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Research paper

Auxiliary dipyridylamide ligand control of dimensionality in copper 5-sulfoisophthalate coordination polymers

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ABSTRACT

Hydrothermal reaction of copper nitrate, sodium 5-sulfoisophthalate (sip), and a long-spanning hydrogen-bonding capable dipyridylamide ligand afforded four coordination polymers whose dimensionality depends critically on the dipyridylamide tether length. The four new phases were structurally characterized via single-crystal X-ray diffraction. { $[Cu_8(sip)_4(pbn)_3(nic)(\mu_3-OH)_2(\mu_2-OH)(\mu_2-H_2O)(H_2O)_4]$ · $5H_2O$ }₁, (**1**, pbn = 1,3-propanediaminebis(nicotinamide), nic = nicotinate) manifests an intriguing 2D slab structure featuring trimeric copper clusters containing bridging hydroxide ions and water molecules along with substantial crystallographic disorder. { $[Cu_3(sip)_2(pbin)_4(H_2O)_4]$ · $14H_2O$ }₁, (**2**, pbin = 1,3-propanediaminebis(isonicotinamide)) shows 1D chain motifs with curled conformation dipyridylamide ligands. { $[Cu_4(\mu_3-OH)_2(sip)_2(hbin)]$ · $2H_2O$ }₁, (**3**, hbin = 1,6-hexanediaminebis(isonicotinamide)) features [$Cu_4(\mu-OH)_2(sip)_2$] butterfly clusters connected into a 3D 3,8-connected network with (4.6^2)₂($4^{2618748^4$) topology. { $[Cu(Hsip)(hbn)(H_2O)]$ · $2H_2O$ }₁, (**4**, hbn = 1,6-hexanediaminebis(nicotinamide)) exhibits a sawtooth (4,4) grid topology. Variable temperature magnetic susceptibility studies on **1** and **3** revealed antiferromagnetic behavior (g = 2.079(6), J = -5.7(2) cm⁻¹ for **1**, g = 2.14(2), $J_1 = -19(1)$ cm⁻¹, $J_2 = -35(2)$ cm⁻¹ for **3**). Thermal decomposition behavior of **1**-4 is also discussed.

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1. Introduction

Investigations into the synthesis of divalent metal coordination polymers remain a focus of inorganic chemistry basic research. These metal-organic crystalline phases have demonstrated significant utility in gas storage [1], as selective adsorbents [2], in drug delivery [3], in heterogeneous catalysis [4], and more recently as detectors of explosive traces for security applications [5]. Nevertheless, the structural chemistry of coordination polymer networks holds tremendous aesthetic appeal beyond a utilitarian perspective [6]. Most previously reported coordination polymers have been constructed from aromatic dicarboxylate ligands in combination with rigid dipyridyl-type ligands, providing two possible means of linking together divalent metal ions into 1D chain, 2D layer, or 3D network topologies [7]. In the cases of copper-based coordination polymers, carboxylate bridges can span the d^9 -configuration metal ions, imparting a mechanism for unpaired electron spin communication via overlap of the magnetic d_{x2-y2} orbitals [8].

Within divalent copper coordination polymers containing the trianionic 5-sulfoisophthalate ligand (sip, Scheme 1), the sulfonate

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moiety can act either as a ligated or unligated anionic component. in addition to the two carboxylate groups that are more likely to bind strongly to copper. The resulting stoichiometric ratio between divalent metal ions and the sip ligands is therefore crucially important in defining the structural topologies of copper/sip crystalline phases. In coordination polymers where a 1:1 ratio between the copper ions and the sip ligand is observed, necessary charge balance must be brought by other structural components. One method is through the inclusion of interstitial metal or organoammonium cations such as in the layered phase { $[Ca(H_2O)_3Cu_2(H_2 O_{6}(sip)_{2}$ $\cdot 2H_{2}O_{n}$ [9] and the zig-zag chain phase {[Cu(sip)] $(H_2O)_4](H_2en)_{0.5}_n$ [10]. Alternatively, protonation of the pyridyl co-ligands can occur, for example as seen in the $2D + 2D \rightarrow 3D$ inclined interpenetrated phase $\{[Cu(sip)(H4-bpmp)(H_2O)] \cdot 4H_2O\}_n$ (4-bpmp = bis(4-pyridylmethyl)piperazine) [11]. In rarer cases, protonation of the sip sulfonate group has been reported, such as in the 1D chain phase $\{[Cu(H_2O)_2(H_{2}Sip)] \cdot 2H_2O \cdot (piperazine)_{1/2}]_n\}$ [12]. The necessity of interstitial cations or ligand protonation can be obviated in compounds with a three-to-two copper/sip ratio, for example in complexes such as $\{[Cu_3(sip)_2(py)_{10}], 2(py)\}$ $13.5H_2O_{ln}$ [13], which adopts a (6,3) honeycomb layer topology. In some other copper-sip coordination polymers, a two-to-one copper/sip ratio is provided by the presence of triply bridging









Scheme 1. Ligands used in this study.

hydroxide ions within tetranuclear copper clusters, as seen in $[Cu_4(OH)_2(sip)_2(2,2'-bipyridine)_2(H_2O)_2]_n$, which possesses an uncommon 3-D rutile $(4.6^2)_2(4^26^{10}8^3)$ topology [10] and in { $[Cu_4(sip)_2(OH)_2(H_2O)_3(4-bpfp)] \cdot H_2O\}_n$ (4-bpfp = bis(4-pyridylformyl) piperazine), which manifests a 3,3,8-connected trinodal lattice with $(3.4^2)(4\ ^2\ 6)(3\ ^24^45\ ^36^97\ ^78\ ^29)$ topology [11]. The longer, more flexible dipyridylamide ligand butane(bisnicotinamide) (bbn) afforded the 2D phase { $[Cu_3(sip)_2(bbn)_3(H_2O)_8] \cdot 6H_2O\}_n$, which shows a 2D + 2D \rightarrow 3D parallel 3,4-connected binodal $(4.6^2)_2(4\ ^26\ ^28\ ^2)$ topology related to a standard (4,4) grid but with regular pillar absences [14]. A similar structure was observed in { $[Cu_3(sip)_2(bbn)_3(H_2O)_8] \cdot 11.5H_2O\}_n$ (hbn = hexane(bisnicotinamide), Scheme 1) [15].

