protons could not be determined in the electron density map, O^{2-} , OH^- and H_2O were assigned based on binding mode, as well as bond angles and lengths, using values that are consistent with literature data.^{44–46} Herein we give a short description of the structures with emphasis on the IBUs and their connection. IBUs are building units comprised of smaller inorganic ions and molecules, such as metal ions, water molecules, hydroxide and other anions and do not contain any carbon atoms of the organic linker molecule. For a more detailed description of the structures see the SI, including the asymmetric units, the coordination environment of the Bi^{3+} ions and the connectivity by the ligand molecule. The Crystallographic data of all title compounds is summarized in Table 3. In the following, the purple polyhedra represent the coordination environment of the Bi^{3+} while the light blue polyhedra show the Bi-O cluster, where the Bi^{3+} ions form the corners of the polyhedra.

Compound **1** with the formula $[\text{Bi}_6\text{O}_6(\text{OH})_2(\text{H}_2\text{O})_4(\text{DSNDC})]$ crystallizes in the orthorhombic space group *Pbcn*. The three symmetry independent Bi^{3+} ions are seven (Bi1) or eight-fold coordinated (Bi2, Bi3). These Bi-O polyhedra are connected by edge and face sharing and form infinite, one dimensional IBUs along the *c*-axis. Each carboxylate and sulfonate group of the linker binds in a chelating fashion type to three and two Bi^{3+} ions, respectively. Each group coordinates to Bi^{3+} ions from four different IBUs so that each IBU is linked to eight other IBUs to form the dense three-dimensional CP (Figure 8).

Figure 8. Molecular structure of the linker H₄DSNDC (left) and crystal structure of **1**. Middle IBU composed of edge and face sharing BiO₇ and BiO₈ polyhedra (purple) and section of the three-dimensional structure (right). Bi atoms are shown in light blue, S atoms in yellow, O atoms in red, C atoms in dark gray, H atoms are excluded for clarity.

Compound **2**, [Bi₂(OH)₂(DSNDC)], crystallizes in the triclinic space group $P\bar{1}$. The Bi³⁺ ion is nine-fold coordinated. The two hydroxide ions connect two Bi³⁺ ions to a dinuclear IBU. These dimeric units form layers in the *a-b*-plane through edge sharing of O4 and O6 of the CSO₃⁻ group. This layer is structurally related to the layers observed in [Bi₂O₂(OH)(NO₃)].⁴⁷ The organic moiety connects the layers to form a dense three-dimensional CP (Figure 9).

Figure 9. Layers formed by three dinuclear $\{\text{Bi}_2(\text{OH})_2\}$ through the connection of SO_3^- groups (left) and three-dimensional structure of compound **2** (right). Bi atoms are shown in light blue, S atoms in yellow, O atoms in red, C atoms in dark gray, H atoms are excluded for clarity. BiO_9 polyhedra are shown in purple.

Compound **3**, $[\text{Bi}_8\text{O}_7(\text{OH})_2(\text{H}_2\text{O})_2(\text{DSNDC})_2]$, crystallizes in the triclinic space group $P\bar{1}$. The eight Bi^{3+} ions and their symmetry related equivalents form the new $\{\text{Bi}_{16}\text{O}_{14}(\text{OH})_4\}$ cluster. Each of these clusters is bonded to two other clusters by two water molecules and a one-dimensional IBU along the a -axis is formed. Each IBU is connected to six other IBUs by the linker molecules and a dense three-dimensional CP is formed (Figure 10).

Figure 10. $\{\text{Bi}_{16}\text{O}_{14}(\text{OH})_4\}$ cluster as a blue polyhedron (left) and three-dimensional structure of compound **3** (right). The linker molecules connect the chains to a dens network. Bi atoms are shown in light blue, S atoms in yellow, O atoms in red, C atoms in dark gray, H atoms are excluded for clarity.

Compound **4**, $[\text{Bi}_7\text{O}_5(\text{OH})_3(\text{H}_2\text{O})_4(\text{DSNDC})_2] \cdot 4\text{H}_2\text{O}$, crystallizes in the monoclinic space group $P2_1/m$. The O^{2-} and OH^- ions connect the seven symmetry independent Bi^{3+} ions to a Bi-O cluster. This cluster is similar to the common $\{\text{Bi}_6\text{O}_4(\text{OH})_4\}$ cluster but distorted and contains one more Bi^{3+} ion (Bi5) connected by one O^{2-} ion (O3). Each of these IBUs is coordinated by eight linker molecules to twelve other IBUs (Figure 11), resulting in a three-dimensional network.

Figure 11. Shown are the seven Bi^{3+} ions of the IBU of compound **4**, six Bi^{3+} ions form the well-known hexanuclear Bi-O polyhedron (blue, left) and the three-dimensional structure (right). Bi atoms are shown in light blue, S atoms in yellow, O atoms in red, C atoms in dark gray, H atoms are excluded for clarity.

