The structures of ordered defects in thiocyanate Prussian Blue analogues

Matthew J. Cliffe, *a,b Evan N. Keyzer, Andrew D. Bond, Maxwell A. Astleb and Clare P. Greya

April 6, 2020

^a Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK;

^b School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, UK;

*To whom correspondence should be addressed; e-mail: matthew.cliffe@nottingham.ac.uk.

Contents

1	Synthetic Procedures 1.1 Synthesis of HSCN 1.2 Synthesis of H ₃ [Bi(SCN) ₆] solution 1.3 Synthesis of 1 1.4 Synthesis of 2 1.5 Synthesis of 3 and 4 1.6 Synthesis of 5 and 6	2 2 2 2 2 2 2 2 2 2
2	Single Crystal X-ray Diffraction	3
3	Powder X-ray Diffraction	5
4	ICP-OES	6
5	STEM-EDX	6
6	Diffuse Reflectance	8

List of Figures

1	Rietveld refinement of mixed phase α - and β Zn ₃ Bi ₂ (SCN) ₆ . * indicates the presence of an
	impurity peak
2	Representative EDX spectrum for compound 2
3	Tauc normalised diffuse reflectance data for determination of band gap 1,2,4,5 & 6 8
4	Diffuse reflectance spectra for compounds 1,2,4,5 & 6

List of Tables

1	Summary of key crystallographic parameters for all compounds	4
2	STEM-EDX elemental ratios in sample 2	6

1 Synthetic Procedures

The synthesis procedures were adapted from those reported in S1.

1.1 Synthesis of HSCN

In a 250 mL round bottom flask, NH₄SCN (5g, 65.7 mmol) was dissolved in 5 mL H₂O and cooled to 0 °C in an ice bath. A H₂SO₄ solution (ca. 7 ml of H₂SO₄ in 12 ml H₂O) was then added dropwise to the cooled NH₄SCN solution. The reaction mixture was stirred for 30 mins before being warmed to room temperature. The aqueous mixture was subsequently extracted with diethyl ether (2×20 ml) and the organic phase was retrieved and its volume reduced by half using a stream of N₂.

1.2 Synthesis of H₃[Bi(SCN)₆] solution

 $Bi_2O_2(CO_3)$ (0.50 g, 0.98 mmol) was suspended in ca. 12 mL H₂O followed by the addition of the HSCN/ether solution. The resulting reaction mixture was stirred vigorously under a slight flow of N₂ until all ether had been removed and the solution had turned bright orange. Any remaining solids were filtered off and the orange solution was placed under a slight vacuum to remove any excess HSCN.

1.3 Synthesis of 1

1 mL of the prepared H₃[Bi(SCN)₆] was added to approximately 50 mg MnCO₃, and left to react overnight. Any excess solids were removed by gravity filtration. The dark red solution was then left to evaporate in a watch glass covered by petri-dish for a period of approximate two weeks until diffraction quality dark orange single crystals formed.

1.4 Synthesis of 2

1mL of the prepared $H_3[Bi(SCN)_6]$ was added to approximately 50 mg $(Co_5(CO_3)_2(OH)_6)$ and left to react overnight. Any excess solids were removed by gravity filtration. The dark red solution was then left to evaporate in a watch glass covered by petri-dish for a period of approximate two weeks until diffraction quality dark orange single crystals formed.

1.5 Synthesis of 3 and 4

Bi(NO₃)₃ · 2.5 H₂O (3 mmol, 1.46 g) was dissolved in 1.5 mL 3M HNO₃, and a solution of NH₄SCN (13.1 mmol, 1.00 g) dissolved in 2 mL of distilled water was added to it, producing a vivid orange solution. Ni(NO₃)₂ · 6 H₂O (7 mmol, 2.036 g) was dissolved in 2 mL of water and then added to to bismuth thiocyanate solution, which on standing produced numerous small very dark orange single crystals of **4** over a period of 15 min. The same route can be used to produce **3**, substituting Co(NO₃) · 6 H₂O.

1.6 Synthesis of 5 and 6

Bi(NO₃)₃ · 2.5 H₂O (3 mmol, 1.46 g) was dissolved in 1.5 mL 3M HNO₃, and a solution of NH₄SCN (13.1 mmol, 1.00 g) dissolved in 2 mL of distilled water was added to it, producing a vivid orange solution. $Zn(NO_3)_2 \cdot 6 H_2O$ (7 mmol, 2.082 g) was dissolved in 2 mL of water and then added to to bismuth thiocyanate solution, which on standing produced an immediate precipitate of numerous orange single crystals of **5** and **6**.

2 Single Crystal X-ray Diffraction

Single crystals were selected and mounted using perfluorinated oil on a polymer-tipped micromount and cooled rapidly to measurement temperature 120 K or 180 K in a stream of cold N_2 using an Oxford Cryosystems open flow cryostat. To enable variable temperature measurements, the crystal used for structures **1** and **1a** was mounted using varnish on a pin.