We thus sought to expand the already rich structural scope of copper sulfoisophthalate coordination polymers by employing some other conformationally flexible dipyridylamide coligands, namely propane(bisnicotinamide) (pbn, Scheme 1), propane (bissionicotinamide) (pbn, Scheme 1), hexane(bissionicotinamide) (hbin, Scheme 1), and hexane(bisnicotinamide). In the course of our investigations we have successfully prepared and structurally characterized four coordination polymers: $\{[Cu_8(sip)_4(pbn)_3(nic) (\mu_3-OH)_2(\mu_2-OH)(\mu_2-H_2O)(H_2O)_4]\cdot5H_2O\}_n$ (1) $\{[Cu_3(sip)_2(pbin)_4 (H_2O)_4]\cdot14H_2O\}_n$ (2), $\{[Cu_4(\mu_3-OH)_2(sip)_2(hbin)]\cdot H_2O\}_n$ (3), and $\{[Cu(Hsip)(hbn)(H_2O)]\cdot2H_2O\}_n$ (4). Thermal properties for all new phases have been assayed, as well as the magnetic properties of 1 and 3 as they possessed trinuclear and tetranuclear copper ion clusters, respectively.

2. Experimental section

2.1. General considerations

Copper nitrate and sodium 5-sulfoisophthalate were commercially obtained. Condensation of 1,3-propanediamine and two molar equivalents of isonicotinoyl chloride hydrochloride in dry pyridine was used to prepare 1,3-propanediaminebis(isonicotinamide) (pbin), which was isolated via CH₂Cl₂ extraction and rotary evaporation [16]. A similar reaction between 1,6-hexanediamine and two molar equivalents of isonicotinoyl chloride hydrochloride in dry pyridine afforded 1,6-hexanediaminebis (isonicotinamide) (hbin) after similar workup. Reacting 1,3propanediamine and two molar equivalents of nicotinoyl chloride hydrochloride in a similar manner afforded 1,3-propanediaminebis(nicotinamide) (pbn); hbn was prepared using 1,6-hexanediamine as the starting diamine. Water was deionized above 3 M Ω cm in-house. IR spectra were recorded on powdered samples using a Perkin Elmer Spectrum One DRIFT instrument. Thermogravimetric analysis was performed on a TA Instruments Q-50 Thermogravimetric Analyzer with a heating rate of 10 °C/min up to 600 °C. Elemental Analysis was carried out using a Perkin Elmer 2400 Series II CHNS/O Analyzer. Variable temperature magnetic susceptibility data for 1 and 3 (2 K-300 K) were collected on a Quantum Design MPMS3 SQUID magnetometer at an applied field of 0.1 T. After each temperature change the sample was kept at the new temperature for five minutes before magnetization measurement to ensure thermal equilibrium. The susceptibility data was corrected for diamagnetism using Pascal's constants [17], and for the diamagnetism of the sample holder.

2.2. Preparation of { $[Cu_8(sip)_4(pbn)_3(nic)(\mu_3-OH)_2(\mu_2-OH)(\mu_2-H_2O)(H_2O)_4] \cdot 5H_2O}_n$ (1)

Cu(NO₃)₂·2.5H₂O (65 mg, 0.28 mmol), sodium 5-sulfoisophthalate (75 mg, 0.28 mmol), and pbn (87 mg, 0.28 mmol) were mixed with 10 mL of distilled H₂O in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120 °C for 24 h, and then was cooled slowly to 25 °C. Blue crystals of **1** (71 mg, 76% yield based on Cu) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for C₈₃H₈₆-Cu₈N₁₃O₄₉S₄ **1**: C, 37.11; H, 3.23; N, 6.78% Found: C, 37.48; H, 3.59; N, 7.00%. IR (cm⁻¹): 3722 (m), 1650 (s), 1617 (m), 1556 (m), 1479 (m), 1431 (m), 1356 (s), 1221 (m), 1183 (m), 1110 (m), 1040 (s), 831 (w), 779 (m), 724 (s).

2.3. Preparation of $\{[Cu_3(sip)_2(pbin)_4(H_2O)_4] \cdot 14H_2O\}_n$ (2)

Cu(NO₃)₂·2.5H₂O (65 mg, 0.28 mmol), sodium 5-sulfoisophthalate (75 mg, 0.28 mmol), and pbin (87 mg, 0.28 mmol) were mixed with 10 mL of distilled H₂O in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120 °C for 24 h, and then was cooled slowly to 25 °C. Blue crystals of **2** (110 mg, 56% yield based on Cu) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for C₇₆-H₁₀₂Cu₃N₁₆O₄₀S₂ **2**: C, 42.77; H, 4.82; N, 10.50% Found: C, 43.61; H, 4.74; N, 10.65%. IR (cm⁻¹): 3280 (m), 1650 (s), 1607 (s), 1557 (s), 1433 (m), 1355 (s), 1199 (s), 1109 (m), 1040 (s), 858 (m), 735 (m), 703 (s).