Compound **5**, $[\text{Bi}_2(\text{OH})_2(\text{OH}_2)_2(\text{DSNDC})(\text{H}_2\text{DSNDC})]$, crystallizes in the triclinic space group $P\bar{1}$. The Bi^{3+} ion is eight-fold coordinated. Two sulfonate groups connect two Bi^{3+} ions to a chain of corner sharing, alternating BiO_8 and two CSO_3 polyhedra along the a -axis. The organic moieties link each of these chains to six other chains and a three-dimensional CP with very small channels along the a -axis with a diameter of 2.6 Å at the widest and 1.1 Å at the narrowest part is formed. Between the carboxylic acid groups hydrogen bonds are formed (Figure 12) which further stabilize the three-dimensional framework.

Figure 12. Crystal structure of compound **5**. Chains of BiO_8 and CSO_3 polyhedra (left), connection of the chains through $\text{H}_2\text{DSNDC}^{2-}$ ions (middle), Hydrogen bonds between the $-\text{COOH}$ groups in red dashed lines (left). Bi atoms are shown in light blue, S atoms in yellow, O atoms in red, C atoms in dark gray, H atoms are excluded for clarity. BiO_8 polyhedra are shown in purple.

Compound **6**, $[\text{Bi}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_{12}(\text{H}_2\text{DSNDC})_3] \cdot x\text{H}_2\text{O}$, crystallizes in the triclinic space group $P\bar{1}$. The three Bi^{+3} ions and their symmetry equivalents form the well-known $\{\text{Bi}_6\text{O}_4(\text{OH})_4\}$ cluster, that was even observed in two-dimensional and three-dimensional CPS.^{25,45} The O^{2-} and OH^- ions are disordered and could not be refined separately. Six different linker molecules coordinate to one cluster and connect each of the IBUs to four others. Thus a two-dimensional CP is formed. The carboxylic acid groups form hydrogen bonds and bridge these layers (Figure 13).

Figure 13. Crystal structure of compound **6**. $\{\text{Bi}_6\text{O}_4(\text{OH})_4\}$ cluster with coordinating water molecules (left), connection of the IBUs in compound **6** by linker molecules through S-O-Bi bonds, thus forming layers in the *ac*-plane (middle). Hydrogen bonds between -COOH groups lead to the interconnection of the layers along the *b*-axis (right). Hydrogen bonds shown as red dashed lines. Bi atoms are shown in light blue, S atoms in yellow, O atoms in red, C atoms in dark gray, H atoms and water molecules are excluded for clarity. Bi_6 polyhedra are shown in blue.

A comparison of structural features observed in the six title compounds is given in Table 4. All compounds form three-dimensional CPs except for compound **6**, which crystallizes as a two-dimensional CP with hydrogen bonds between the layers. The observed IBUs differ in all structures and range from mononuclear BiO_8 polyhedra to infinite Bi-O chains (Figure S33) demonstrating the high flexibility of the Bi coordination environment. The density, taken from crystal structure data, lies between 2.5 g/cm^3 for compound **5** and 4.6 g/cm^3 for compound **1** (Table 4). In all compounds the sulfonate groups bridge at least two Bi^{3+} ions in a $[2,110]$ fashion, three Bi^{3+} ions in $[3,211]$ or $[3,221]$ or four in $[4,221]$ bonding mode, described in the *Harris* notation (Figure 14).⁴⁸ An even larger structural diversity is found in the binding mode of the carboxylate

groups. These range from [4,32] and [3,22] to [2,21] and [1,11]. The -COOH groups in compounds **5** and **6** do not coordinate to the Bi^{3+} ions but form dimeric units through hydrogen bonds.

Table 4. Comparison of some structural properties of the six title compounds.

	IBU	Density [g/cm ³]	Pores [Å]	Ratio of Bi^{3+} and linker	Harris notation of Sulfonate	Carboxylate
Compound 1	$\{\text{Bi}_3\text{O}_3(\text{OH})\}_\infty$	4.6	no	6:1	[2,111]	[3,22]
Compound 2	$\{\text{Bi}_2(\text{OH})_2\}$	3.5	no	2:1	[3,221]	[1,11]
Compound 3	$\{\text{Bi}_{16}\text{O}_{14}(\text{OH})_4\}$	4.3	no	4:1	[2,110], [3,211], [4,221]	[2,21], [3,22], [4,32]
Compound 4	$\{\text{Bi}_7\text{O}_5(\text{OH})_3\}$	3.8	4.2	7:2	[2,110], [4,221]	[2,21], [3,22]
Compound 5	$\{\text{BiO}_8\}$	2.5	2.6	1:1	[2,110]	[1,11] COOH
Compound 6	$\{\text{Bi}_6\text{O}_4(\text{OH})_4\}$	2.6*	11	2:1	[2,110]	COOH

* framework density, occluded water molecules were not taken into account

Figure 14. The binding modes of sulfonate and carboxylate groups in the six title compounds using the Harris notation.⁴²