Single-crystal X-ray diffraction data for **2**, **4**, **5** and **6** were collected using a Nonius KappaCCD diffractometer, using graphite monochromated MoK α radiation ($\lambda = 0.7107$ Å). Data for **1** and **1a** were collected using a on a Bruker D8-Quest PHOTON-100 diffractometer equipped with an Incoatec I μ S Cu microsource ($\lambda = 1.54056$ Å). Data for **3** were collected using Single crystal X-ray diffraction data were collected on an Oxford Diffraction GV1000 (AtlasS2 CCD area detector, mirror-monochromated Cu-K $_{\alpha}$ radiation source ($\lambda = 1.54184$ Å). Structure solution was carried out using SHELXT and refinement with SHELXL, within the OLEX2 graphical interface. ^{S2-4} For crystal **1**, hydrogen atoms were refined with constrained geometries and riding thermal parameters, however the disorder present in samples **2**–**4** meant that hydrogen atoms could not be located, aside from an NH₄ cation in **4**. Disordered sites in structures **1**, **2**, **3** and **4** were modelled at half occupancy.

Compound	1	, , ,	้1a		2	
Formula	Mn ₂ Bi(SCN) ₇ 7 H ₂ O	Mn ₂ Bi(SCN)	$_{7}7 H_{2}O$	Co ₉ Bi ₆ (SCN) ₃₆ (H	₂ O) ₃₈	
Molar mass	851.54		851.54	45	35.47	
Crystal System	Monoclinic	Mo	noclinic	Tr	iclinic	
Space Group	$P2_1/n$		$P2_1/n$		P1	
Crystal Colour	dark orange	dark	orange	dark o	range	
2	4		4		1	
Radiation	$Cu K_{\alpha}$		$Cu K_{\alpha}$	N	No K $_{\alpha}$	
Temperature (K)	300		180		180	
a (A)	8.3698(3)	8.3	3065(2)	12.020	09 (2)	
b (A)	26.0037(9)	25.8	8428(6)	12.16	13 (2)	
c (Å)	12.2466(4)	12.2	2664(3)	23.83	19 (4)	
lpha (Å)	90		90	94.20	00 (1)	
β (Å)	91.208(2)	90.23	360(10)	94.00	03 (1)	
γ (Å)	90		90	91.4	52 (1)	
V (Å ³)	2664.83(16)	2633	8.12(11)	3464.52	2 (10)	
Measured reflections	30850		33300	2	21789	
Independent reflections	4712		4657	1	3585	
$R_{ m int}$	0.1315		0.080		0.035	
$R[F^2 > 2\sigma(F^2)]$	0.0553		0.038		0.059	
S	1.013		1.03		1.13	
CCDC number						
Compound		3		4	5	6
Compound Formula	Co ₅ Bi ₆ (SCN) ₃₀ 3 NH ₄ ·	3 16 H₂O Nig	₅Bi ₆ (SCN	4 I) ₃₀ 3 NH ₄ · 16 H ₂ O	5 α-Zn ₃ Bi ₂ (SCN) ₁₂	6 β-Zn ₃ Bi ₂ (SCN) ₁₂
Compound Formula Molar mass	Co ₅ Bi ₆ (SCN) ₃₀ 3 NH ₄ · 3	3 16 H ₂ O Nig 3438.91	₅Bi ₆ (SCN	4 I) ₃₀ 3 NH ₄ · 16 H ₂ O 3512.13	5 α-Zn ₃ Bi ₂ (SCN) ₁₂ 1311.03	6 β-Zn ₃ Bi ₂ (SCN) ₁₂ 1311.03
Compound Formula Molar mass Crystal System	Co ₅ Bi ₆ (SCN) ₃₀ 3 NH ₄ . 3	3 16 H₂O Nig 3438.91 Triclinic	₅Bi ₆ (SCN	4 I) ₃₀ 3 NH ₄ · 16 H ₂ O 3512.13 Triclinic	5 α-Zn ₃ Bi ₂ (SCN) ₁₂ 1311.03 Monoclinic	6 β-Zn ₃ Bi ₂ (SCN) ₁₂ 1311.03 Monoclinic
Compound Formula Molar mass Crystal System Space Group	Co ₅ Bi ₆ (SCN) ₃₀ 3 NH ₄ · 3	3 16 H₂O Ni 3438.91 Triclinic P1	₅ Bi ₆ (SCN	4 1) ₃₀ 3 NH ₄ · 16 H ₂ O 3512.13 Triclinic P1	5 α-Zn ₃ Bi ₂ (SCN) ₁₂ 1311.03 Monoclinic C2/c	6 β-Zn ₃ Bi ₂ (SCN) ₁₂ 1311.03 Monoclinic P2 ₁ /c