2.4. Preparation of $\{[Cu_4(\mu_3-OH)_2(sip)_2(hbin)] \cdot H_2O\}_n$ (3)

Cu(NO₃)₂·2.5H₂O (65 mg, 0.28 mmol), sodium 5-sulfoisophthalate (75 mg, 0.28 mmol), and hbin (91 mg, 0.28 mmol) were mixed with 10 mL of distilled H₂O in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120 °C for 24 h, and then was cooled slowly to 25 °C. Blue crystals of **3** (54 mg, 69% yield based on Cu) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for C₃₄H₃₄-Cu₄N₄O₂₀S₂ **3**: C, 35.92; H, 3.01; N, 4.93% Found: C, 35.41; H, 3.47; N, 5.11%. IR (cm⁻¹): 3288 (w), 2935 (w), 1638 (m), 1612 (s), 1551 (s), 1435 (m), 1359 (s), 1191 (s), 1099 (m), 1040 (s), 776 (m), 722 (s), 688 (s).

2.5. Preparation of $\{[Cu(Hsip)(hbn)(H_2O)] \cdot 2H_2O\}_n$ (4)

Cu(NO₃)₂·2.5H₂O (65 mg, 0.28 mmol), sodium 5-sulfoisophthalate (75 mg, 0.28 mmol), and hbn (91 mg, 0.28 mmol) were mixed with 10 mL of distilled H₂O in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120 °C for 24 h, and then was cooled slowly to 25 °C. Blue crystals of **4** (140 mg, 73% yield based on Cu) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for C₂₆H₃₂-CuN₄O₁₂S **4**: C, 45.38; H, 4.69; N, 8.14% Found: C, 45.68; H, 4.45; N, 8.23%. IR (cm⁻¹): 3269 (m), 2933 (w), 1652 (m), 1605 (m), 1547 (s), 1433 (m), 1358 (s), 1166 (s), 1104 (m), 1035 (s), 996 (w), 838 (w), 695 (s).

3. X-ray crystallography

Diffraction data for 1-4 were collected on a Bruker-AXS SMART-CCD X-ray diffractometer using graphite-monochromated Mo-Ka radiation ($\lambda = 0.71073$ Å) at 173 K. The data were processed via SAINT [18], and subjected for Lorentz and polarization effect and absorption corrections using SADABS [19]. The structures were solved using direct methods with SHELXTL [20] within the OLEX2 crystallographic software suite [21]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined isotropically with a riding model. The Cu atoms in 2 were disordered over two sets of positions and modeled with a 95:5 ratio in terms of major-to-minor disorder components. The sulfonate groups and one of the pbin ligand trimethylene tethers in 2 were disordered in a 50:50 ratio, and were modeled successfully with partial occupancies. The amide carbonyl oxygen atoms in 4 were disordered in a 50:50 ratio, and were modeled successfully with partial occupancies. Crystallographic details for **1–4** are given in Table 1.

Table 1

Crystal and Structure Refinement Data for 1-4.