Synthesis-structure trends

The combination of the results of the HT and in situ PXRD investigations with the ones of the crystal structure determinations allows us to set up some synthesis-structure-relationships. From the HT experiments, the trends presented in Figure 1, right, are representative since all six title compounds are obtained in this section of the parameter field. Since high reaction temperatures (180 °C) and long reaction times (48 h) were used, we anticipate the formation of – under these reaction conditions - thermodynamically stable reaction products. Under acidic conditions, the overall concentration and the molar ratio Bi^{3+} to H_4DSNDC have the following influence on the crystal density (Table 4, Figure 15). The highest value is found in compound **1**, which forms at low reactant concentrations. Interestingly the molar metal to linker ratio in the title compounds is not directly related to the ratio of starting materials (e.g. compound **1** has a composition of 6:1 but also forms at 1:6 metal to linker ratios). With increasing linker concentration, the density of the obtained structures decreases in the order of compound **3**, **4** and **2**. Compounds **5** and **6** do not fall within this trend, thus having a lower density than compound **2**, which is easily explained by the presence of small cavities in their structures (see SI). The IBUs of the reported structures range from mononuclear and dinuclear complexes to different Bi-O clusters and infinite Bi-O chains (Figure S33). The size of the IBUs seems to correlate with the overall concentration of starting materials. The largest IBU is the infinite Bi-O chain in compound **1**. Slightly higher concentrations afford compound **3** with a Bi-O cluster containing 16 Bi^{3+} ions. A further increase of the concentration leads to compound **4** with heptanuclear Bi-O clusters. At higher metal concentrations compound **6** with hexanuclear Bi-O clusters is formed. The highest studied concentrations resulted in compound **2** with dimeric IBUs.

Figure 15. Reproduction of Figure 1, right including the observed synthesis-structure-trends The red arrow represents the increase of crystal density with decreasing linker concentration ($2 \rightarrow 4 \rightarrow 3 \rightarrow 1$) and the blue arrow represents the increase of IBUs with lower overall concentrations ($2 \rightarrow 6 \rightarrow 4 \rightarrow 3 \rightarrow 1$).

The results of the *in situ* PXRD investigations allow us to extract kinetic synthesis-structure information (Figure 7). Compound **6** is predominantly observed at short reaction times (R1 to R5). It contains the hexanuclear Bi-O cluster, which is well known to form under these reaction conditions and is predominant to aqueous bismuth chemistry. In addition compound **6** contains exclusively non-coordinating -COOH-groups. Hence, the rapid formation of **6** is just the assembly of building units that are available in solution. Under more acidic conditions and a high reaction temperature of 180 °C (R4), the decomposition of the hexanuclear cluster takes place. Subsequently compound **5** is formed which contains mononuclear complexes and -COO⁻ as well as -COOH-groups. At lower concentrations of 2:2 and 120 or 150 °C (R1 and R2) compound **6**

dissolves and a transformation into compound **4** is observed. In this transformation the $\{\text{Bi}_6\text{O}_4(\text{OH})_4\}$ cluster is probably not fully dissolved but extended by condensation of an additional Bi^{3+} ion to form the $\{\text{Bi}_7\text{O}_5(\text{OH})_3\}$ cluster. In the reactions R3 and R5* the influence of higher reaction temperatures of 180 °C and the addition of base was studied. As expected both parameters have a similar effect on the product formation since compound **1** is formed which has the highest degree of condensation in the IBU and the highest crystal density. Nevertheless, in R3, i.e. at long reaction times an additional transformation to **2** takes place. This can be explained by the larger linker concentration in the reaction mixture since in compounds **1** and **2** metal to linker ratios of 6:1 and 2:1 are observed, respectively. Hence, the higher concentration of linker molecules in solution leads to this transformation of **1** to **2**.

Conclusion

Through the combination of systematic HT studies and five *in situ* PXRD measurements the crystallization and transformation of six new bismuth CPs was investigated. The crystal structure of all six compounds were determined and the large structural flexibility of Bi^{3+} chemistry is reflected in the various IBUs and their connectivity. The IBUs range from the common mononuclear and dinuclear IBUs and hexanuclear Bi-O clusters to up to now unreported $\{\text{Bi}_7\text{O}_5(\text{OH})_3\}$ and $\{\text{Bi}_{16}\text{O}_{14}(\text{OH})_4\}$ clusters and a one-dimensional Bi-O chain. The HT and *in situ* studies demonstrated the complexity of the reactions system and the role of reaction temperature and time as well as overall concentrations and molar ratios metal to linker. This information in combination with the crystals structures allowed us to set up synthesis-structure trends, such as high crystal density at low concentrations or the decomposition of the $\{\text{Bi}_6\text{O}_4(\text{OH})_4\}$ cluster at long reaction times.

ASSOCIATED CONTENT

The **Supporting Information** is available free of charge on the ACS Publications website at DOI: XXX. It contains detailed structure descriptions, powder X-ray diffraction patterns, IR spectra and results of the TG/DTA measurements of the title compounds. CCDC 1837217-1837222 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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SYNOPSIS

The complexity of the parameter space of the chemical system Bi^{3+} / 4,8-disulfononaphthalene-2,6-dicarboxylic acid (H_4DSNDC) / H_2O / HNO_3 or NaOH was established and the fields of formation of six new coordination polymers with various inorganic building units - demonstrating the high variability of Bi-O structural chemistry - were located. Precise control of reactant ratios as well as reaction time and temperature are important parameters and the influence of reaction time was studied via *in situ* PXRD measurements.