Compound Formula Molar mass Crystal System Space Group Crystal Colour	Co ₅ Bi ₆ (SCN) ₃₀ 3 NH ₄ · 3 3 dark	3 16 H₂O Niạ 3438.91 Triclinic <i>P</i> 1 orange	₅Bi ₆ (SCN	4 I) ₃₀ 3 NH₄ · 16 H₂O 3512.13 Triclinic P1 dark orange	5 α-Zn ₃ Bi ₂ (SCN) ₁₂ 1311.03 Monoclinic C2/c orange	6 β-Zn ₃ Bi ₂ (SCN) ₁₂ 1311.03 Monoclinic P2 ₁ /c orange
Compound Formula Molar mass Crystal System Space Group Crystal Colour Z	Co₅Bi ₆ (SCN) ₃₀ 3 NH ₄ · 3 3 dark	3 16 H ₂ O Nia 3438.91 Triclinic <i>P</i> 1 orange 1	₅Bi ₆ (SCN	4 I) ₃₀ 3 NH₄ · 16 H₂O 3512.13 Triclinic P1 dark orange 1	5 α-Zn ₃ Bi ₂ (SCN) ₁₂ 1311.03 Monoclinic C2/c orange 4	β-Zn ₃ Bi ₂ (SCN) ₁₂ 1311.03 Monoclinic $P2_1/c$ orange 4
Compound Formula Molar mass Crystal System Space Group Crystal Colour Z Radiation	Co₅Bi ₆ (SCN) ₃₀ 3 NH ₄ · 3 3 dark	$\begin{array}{c c} 3 \\ 16 \mathrm{H_2O} & \mathrm{Nis} \\ 3438.91 \\ \hline \mathrm{Triclinic} \\ P\overline{1} \\ \mathrm{orange} \\ 1 \\ \mathrm{Cu} \mathrm{K}_{\alpha} \end{array}$	₅Bi ₆ (SCN	4 I) ₃₀ 3 NH₄ · 16 H₂O 3512.13 Triclinic <i>P</i> 1 dark orange 1 Mo K _α	5 α-Zn ₃ Bi ₂ (SCN) ₁₂ 1311.03 Monoclinic C2/c orange 4 Mo K _α	6 β-Zn ₃ Bi ₂ (SCN) ₁₂ 1311.03 Monoclinic P2 ₁ /c orange 4 Mo K _α
Compound Formula Molar mass Crystal System Space Group Crystal Colour Z Radiation Temperature (K)	Co₅Bi ₆ (SCN) ₃₀ 3 NH₄ · 3 dark	$\begin{array}{c c} 3 \\ 16 \mathrm{H_2O} & \mathrm{Ni}_{\mathrm{s}} \\ 3438.91 \\ \mathrm{Triclinic} \\ P\overline{1} \\ \mathrm{orange} \\ 1 \\ \mathrm{Cu} \mathrm{K}_{\alpha} \\ 120 \end{array}$	₅Bi ₆ (SCN	$\begin{array}{c} & {\bf 4} \\ {1\!$	$3 \\ \alpha$ -Zn ₃ Bi ₂ (SCN) ₁₂ 1311.03 Monoclinic C2/c orange 4 Mo K _{α} 109	β-Zn ₃ Bi ₂ (SCN) ₁₂ 1311.03 Monoclinic $P2_1/c$ orange 4 Mo K _α 180
Compound Formula Molar mass Crystal System Space Group Crystal Colour Z Radiation Temperature (K) a (Å)	Co₅Bi ₆ (SCN) ₃₀ 3 NH₄ · 3 dark 11.9	$\begin{array}{c c} {\bf 3} \\ 16 {\rm H_2O} & {\rm Ni}_8 \\ 3438.91 \\ {\rm Triclinic} \\ P\overline{1} \\ {\rm orange} \\ 1 \\ {\rm Cu} {\rm K}_\alpha \\ 120 \\ {\rm v106} \ (3) \end{array}$	₅Bi ₆ (SCN	$\begin{array}{c} & {\color{red} 4} \\ 1_{30} 3 \text{NH}_4 \cdot 16 \text{H}_2\text{O} \\ 3512.13 \\ \text{Triclinic} \\ P\overline{1} \\ \text{dark orange} \\ 1 \\ \text{Mo } \text{K}_{\alpha} \\ 111 \\ 11.8567 \ (2) \end{array}$	$\begin{array}{c} {\bf 5} \\ \alpha \mbox{-} Zn_3 \mbox{Bi}_2(SCN)_{12} \\ 1311.03 \\ Monoclinic \\ C2/c \\ orange \\ 4 \\ Mo \ K_{\alpha} \\ 109 \\ 26.3104 \ (4) \end{array}$	β-Zn ₃ Bi ₂ (SCN) ₁₂ 1311.03 Monoclinic $P2_1/c$ orange 4 Mo K _α 180 17.7331 (6)
Compound Formula Molar mass Crystal System Space Group Crystal Colour Z Radiation Temperature (K) a (Å) b (Å)	Co₅Bi ₆ (SCN) ₃₀ 3 NH₄ · 3 dark 11.9 11.9	$\begin{array}{c c} 3 \\ \hline 16 \mathrm{H_2O} & \mathrm{Ni}_{\mathrm{S}} \\ 3438.91 \\ \mathrm{Triclinic} \\ P\overline{1} \\ \mathrm{orange} \\ 1 \\ \mathrm{Cu} \mathrm{K}_{\alpha} \\ 120 \\ \mathrm{1106} \ (3) \\ \mathrm{3822} \ (3) \end{array}$	₅Bi ₆ (SCN	$\begin{array}{c} & {\color{black} 4} \\ 1 \\ 1 \\ 3 \\ 3 \\ 3 \\ 3 \\ 3 \\ 3 \\ 3 \\ 3$	$\begin{array}{c} {\bf 5} \\ \alpha \mbox{-} Zn_3 Bi_2(SCN)_{12} \\ 1311.03 \\ Monoclinic \\ C2/c \\ orange \\ 4 \\ Mo K_{\alpha} \\ 109 \\ 26.3104 \ (4) \\ 8.4587 \ (1) \end{array}$	β-Zn ₃ Bi ₂ (SCN) ₁₂ 1311.03 Monoclinic $P2_1/c$ orange 4 Mo K _α 180 17.7331 (6) 13.6501 (4)