Data	1	2
Empirical Formula	C83H86Cu8N13O49S4	C76H102Cu3N16O40S2
Formula Weight	2686.21	2134.47
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	P1
a (Å)	9.6997(15)	13.723(5)
b (A)	40.083(6)	14.264(6)
c (A)	12.788(2)	14.747(6)
α (°)	90 100 652(2)	66.401(5)
p (°)	90	62 127(5)
$V(Å^3)$	4886 3(13)	2308 4(16)
Z	2	1
$D (g cm^{-3})$	1.824	1.535
μ (mm ⁻¹)	1.900	0.830
Min./max. transmission	0.8713	0.8696
hkl ranges	$-11 \le h \le 11$,	$-16 \leq h \leq 16$,
	$-48 \leq k \leq 48$,	$-17 \le k \le 17$,
	$-15 \le l \le 15$	$-17 \le l \le 17$
Total reflections	39,636	37,507
Unique reflections	8984	8594
R(IIII) Parameters	649	0.2179 504
R_1 (all data)	0 1506	0 2 2 5 3
$R_1 (I > 2\sigma(I))$	0.0795	0.1267
wR_2 (all data)	0.2437	0.3888
$wR_2 (I > 2\sigma(I))$	0.1976	0.3407
Max/min residual (e ⁻ /Å ³)	2.079 / -1.967	1.906 / -1.087
G.O.F.	1.043	1.047
Data	3	4
Data Empirical Formula	3 C ₃₄ H ₃₄ Cu ₄ N ₄ O ₂₀ S ₂	4 C ₂₆ H ₃₂ CuN ₄ O ₁₂ S
Data Empirical Formula Formula Weight	3 C ₃₄ H ₃₄ Cu ₄ N ₄ O ₂₀ S ₂ 1118.91	4 C ₂₆ H ₃₂ CuN ₄ O ₁₂ S 688.15
Data Empirical Formula Formula Weight Crystal system	3 C ₃₄ H ₃₄ Cu ₄ N ₄ O ₂₀ S ₂ 1118.91 monoclinic	4 C ₂₆ H ₃₂ CuN ₄ O ₁₂ S 688.15 monoclinic
Data Empirical Formula Formula Weight Crystal system Space group	3 C ₃₄ H ₃₄ Cu ₄ N ₄ O ₂₀ S ₂ 1118.91 monoclinic P ₂₁ /n	4 C ₂₆ H ₃₂ CuN ₄ O ₁₂ S 688.15 monoclinic <i>P</i> 2 ₁
Data Empirical Formula Formula Weight Crystal system Space group a (Å) b (Å)	3 C ₃₄ H ₃₄ Cu ₄ N ₄ O ₂₀ S ₂ 1118.91 monoclinic P2 ₁ /n 10.657(3) 15 109(4)	$\frac{4}{C_{26}H_{32}CuN_4O_{12}S}$ 688.15 monoclinic <i>P</i> 2 ₁ 9.2962(12) 14.042(2)
Data Empirical Formula Formula Weight Crystal system Space group a (Å) b (Å) c (Å)	3 C ₃₄ H ₃₄ Cu ₄ N ₄ O ₂₀ S ₂ 1118.91 monoclinic <i>P</i> 2 ₁ / <i>n</i> 10.657(3) 15.108(4) 12.213(3)	$\begin{array}{c} 4 \\ \\ C_{26}H_{32}CuN_4O_{12}S \\ 688.15 \\ \\ monoclinic \\ P2_1 \\ 9.2962(12) \\ 14.942(2) \\ 10.7457(14) \end{array}$
Data Empirical Formula Formula Weight Crystal system Space group a (Å) b (Å) c (Å) α (°)	3 C ₃₄ H ₃₄ Cu ₄ N ₄ O ₂₀ S ₂ 1118.91 monoclinic <i>P</i> 2 ₁ / <i>n</i> 10.657(3) 15.108(4) 12.213(3) 90	4 C ₂₆ H ₃₂ CuN ₄ O ₁₂ S 688.15 monoclinic <i>P</i> 2 ₁ 9.2962(12) 14.942(2) 10.7457(14) 90
Data Empirical Formula Formula Weight Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°)	3 C ₃₄ H ₃₄ Cu ₄ N ₄ O ₂₀ S ₂ 1118.91 monoclinic <i>P</i> 2 ₁ / <i>n</i> 10.657(3) 15.108(4) 12.213(3) 90 93.513(4)	$\begin{array}{c} \textbf{4} \\ \hline C_{26}H_{32}CuN_4O_{12}S \\ 688.15 \\ monoclinic \\ P2_1 \\ 9.2962(12) \\ 14.942(2) \\ 10.7457(14) \\ 90 \\ 92.091(2) \end{array}$
Data Empirical Formula Formula Weight Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°)	3 C ₃₄ H ₃₄ Cu ₄ N ₄ O ₂₀ S ₂ 1118.91 monoclinic <i>P</i> 2 ₁ / <i>n</i> 10.657(3) 15.108(4) 12.213(3) 90 93.513(4) 90	4 C ₂₆ H ₃₂ CuN ₄ O ₁₂ S 688.15 monoclinic <i>P</i> 2 ₁ 9.2962(12) 14.942(2) 10.7457(14) 90 92.091(2) 90
Data Empirical Formula Formula Weight Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°) V (Å3)	3 C ₃₄ H ₃₄ Cu ₄ N ₄ O ₂₀ S ₂ 1118.91 monoclinic <i>P</i> 2 ₁ / <i>n</i> 10.657(3) 15.108(4) 12.213(3) 90 93.513(4) 90 1962.5(9)	$\begin{array}{c} \textbf{4} \\ \hline C_{26}H_{32}CuN_4O_{12}S \\ 688.15 \\ monoclinic \\ P2_1 \\ 9.2962(12) \\ 14.942(2) \\ 10.7457(14) \\ 90 \\ 92.091(2) \\ 90 \\ 1491.6(3) \end{array}$
Data Empirical Formula Formula Weight Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°) V (Å3) Z	3 C ₃₄ H ₃₄ Cu ₄ N ₄ O ₂₀ S ₂ 1118.91 monoclinic <i>P</i> 2 ₁ / <i>n</i> 10.657(3) 15.108(4) 12.213(3) 90 93.513(4) 90 1962.5(9) 2	$\begin{array}{c} \textbf{4} \\ \hline C_{26}H_{32}CuN_4O_{12}S \\ 688.15 \\ monoclinic \\ P2_1 \\ 9.2962(12) \\ 14.942(2) \\ 10.7457(14) \\ 90 \\ 92.091(2) \\ 90 \\ 1491.6(3) \\ 2 \end{array}$