Compound Formula Molar mass Crystal System Space Group Crystal Colour Z Radiation Temperature (K) a (Å) b (Å) c (Å)	Co₅Bi ₆ (SCN) ₃₀ 3 NH₄ · 3 dark 11.9 11.9 8.4	$\begin{array}{c c} 3 \\ \hline 16 \ \mathrm{H_2O} & \mathrm{Ni}_{\mathrm{S}} \\ 3438.91 \\ \mathrm{Triclinic} \\ P\overline{1} \\ \mathrm{orange} \\ 1 \\ \mathrm{Cu} \ \mathrm{K}_{\alpha} \\ 120 \\ \mathrm{1106} \ (3) \\ 3822 \ (3) \\ .250 \ (5) \end{array}$	₅Bi ₆ (SCN	$\begin{array}{c} & {\color{black} 4} \\ {\color{black} 1} \\ {\color{black} 1} \\ {\color{black} 3} \\ {\color{black} 3} \\ {\color{black} 3} \\ {\color{black} 1} \\ {\color{black} 1} \\ {\color{black} 3} \\ {\color{black} 1} \\ {\color{black} 1}$	$\begin{array}{c} & 5 \\ \hline \alpha \text{-Zn}_3 \text{Bi}_2(\text{SCN})_{12} \\ 1311.03 \\ \text{Monoclinic} \\ C2/c \\ \text{orange} \\ 4 \\ \text{Mo } \text{K}_{\alpha} \\ 109 \\ 26.3104 \ (4) \\ 8.4587 \ (1) \\ 15.7403 \ (3) \end{array}$	$\frac{6}{\beta - Zn_3Bi_2(SCN)_{12}}$ 1311.03 Monoclinic $P2_1/c$ orange 4 Mo K _α 180 17.7331 (6) 13.6501 (4) 16.4375 (4)
CompoundFormulaMolar massCrystal SystemSpace GroupCrystal ColourZRadiationTemperature (K) a (Å) b (Å) c (Å) α (Å)	Co₅Bi ₆ (SCN) ₃₀ 3 NH₄ · 3 dark 11.9 11.9 8.4 83.	$\begin{array}{c c} 3 \\ \hline 16 \ \mathrm{H_2O} & \mathrm{Ni}_{\mathrm{S}} \\ 3438.91 \\ \mathrm{Triclinic} \\ P\overline{1} \\ \mathrm{orange} \\ 1 \\ \mathrm{Cu} \ \mathrm{K}_{\alpha} \\ 120 \\ \mathrm{1106} \ \mathbf{(3)} \\ 3822 \ \mathbf{(3)} \\ .250 \ \mathbf{(5)} \\ 935 \ \mathbf{(2)} \end{array}$	₅Bi ₆ (SCN	$\begin{array}{c} & {\color{black} 4} \\ 1 \\ 1 \\ 3 \\ 3 \\ 3 \\ 1 \\ 3 \\ 3 \\ 1 \\ 1$	$\begin{array}{c} {\bf 5} \\ \alpha \mbox{-} Zn_3 Bi_2(SCN)_{12} \\ 1311.03 \\ Monoclinic \\ C2/c \\ orange \\ 4 \\ Mo K_{\alpha} \\ 109 \\ 26.3104 \ (4) \\ 8.4587 \ (1) \\ 15.7403 \ (3) \\ 90 \end{array}$	$\frac{6}{\beta - Zn_3Bi_2(SCN)_{12}}$ 1311.03 Monoclinic $P2_1/c$ orange 4 Mo K _α 180 17.7331 (6) 13.6501 (4) 16.4375 (4) 90
CompoundFormulaMolar massCrystal SystemSpace GroupCrystal ColourZRadiationTemperature (K) a (Å) b (Å) c (Å) α (Å) β (Å)	Co₅Bi ₆ (SCN) ₃₀ 3 NH₄ · 3 dark 11.9 11.9 8.4 83. 76.	$\begin{array}{c c} 3 \\ \hline 16 \ \mathrm{H_2O} & \mathrm{Ni}_{\mathrm{S}} \\ 3438.91 \\ \mathrm{Triclinic} \\ P\overline{1} \\ \mathrm{orange} \\ 1 \\ \mathrm{Cu} \ \mathrm{K}_{\alpha} \\ 120 \\ \mathrm{1106} \ \mathbf{(3)} \\ 3822 \ \mathbf{(3)} \\ .250 \ \mathbf{(5)} \\ 935 \ \mathbf{(2)} \\ 504 \ \mathbf{(2)} \end{array}$	₅Bi ₆ (SCN	$\begin{array}{c} & {\color{black} 4} \\ 1 \\ 1 \\ 3 \\ 3 \\ 3 \\ 1 \\ 3 \\ 3 \\ 1 \\ 1$	$\begin{array}{c} {\bf 5} \\ \alpha \mbox{-} Zn_3 Bi_2(SCN)_{12} \\ 1311.03 \\ Monoclinic \\ C2/c \\ orange \\ 4 \\ Mo K_{\alpha} \\ 109 \\ 26.3104 \ (4) \\ 8.4587 \ (1) \\ 15.7403 \ (3) \\ 90 \\ 93.630 \end{array}$	β-Zn ₃ Bi ₂ (SCN) ₁₂ 1311.03 Monoclinic $P2_1/c$ orange 4 Mo K _α 180 17.7331 (6) 13.6501 (4) 16.4375 (4) 90 114.3971 (12)
Compound Formula Molar mass Crystal System Space Group Crystal Colour Z Radiation Temperature (K) a (Å) b (Å) c (Å) α (Å) β (Å) γ (Å)	Co₅Bi ₆ (SCN) ₃₀ 3 NH₄ · . 3 dark 11.9 11.9 8.4 83. 76. 85.	3 16 H ₂ O Nia 3438.91 Triclinic $P\overline{1}$ orange 1 Cu K _{α} 120 106 (3) 1382 (3) 250 (5) 935 (2) 504 (2) 384 (2) (2)	₅Bi ₆ (SCN	$\begin{array}{c} & {\color{black} 4} \\ 1 \\ 1 \\ 3 \\ 3 \\ 3 \\ 1 \\ 3 \\ 3 \\ 1 \\ 1$	$\begin{array}{c} {\bf 5} \\ \alpha \mbox{-} Zn_3 Bi_2(SCN)_{12} \\ 1311.03 \\ Monoclinic \\ C2/c \\ orange \\ 4 \\ Mo K_{\alpha} \\ 109 \\ 26.3104 \ (4) \\ 8.4587 \ (1) \\ 15.7403 \ (3) \\ 90 \\ 93.630 \\ 90 \end{array}$	$\frac{6}{\beta - Zn_3Bi_2(SCN)_{12}}$ 1311.03 Monoclinic $P2_1/c$ orange 4 Mo K _α 180 17.7331 (6) 13.6501 (4) 16.4375 (4) 90 114.3971 (12) 90
CompoundFormulaMolar massCrystal SystemSpace GroupCrystal ColourZRadiationTemperature (K) a (Å) b (Å) c (Å) α (Å) β (Å) γ (Å) V (Å) V (Å)	Co₅Bi ₆ (SCN) ₃₀ 3 NH₄ · . 3 dark 11.9 11.9 8.4 83. 76. 85. 2529.	3 16 H ₂ O Nia 3438.91 Triclinic $P\overline{1}$ orange 1 Cu K _{α} 120 106 (3) 1382 (3) .250 (5) 935 (2) .504 (2) .384 (2) .04 (12)	₅Bi ₆ (SCN	$\begin{array}{c} \label{eq:2} \begin{tabular}{lllllllllllllllllllllllllllllllllll$	$\begin{array}{c} 5 \\ \alpha\text{-Zn}_3\text{Bi}_2(\text{SCN})_{12} \\ 1311.03 \\ \text{Monoclinic} \\ C2/c \\ \text{orange} \\ 4 \\ \text{Mo K}_{\alpha} \\ 109 \\ 26.3104 (4) \\ 8.4587 (1) \\ 15.7403 (3) \\ 90 \\ 93.630 \\ 90 \\ 3496.00 (9) \end{array}$	
CompoundFormulaMolar massCrystal SystemSpace GroupCrystal ColourZRadiationTemperature (K) a (Å) b (Å) c (Å) α (Å) β (Å) γ (Å) γ (Å) V (Å3)Measured reflections	Co₅Bi ₆ (SCN) ₃₀ 3 NH₄ · 3 dark 11.9 11.9 8.4 83. 76. 85. 2529.	$\begin{array}{c c} 3 \\ 16 \ \mathrm{H_2O} & \mathrm{Ni}_{\mathrm{s}} \\ 3438.91 \\ \mathbf{Triclinic} \\ P\overline{1} \\ \mathbf{orange} \\ 1 \\ \mathbf{Cu} \ \mathrm{K}_{\alpha} \\ 120 \\ 106 \ \mathbf{(3)} \\ 382 \ \mathbf{(3)} \\ 250 \ \mathbf{(5)} \\ 935 \ \mathbf{(2)} \\ 504 \ \mathbf{(2)} \\ 384 \ \mathbf{(2)} \\ 04 \ \mathbf{(12)} \\ 37154 \end{array}$	₅Bi ₆ (SCN	$\begin{array}{c} & {\color{black} 4} \\ {\color{black} 1} \\ {\color{black} 3} \\ {\color{black} 3} \\ {\color{black} 3} \\ {\color{black} 3} \\ {\color{black} 1} \\ {\color{black} 1}$	$\begin{array}{c} & 5\\ \hline \alpha \text{-}Zn_3\text{Bi}_2(\text{SCN})_{12}\\ 1311.03\\ \text{Monoclinic}\\ C2/c\\ \text{orange}\\ 4\\ \text{Mo K}_{\alpha}\\ 109\\ 26.3104 \ (4)\\ 8.4587 \ (1)\\ 15.7403 \ (3)\\ 90\\ 93.630\\ 90\\ 3496.00 \ (9)\\ 7507 \end{array}$	$\frac{6}{\beta - Zn_3Bi_2(SCN)_{12}}$ 1311.03 Monoclinic $P2_1/c$ orange 4 Mo K _α 180 17.7331 (6) 13.6501 (4) 16.4375 (4) 90 114.3971 (12) 90 3623.55 (19) 12934