Data Empirical Formula Formula Weight Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°) V (Å3) Z D (g cm ⁻³)	3 C ₃₄ H ₃₄ Cu ₄ N ₄ O ₂₀ S ₂ 1118.91 monoclinic <i>P</i> 2 ₁ / <i>n</i> 10.657(3) 15.108(4) 12.213(3) 90 93.513(4) 90 1962.5(9) 2 1.893 2892	4 C ₂₆ H ₃₂ CuN ₄ O ₁₂ S 688.15 monoclinic P2 ₁ 9.2962(12) 14.942(2) 10.7457(14) 90 92.091(2) 90 1491.6(3) 2 1.532 0.057
Data Empirical Formula Formula Weight Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°) V (Å3) Z D (g cm ⁻³) μ (mm ⁻¹)	3 C ₃₄ H ₃₄ Cu ₄ N ₄ O ₂₀ S ₂ 1118.91 monoclinic <i>P</i> 2 ₁ / <i>n</i> 10.657(3) 15.108(4) 12.213(3) 90 93.513(4) 90 1962.5(9) 2 1.893 2.333 0.9797	4 C ₂₆ H ₃₂ CuN ₄ O ₁₂ S 688.15 monoclinic P2 ₁ 9.2962(12) 14.942(2) 10.7457(14) 90 92.091(2) 90 1491.6(3) 2 1.532 0.871 0.9704
Data Empirical Formula Formula Weight Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°) γ (°) V (Å3) Z D (g cm ⁻³) μ (mm ⁻¹) Min./max. transmission	3 $C_{34}H_{34}Cu_4N_4O_{20}S_2$ 1118.91 monoclinic $P_{2_1/n}$ 10.657(3) 15.108(4) 12.213(3) 90 93.513(4) 90 1962.5(9) 2 1.893 2.333 0.8787 13.45 (b < 12)	$\begin{array}{c} \textbf{4} \\ \hline C_{26}H_{32}CuN_4O_{12}S \\ 688.15 \\ monoclinic \\ P_{21} \\ 9.2962(12) \\ 14.942(2) \\ 10.7457(14) \\ 90 \\ 92.091(2) \\ 90 \\ 1491.6(3) \\ 2 \\ 1.532 \\ 0.871 \\ 0.8784 \\ 11 < b < 11 \end{array}$
Data Empirical Formula Formula Weight Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°) γ (°) γ (°) V (Å ³) Z D (g cm ⁻³) μ (mm ⁻¹) Min,/max. transmission hkl ranges	3 $C_{34}H_{34}Cu_4N_4O_{20}S_2$ 1118.91 monoclinic $P_{2_1/n}$ 10.657(3) 15.108(4) 12.213(3) 90 93.513(4) 90 1962.5(9) 2 1.893 2.333 0.8787 $-12 \le h \le 12$, $-18 \le k \le 18$	$\begin{array}{c} \textbf{4} \\ \hline C_{26}H_{32}CuN_4O_{12}S \\ 688.15 \\ monoclinic \\ P2_1 \\ 9.2962(12) \\ 14.942(2) \\ 10.7457(14) \\ 90 \\ 92.091(2) \\ 90 \\ 1491.6(3) \\ 2 \\ 1.532 \\ 0.871 \\ 0.8784 \\ -11 \leq h \leq 11, \\ -18 \leq k \leq 18 \end{array}$
Data Empirical Formula Formula Weight Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°) γ (°) γ (Å) Z D (g cm ⁻³) μ (mm ⁻¹) Min./max. transmission hkl ranges	$\begin{array}{c} \textbf{3} \\ \hline \\ C_{34}H_{34}Cu_4N_4O_{20}S_2 \\ 1118.91 \\ monoclinic \\ P2_1/n \\ 10.657(3) \\ 15.108(4) \\ 12.213(3) \\ 90 \\ 93.513(4) \\ 90 \\ 1962.5(9) \\ 2 \\ 1.893 \\ 2.333 \\ 0.8787 \\ -12 \leq h \leq 12, \\ -18 \leq k \leq 18, \\ -14 \leq l \leq 14 \end{array}$	$\begin{array}{c} \textbf{4} \\ \hline C_{26}H_{32}CuN_4O_{12}S \\ 688.15 \\ monoclinic \\ P2_1 \\ 9.2962(12) \\ 14.942(2) \\ 10.7457(14) \\ 90 \\ 92.091(2) \\ 90 \\ 1491.6(3) \\ 2 \\ 1.532 \\ 0.871 \\ 0.8784 \\ -11 \leq h \leq 11, \\ -18 \leq k \leq 18, \\ -12 \leq l \leq 12 \end{array}$
Data Empirical Formula Formula Weight Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°) γ (°) γ (Å) Z D (g cm ⁻³) μ (mm ⁻¹) Min./max. transmission hkl ranges	$\begin{array}{c} \textbf{3} \\ \hline \\ C_{34}H_{34}Cu_4N_4O_{20}S_2 \\ 1118.91 \\ monoclinic \\ P2_1/n \\ 10.657(3) \\ 15.108(4) \\ 12.213(3) \\ 90 \\ 93.513(4) \\ 90 \\ 1962.5(9) \\ 2 \\ 1.893 \\ 2.333 \\ 0.8787 \\ -12 \leq h \leq 12, \\ -18 \leq k \leq 18, \\ -14 \leq l \leq 14 \\ 25148 \end{array}$	$\begin{array}{c} \textbf{4} \\ \hline C_{26}H_{32}CuN_4O_{12}S \\ 688.15 \\ monoclinic \\ P2_1 \\ 9.2962(12) \\ 14.942(2) \\ 10.7457(14) \\ 90 \\ 92.091(2) \\ 90 \\ 1491.6(3) \\ 2 \\ 1.532 \\ 0.871 \\ 0.8784 \\ -11 \leq h \leq 11, \\ -18 \leq k \leq 18, \\ -12 \leq l \leq 12 \\ 12202 \end{array}$