Compound Formula Molar mass Crystal System Space Group Crystal Colour Z Radiation Temperature (K) a (Å) b (Å) c (Å) α (Å) β (Å) γ (Å) V (Å ³) Measured reflections Independent reflections	Co₅Bi ₆ (SCN) ₃₀ 3 NH₄ · 3 dark 11.9 11.9 8.4 83. 76. 85. 2529.	$\begin{array}{c c} 3 \\ \hline 16 \ \mathrm{H_2O} & \mathrm{Ni}_{\mathrm{s}} \\ \hline 3438.91 \\ \hline \mathrm{Triclinic} \\ P\overline{1} \\ \mathrm{orange} \\ 1 \\ \mathrm{Cu} \ \mathrm{K}_{\alpha} \\ 120 \\ \mathrm{r106} \ (3) \\ 382 \ (3) \\ 250 \ (5) \\ 935 \ (2) \\ 504 \ (2) \\ 384 \ (2) \\ 04 \ (12) \\ 37154 \\ 9921 \\ \end{array}$	₅Bi ₆ (SCN	$\begin{array}{r} & {\color{red} 4} \\ {\color{black} 1} \\ {\color{black} 3} \\ {\color{black} 3} \\ {\color{black} 3} \\ {\color{black} 3} \\ {\color{black} 1} \\$	$\begin{array}{c} & 5\\ \hline \alpha \text{-}Zn_3\text{Bi}_2(\text{SCN})_{12}\\ 1311.03\\ \text{Monoclinic}\\ C2/c\\ \text{orange}\\ 4\\ \text{Mo K}_{\alpha}\\ 109\\ 26.3104 \ (4)\\ 8.4587 \ (1)\\ 15.7403 \ (3)\\ 90\\ 93.630\\ 90\\ 3496.00 \ (9)\\ 7507\\ 3975 \end{array}$	$\begin{array}{c} 6 \\ \beta\text{-Zn}_3\text{Bi}_2(\text{SCN})_{12} \\ 1311.03 \\ \text{Monoclinic} \\ P2_1/c \\ \text{orange} \\ 4 \\ \text{Mo K}_{\alpha} \\ 180 \\ 17.7331 (6) \\ 13.6501 (4) \\ 16.4375 (4) \\ 90 \\ 114.3971 (12) \\ 90 \\ 3623.55 (19) \\ 12934 \\ 7822 \end{array}$
Compound Formula Molar mass Crystal System Space Group Crystal Colour Z Radiation Temperature (K) a (Å) b (Å) c (Å) α (Å) β (Å) γ (Å) γ (Å) Weasured reflections Independent reflections R_{int}	Co₅Bi ₆ (SCN) ₃₀ 3 NH₄ · 3 dark 11.9 11.9 8.4 83. 76. 85. 2529.	$\begin{array}{c c} 3 \\ \hline 16 \ \mathrm{H_2O} & \mathrm{Ni}_{\mathrm{s}} \\ \hline 3438.91 \\ \hline \mathrm{Triclinic} \\ P\overline{1} \\ \mathrm{orange} \\ 1 \\ \mathrm{Cu} \ \mathrm{K}_{\alpha} \\ 120 \\ \mathrm{r106} \ (3) \\ 382 \ (3) \\ .250 \ (5) \\ 935 \ (2) \\ 504 \ (2) \\ .384 \ (2) \\ .04 \ (12) \\ .37154 \\ .9921 \\ 0.047 \\ \end{array}$	₅Bi ₆ (SCN	$\begin{array}{c} & {\color{black} 4} \\ {\color{black} 4} \\ {\color{black} 1} \\ {\color{black} 3} \\ {\color{black} 3} \\ {\color{black} 3} \\ {\color{black} 1} \\ {\color{black} 1}$	$\begin{array}{c} & 5\\ \hline \alpha \text{-}Zn_3\text{Bi}_2(\text{SCN})_{12}\\ 1311.03\\ \text{Monoclinic}\\ C2/c\\ \text{orange}\\ 4\\ \text{Mo K}_{\alpha}\\ 109\\ 26.3104 (4)\\ 8.4587 (1)\\ 15.7403 (3)\\ 90\\ 93.630\\ 90\\ 3496.00 (9)\\ 7507\\ 3975\\ 0.029\\ \end{array}$	$\begin{array}{c} 6 \\ \beta\text{-Zn}_3\text{Bi}_2(\text{SCN})_{12} \\ 1311.03 \\ \text{Monoclinic} \\ P2_1/c \\ \text{orange} \\ 4 \\ \text{Mo K}_{\alpha} \\ 180 \\ 17.7331 (6) \\ 13.6501 (4) \\ 16.4375 (4) \\ 90 \\ 114.3971 (12) \\ 90 \\ 3623.55 (19) \\ 12934 \\ 7822 \\ 0.052 \end{array}$
CompoundFormulaMolar massCrystal SystemSpace GroupCrystal ColourZRadiationTemperature (K) a (Å) b (Å) c (Å) α (Å) β (Å) γ (Å) V (Å ³)Measured reflectionsIndependent reflections R_{int} $R[F^2 > 2\sigma(F^2)]$	Co₅Bi ₆ (SCN) ₃₀ 3 NH ₄ . 3 dark 11.9 11.9 8.4 83. 76. 85. 2529.	$\begin{array}{c c} 3 \\ \hline 16 \ \mathrm{H_2O} & \mathrm{Ni}_{\mathrm{s}} \\ \hline 3438.91 \\ \hline \mathrm{Triclinic} \\ P\overline{1} \\ \mathrm{orange} \\ 1 \\ \mathrm{Cu} \ \mathrm{K}_{\alpha} \\ 120 \\ \mathrm{old} \ (3) \\ \hline 382 \ (3) \\ 250 \ (5) \\ 935 \ (2) \\ 504 \ (2) \\ 37154 \\ 9921 \\ 0.047 \\ 0.031 \\ \end{array}$	₅Bi ₆ (SCN	$\begin{array}{c} & {\color{black} 4} \\ {\color{black} 4} \\ {\color{black} 1} \\ {\color{black} 3} \\ {\color{black} 3} \\ {\color{black} 3} \\ {\color{black} 1} \\ {\color{black} 1}$	$\begin{array}{c} & 5\\ \hline \alpha \text{-}Zn_3Bi_2(\text{SCN})_{12}\\ 1311.03\\ \text{Monoclinic}\\ & C2/c\\ \text{orange}\\ 4\\ \text{Mo K}_{\alpha}\\ 109\\ 26.3104 (4)\\ 8.4587 (1)\\ 15.7403 (3)\\ 90\\ 93.630\\ 90\\ 3496.00 (9)\\ 7507\\ 3975\\ 0.029\\ 0.026\\ \end{array}$	$\begin{array}{c} 6 \\ \beta\text{-Zn}_3\text{Bi}_2(\text{SCN})_{12} \\ 1311.03 \\ \text{Monoclinic} \\ P2_1/c \\ \text{orange} \\ 4 \\ \text{Mo K}_{\alpha} \\ 180 \\ 17.7331 (6) \\ 13.6501 (4) \\ 16.4375 (4) \\ 90 \\ 114.3971 (12) \\ 90 \\ 3623.55 (19) \\ 12934 \\ 7822 \\ 0.052 \\ 0.051 \end{array}$
$\label{eq:compound} \hline \begin{array}{c} \mbox{Compound} \\ \hline \mbox{Formula} \\ \mbox{Molar mass} \\ \mbox{Crystal System} \\ \mbox{Space Group} \\ \mbox{Crystal Colour} \\ \hline \mbox{Z} \\ \hline \mbox{Radiation} \\ \hline \mbox{Temperature (K)} \\ \mbox{a (Å)} \\ \mbox{b (Å)$} \\ \mbox{$c$ (Å)$} \\ \mbox{$c$ (Å)$} \\ \mbox{$\alpha$ (Å)$} \\ \mbox{$\beta$ (Å)$} \\ \mbox{$\gamma$ (Å)$} \\ \mbox{$\gamma$ (Å)$} \\ \mbox{$\gamma$ (Å)$} \\ \mbox{$\gamma$ (Å)$} \\ \mbox{$V$ (Å^3)$} \\ \hline \mbox{Measured reflections} \\ \hline \mbox{Independent reflections} \\ \hline \mbox{$R_{\rm int}$} \\ \mbox{$R[F^2 > 2\sigma(F^2)]$} \\ \mbox{S} \\ \hline \mbox{S} \end{array}$	Co₅Bi ₆ (SCN) ₃₀ 3 NH ₄ . 3 dark 11.9 11.9 8.4 83. 76. 85. 2529.	$\begin{array}{c c} 3 \\ \hline 16 \ \mathrm{H_2O} & \mathrm{Ni}_{\mathrm{s}} \\ \hline 3438.91 \\ \hline \mathrm{Triclinic} \\ P\overline{1} \\ \mathrm{orange} \\ 1 \\ \mathrm{Cu} \ \mathrm{K}_{\alpha} \\ 120 \\ \mathrm{106} \ (3) \\ 382 \ (3) \\ 250 \ (5) \\ 935 \ (2) \\ 504 \ (2) \\ 384 \ (2) \\ 04 \ (12) \\ 37154 \\ 9921 \\ 0.047 \\ 0.031 \\ 1.03 \\ \end{array}$	₅Bi ₆ (SCN	$\begin{array}{c} & {\color{black} 4} \\ {\color{black} 4} \\ {\color{black} 1} \\ {\color{black} 3} \\ {\color{black} 3} \\ {\color{black} 3} \\ {\color{black} 1} \\ {\color{black} 1}$	$\begin{array}{c} & 5\\ \hline \alpha \text{-}Zn_3Bi_2(\text{SCN})_{12}\\ 1311.03\\ \text{Monoclinic}\\ & C2/c\\ \text{orange}\\ 4\\ \text{Mo K}_{\alpha}\\ 109\\ 26.3104 (4)\\ 8.4587 (1)\\ 15.7403 (3)\\ 90\\ 93.630\\ 90\\ 3496.00 (9)\\ 7507\\ 3975\\ 0.029\\ 0.026\\ 1.07\\ \end{array}$	$\begin{array}{c} 6 \\ \beta\text{-Zn}_3\text{Bi}_2(\text{SCN})_{12} \\ 1311.03 \\ \text{Monoclinic} \\ P2_1/c \\ \text{orange} \\ 4 \\ \text{Mo K}_{\alpha} \\ 180 \\ 17.7331 (6) \\ 13.6501 (4) \\ 16.4375 (4) \\ 90 \\ 114.3971 (12) \\ 90 \\ 3623.55 (19) \\ 12934 \\ 7822 \\ 0.052 \\ 0.051 \\ 1.05 \end{array}$