Data Empirical Formula Formula Weight Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°) V (Å3) Z D (g cm ⁻³) μ (mm ⁻¹) Min./max. transmission hkl ranges	$\begin{array}{c} \textbf{3} \\ \hline \\ C_{34}H_{34}Cu_4N_4O_{20}S_2 \\ 1118.91 \\ monoclinic \\ P2_1/n \\ 10.657(3) \\ 15.108(4) \\ 12.213(3) \\ 90 \\ 93.513(4) \\ 90 \\ 1962.5(9) \\ 2 \\ 1.893 \\ 2.333 \\ 0.8787 \\ -12 \leq h \leq 12, \\ -18 \leq k \leq 18, \\ -14 \leq l \leq 14 \\ 25148 \\ 3596 \\ \end{array}$	$\begin{array}{c} \textbf{4} \\ \hline C_{26}H_{32}CuN_4O_{12}S \\ 688.15 \\ monoclinic \\ P2_1 \\ 9.2962(12) \\ 14.942(2) \\ 10.7457(14) \\ 90 \\ 92.091(2) \\ 90 \\ 1491.6(3) \\ 2 \\ 1.532 \\ 0.871 \\ 0.8784 \\ -11 \leq h \leq 11, \\ -18 \leq k \leq 18, \\ -11 \leq l \leq 12 \\ 12202 \\ 5459 \\ \end{array}$
Data Empirical Formula Formula Weight Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°) V (Å3) Z D (g cm ⁻³) μ (mm ⁻¹) Min./max. transmission hkl ranges Total reflections Unique reflections R (int)	$\begin{array}{c} \textbf{3} \\ \hline \\ C_{34}H_{34}Cu_4N_4O_{20}S_2 \\ 1118.91 \\ monoclinic \\ P2_1/n \\ 10.657(3) \\ 15.108(4) \\ 12.213(3) \\ 90 \\ 93.513(4) \\ 90 \\ 1962.5(9) \\ 2 \\ 1.893 \\ 2.333 \\ 0.8787 \\ -12 \leq h \leq 12, \\ -18 \leq k \leq 18, \\ -14 \leq l \leq 14 \\ 25148 \\ 3596 \\ 0.0756 \\ \end{array}$	$\begin{array}{c} \textbf{4} \\ \hline C_{26}H_{32}CuN_4O_{12}S \\ 688.15 \\ monoclinic \\ P2_1 \\ 9.2962(12) \\ 14.942(2) \\ 10.7457(14) \\ 90 \\ 92.091(2) \\ 90 \\ 1491.6(3) \\ 2 \\ 1.532 \\ 0.871 \\ 0.8784 \\ -11 \leq h \leq 11, \\ -18 \leq k \leq 18, \\ -11 \leq l \leq 12 \\ 12202 \\ 5459 \\ 0.0570 \\ \end{array}$
Data Empirical Formula Formula Weight Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°) V (Å3) Z D (g cm ⁻³) μ (mm ⁻¹) Min./max. transmission hkl ranges Total reflections Unique reflections R (int) Parameters	$\begin{array}{c} \textbf{3} \\ \hline \\ C_{34}H_{34}Cu_4N_4O_{20}S_2 \\ 1118.91 \\ monoclinic \\ P2_1/n \\ 10.657(3) \\ 15.108(4) \\ 12.213(3) \\ 90 \\ 93.513(4) \\ 90 \\ 1962.5(9) \\ 2 \\ 1.893 \\ 2.333 \\ 0.8787 \\ -12 \leq h \leq 12, \\ -18 \leq k \leq 18, \\ -14 \leq l \leq 14 \\ 25148 \\ 3596 \\ 0.0756 \\ 292 \\ \end{array}$	$\begin{array}{c} \textbf{4} \\ \hline C_{26}H_{32}CuN_4O_{12}S \\ 688.15 \\ monoclinic \\ P2_1 \\ 9.2962(12) \\ 14.942(2) \\ 10.7457(14) \\ 90 \\ 92.091(2) \\ 90 \\ 1491.6(3) \\ 2 \\ 1.532 \\ 0.871 \\ 0.8784 \\ -11 \leq h \leq 11, \\ -18 \leq k \leq 18, \\ -11 \leq l \leq 12 \\ 12202 \\ 5459 \\ 0.0570 \\ 405 \end{array}$
Data Empirical Formula Formula Weight Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°) V (Å3) Z D (g cm ⁻³) μ (mm ⁻¹) Min./max. transmission hkl ranges Total reflections Unique reflections R(int) Parameters R_1 (all data)	$\begin{array}{c} \textbf{3} \\ \hline \\ C_{34}H_{34}Cu_4N_4O_{20}S_2 \\ 1118.91 \\ monoclinic \\ P2_1/n \\ 10.657(3) \\ 15.108(4) \\ 12.213(3) \\ 90 \\ 93.513(4) \\ 90 \\ 1962.5(9) \\ 2 \\ 1.893 \\ 2.333 \\ 0.8787 \\ -12 \leq h \leq 12, \\ -18 \leq k \leq 18, \\ -14 \leq l \leq 14 \\ 25148 \\ 3596 \\ 0.0756 \\ 292 \\ 0.0609 \\ 0.0455 \\ \end{array}$	$\begin{array}{c} \textbf{4} \\ \hline C_{26}H_{32}CuN_4O_{12}S \\ 688.15 \\ monoclinic \\ P2_1 \\ 9.2962(12) \\ 14.942(2) \\ 10.7457(14) \\ 90 \\ 92.091(2) \\ 90 \\ 1491.6(3) \\ 2 \\ 1.532 \\ 0.871 \\ 0.8784 \\ -11 \leq h \leq 11, \\ -18 \leq k \leq 18, \\ -11 \leq l \leq 12 \\ 12202 \\ 5459 \\ 0.0570 \\ 405 \\ 0.0722 \\ 0.9745 \\ \end{array}$
Data Empirical Formula Formula Weight Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°) V (Å3) Z D (g cm ⁻³) μ (mm ⁻¹) Min./max. transmission hkl ranges Total reflections Unique reflections R_i (all data) R_1 ($l > 2\sigma(l)$) w ($l < d xz$)	$\begin{array}{c} \textbf{3} \\ \hline \\ C_{34}H_{34}Cu_4N_4O_{20}S_2 \\ 1118.91 \\ monoclinic \\ P_{2_1/n} \\ 10.657(3) \\ 15.108(4) \\ 12.213(3) \\ 90 \\ 93.513(4) \\ 90 \\ 1962.5(9) \\ 2 \\ 1.893 \\ 2.333 \\ 0.8787 \\ -12 \leq h \leq 12, \\ -18 \leq k \leq 18, \\ -14 \leq l \leq 14 \\ 25148 \\ 3596 \\ 0.0756 \\ 292 \\ 0.0609 \\ 0.0455 \\ 0.1100 \\ \end{array}$	$\begin{array}{c} \textbf{4} \\ \hline C_{26}H_{32}CuN_4O_{12}S \\ 688.15 \\ monoclinic \\ P2_1 \\ 9.2962(12) \\ 14.942(2) \\ 10.7457(14) \\ 90 \\ 92.091(2) \\ 90 \\ 1491.6(3) \\ 2 \\ 1.532 \\ 0.871 \\ 0.8784 \\ -11 \leq h \leq 11, \\ -18 \leq k \leq 18, \\ -11 \leq h \leq 12, \\ 12202 \\ 5459 \\ 0.0570 \\ 405 \\ 0.0722 \\ 0.0515 \\ 0.1152 \end{array}$