ESI Table 1: Summary of key crystallographic parameters for all compounds

Cu K_{α}, $\lambda = 1.54056$ Å, Mo K_{α}, $\lambda = 0.71073$ Å.

3 Powder X-ray Diffraction

A high-resolution synchrotron X-ray powder diffraction measurement on a ground powder of $Zn_3Bi_2(NCS)_{12}$ was carried out at beamline 11-BM at the Advanced Photon Source (APS) using a wavelength of 0.414537 Å. The sample was loaded into a 0.8 mm diameter Kapton capillary. Rietveld refinement of the data was carried out using Topas Academic 4.1.^{S5, S6} Lattice parameters were allowed to refine freely along with isotropic displacement parameters for Bi atoms and terms accounting for crystallite size broadening and crystallographic strain. The presence of a minor tertiary phase was modelled using independently refining peaks, which we were unable to index as a separate phase.



ESI Fig. 1: Rietveld refinement of mixed phase α - and β Zn₃Bi₂(SCN)₆. * indicates the presence of an impurity peak.

4 ICP-OES

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was recorded on a Perkin Elmer, Optima 2000 DV ICP-OES with S10 autosampler. Samples and standards were prepared with a final solution composition of 2% nitric acid. Metal content was kept below 50 mg/L for ICP measurements as at higher concentrations a precipitate would form which would not dissolve in limited volumes of acids. Found for sample **2** Bi 27.35%, Co 17.97%, Ca 0.0%, Ni 0.0% and Ti 0.0%.

5 STEM-EDX

Energy dispersive X-ray (EDX) spectroscopy was acquired using dark field scanning transmission electron microscopy (STEM), performed using a JEOL JEM-2100+ microscope operated at 200 kV and an Oxford Instruments XMaxN 100TLE X-ray microanalysis system. Samples were deposited onto copper grid mounted "lacey" carbon films (Agar) and the beam was condensed to areas suspended over holes of the amorphous carbon to negate the contribution to the carbon signal from the support film. Copper contributions from the grid were discounted from the analysis. The measured proportions of light atoms (C, N and O) will have contributions from the carbon film and as these measurements were carried out under high vacuum, it is likely a significant proportion of lattice water will have been lost.

Element	Wt%	At%	At. Ratio	At. Ratio (calc.)
Bi	19.87	2.02	2	2
Co	9.74	3.51	3.47	3
S	20.14	13.32	13.19	12
С	23.9	42.18	41.76	12
Ν	21.61	32.71	33.39	12
0	4.72	6.25	6.19	12.67
Ca	0.02	0.01	0.01	0
Ti	0	0	0	0
Ni	0	0	0	0

ESI Table 2: STEM-EDX elemental ratios in sample 2



ESI Fig. 2: Representative EDX spectrum for compound 2

6 Diffuse Reflectance

Diffuse reflectance measurements were carried out on finely ground powdered samples, diluted to 10 wt% with BaSO₄ to remove effects of strong absorption, using a Varian Cary 50 UV-vis spectrometer equipped with a diffuse reflectance accessory (DRA) probe (Barrelino, Harrick Scientific) measured over the range 350–1000 nm. All measurements were performed under standard ambient conditions. The absorption onsets were determined by extrapolation from a Tauc plot, using the Tauc exponent for a direct band gap.



ESI Fig. 3: Tauc normalised diffuse reflectance data for determination of band gap 1,2,4,5 & 6



ESI Fig. 4: Diffuse reflectance spectra for compounds 1,2,4,5 & 6

References

- (S1) M. J. Cliffe, et al., Chemical Science 10, 793 (2019).
- (S2) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **42**, 339 (2009).
- (S3) G. M. Sheldrick, Acta Crystallogr. A71, 3 (2015).
- (S4) G. M. Sheldrick, Acta Crystallogr. C71, 3 (2015).
- (S5) H. Rietveld, J. Appl. Crystallogr. 2, 65 (1969).
- (S6) A. Coelho, J. Appl. Crystallogr. 36, 86 (2003).