DataEmpirical FormulaFormula WeightCrystal systemSpace group a (Å) b (Å) c (Å) α (°) β (°) γ (°) γ (°) γ (Å) Z D (g cm ⁻³) μ (mm ⁻¹)Min./max. transmission hkl rangesTotal reflectionsUnique reflections $R(int)$ Parameters R_1 (all data) R_1 ($l > 2\sigma(l)$) wP_2 (all data)	$\begin{array}{c} \textbf{3} \\ \hline C_{34}H_{34}Cu_4N_4O_{20}S_2 \\ 1118.91 \\ monoclinic \\ P_{21/n} \\ 10.657(3) \\ 15.108(4) \\ 12.213(3) \\ 90 \\ 93.513(4) \\ 90 \\ 93.513(4) \\ 90 \\ 1962.5(9) \\ 2 \\ 1.893 \\ 2.333 \\ 0.8787 \\ -12 \leq h \leq 12, \\ -18 \leq k \leq 18, \\ -14 \leq l \leq 14 \\ 25148 \\ 3596 \\ 0.0756 \\ 292 \\ 0.0609 \\ 0.0455 \\ 0.1199 \\ 0.1084 \end{array}$	$\begin{array}{c} \textbf{4} \\ \hline C_{26}H_{32}CuN_4O_{12}S \\ 688.15 \\ monoclinic \\ P_{21} \\ 9.2962(12) \\ 14.942(2) \\ 10.7457(14) \\ 90 \\ 92.091(2) \\ 90 \\ 1491.6(3) \\ 2 \\ 1.532 \\ 0.871 \\ 0.8784 \\ -11 \leq h \leq 11, \\ -18 \leq k \leq 18, \\ -12 \leq l \leq 12 \\ 12202 \\ 5459 \\ 0.0570 \\ 405 \\ 0.0722 \\ 0.0515 \\ 0.1158 \\ 0.1020 \end{array}$
DataEmpirical FormulaFormula WeightCrystal systemSpace group a (Å) b (Å) c (Å) α (°) β (°) γ (°) γ (Å) Z D (g cm ⁻³) μ (mm ⁻¹)Min./max. transmission hkl rangesTotal reflectionsUnique reflections $R(int)$ Parameters R_1 (all data) R_1 ($l > 2\sigma(l)$) wR_2 (all data) wR_2 (1 > 2 $\sigma(l)$) wR_2 (l > 2 $\sigma(l)$)	$\begin{array}{c} \textbf{3} \\ \hline C_{34}H_{34}Cu_4N_4O_{20}S_2 \\ 1118.91 \\ monoclinic \\ P_{21/n} \\ 10.657(3) \\ 15.108(4) \\ 12.213(3) \\ 90 \\ 93.513(4) \\ 90 \\ 1962.5(9) \\ 2 \\ 1.893 \\ 2.333 \\ 0.8787 \\ -12 \leq h \leq 12, \\ -18 \leq k \leq 18, \\ -14 \leq l \leq 14 \\ 25148 \\ 3596 \\ 0.0756 \\ 292 \\ 0.0609 \\ 0.0455 \\ 0.1199 \\ 0.1084 \\ 1.148/-0.491 \\ \end{array}$	$\begin{array}{c} \textbf{4} \\ \hline C_{26}H_{32}CuN_4O_{12}S \\ 688.15 \\ monoclinic \\ P_{21} \\ 9.2962(12) \\ 14.942(2) \\ 10.7457(14) \\ 90 \\ 92.091(2) \\ 90 \\ 1491.6(3) \\ 2 \\ 1.532 \\ 0.871 \\ 0.8784 \\ -11 \leq h \leq 11, \\ -18 \leq k \leq 18, \\ -12 \leq l \leq 12 \\ 12202 \\ 5459 \\ 0.0570 \\ 405 \\ 0.0722 \\ 0.0515 \\ 0.1158 \\ 0.1039 \\ 0.726(-0.425 \\ 0.0725 \\ 0.0725 \\ 0.0725 \\ 0.0725 \\ 0.0725 \\ 0.0725 \\ 0.0726 \\ 0.0725 \\ 0.0725 \\ 0.0725 \\ 0.0725 \\ 0.0725 \\ 0.0726 \\ 0.0725 \\ 0.0725 \\ 0.0726 \\ 0.0725 \\ 0.072$
DataEmpirical FormulaFormula WeightCrystal systemSpace group a (Å) b (Å) c (Å) α (°) β (°) γ (°) γ (Å) Z D (g cm ⁻³) μ (mm ⁻¹)Min./max. transmission hkl rangesTotal reflectionsUnique reflections $R(int)$ Parameters R_1 (all data) R_1 ($l > 2\sigma(l)$) wR_2 (all data) wR_2 (1 > 2 $\sigma(l)$)Max/min residual ($e^{-}/Å^3$)G.O.F.	$\begin{array}{c} \textbf{3} \\ \hline C_{34}H_{34}Cu_4N_4O_{20}S_2 \\ 1118.91 \\ monoclinic \\ P_{21/n} \\ 10.657(3) \\ 15.108(4) \\ 12.213(3) \\ 90 \\ 93.513(4) \\ 90 \\ 93.513(4) \\ 90 \\ 1962.5(9) \\ 2 \\ 1.893 \\ 2.333 \\ 0.8787 \\ -12 \leq h \leq 12, \\ -18 \leq k \leq 18, \\ -14 \leq l \leq 14 \\ 25148 \\ 3596 \\ 0.0756 \\ 292 \\ 0.0609 \\ 0.0455 \\ 0.1199 \\ 0.1084 \\ 1.148/-0.491 \\ 1.086 \\ \end{array}$	$\begin{array}{c} \textbf{4} \\ \hline C_{26}H_{32}CuN_4O_{12}S \\ 688.15 \\ monoclinic \\ P_2 \\ 9.2962(12) \\ 14.942(2) \\ 10.7457(14) \\ 90 \\ 92.091(2) \\ 90 \\ 1491.6(3) \\ 2 \\ 1.532 \\ 0.871 \\ 0.8784 \\ -11 \leq h \leq 11, \\ -18 \leq k \leq 18, \\ -12 \leq l \leq 12 \\ 12202 \\ 5459 \\ 0.0570 \\ 405 \\ 0.0722 \\ 0.0515 \\ 0.1158 \\ 0.1039 \\ 0.726/-0.425 \\ 1.013 \\ \end{array}$

4. Results and discussion

4.1. Synthesis and spectra

Crystalline samples of **1–4** were produced by the hydrothermal reaction of copper nitrate, sodium 5-sulfoisophthalate, and the requisite dipyridylamide ligand. The infrared spectra of **1–4** were consistent with their structural components as determined by single-crystal X-ray diffraction. Intense, broadened asymmetric and symmetric C–O stretching bands within the carboxylate ligands were observed at 1555 and 1356 cm⁻¹ for **1**, at 1557 and 1355 cm⁻¹ for **2**, at 1551 and 1359 cm⁻¹ for **3**, and at 1547 and 1358

cm⁻¹ for **4**. Medium intensity bands in the range of ~1600 cm⁻¹ to ~1300 cm⁻¹ were ascribed to stretching modes of the pyridyl rings of the dipyridylamide ligands [22]. Features corresponding to C–H bending and ring puckering within the pyridyl moieties exist in the region between ~900 and ~650 cm⁻¹. Broad, weak spectral bands in the vicinity of ~3000–3400 cm⁻¹ indicate the presence of bound and unbound water molecules. The C=O stretching bands of the amide groups of the dipyridylamide ligands appeared at 1650 cm⁻¹, 1649 cm⁻¹, 1638 cm⁻¹, and 1652 cm⁻¹ for **1–4**, respectively.

4.2. Structural description of { $[Cu_8(sip)_4(pbn)_3(nic)(\mu_3-OH)_2(\mu_2-OH)(\mu_2-H_2O)(H_2O)_4]$ -5H₂O}_n (**1**)

The complicated asymmetric unit of compound **1** contains four divalent copper atoms in disparate coordination environments (Cu1, Cu2, Cu3, Cu4), two sip ligands (sip-A, sip-B), a pbn ligand whose central aliphatic tether is disordered equally over two sets of positions (pbn-A), another pbn ligand best refined at half occupancy (pbn-B), a nicotinate ligand best refined at half occupancy,



Fig. 1. [Cu₃(OCO)₂(OSO)(µ₃-OH)(µ₂-OH/H₂O)(pbn)] trinuclear unit in 1 showing complete coordination environments at Cu1, Cu2, and Cu3 atoms. Thermal ellipsoids are drawn at 50% probability.



Fig. 2. Coordination environment at Cu4 atoms in 1. Thermal ellipsoids are drawn at 50% probability.

two bound water molecules, one μ_2 -bridging oxygen atom, and one μ_3 -bridging hydroxide ion. To provide charge neutrality in the compound, it must be the case that one half of these μ_2 -bridging oxygen atoms are hydroxide ions, and the other half are μ_2 bridging water molecules. There are also net two and one-half water molecules of crystallization residing within the asymmetric unit. The nic ligand was formed from the *in situ* hydrolysis of some of the pbn precursor ligands [23].

The Cu1 atoms display a {CuNO₄} square pyramidal coordination environment ($\tau = 0.06$ [24]) with the apical position taken up by a bound water molecule. Within the basal plane, the μ_2 -bridging disordered hydroxide/water molecule group, and the μ_3 -bridging hydroxide occupy cis positions. The other two cis positions at Cu1 are filled by a carboxylate oxygen atom donor from a sip-A ligand and a pyridyl nitrogen donor atom from a pbn-A ligand. The Cu2 atoms display a more distorted {CuNO₄} square pyramidal coordination environment ($\tau = 0.35$), with the apical position filled by a sulfonate oxygen atom from a sip-A ligand. Again, a μ_2 -bridging disordered hydroxide/water molecule, and a μ_3 -bridging hydroxide ion occupy cis positions in the basal plane. The remaining two cis coordination sites at Cu2 are occupied by a pyridyl nitrogen donor atom belonging to the other pyridyl ring of pbn-A ligands, and a carboxylate oxygen donor atom from a sip-B ligand. The Cu3 atoms display a less distorted {CuNO₄} square pyramidal coordination environment ($\tau = 0.04$), again with its apical position filled by a sulfonate oxygen atom from a sip-A ligand. The basal plane at Cu3 contains a μ_3 -bridging hydroxide ion trans to a pyridyl nitrogen donor atom from either a nic ligand or a pbn-B ligand, depending on the particular disorder conformation. The remaining two trans basal coordination sites are filled by carboxylate oxygen atoms, one from a sip-A ligand and the other from a sip-B ligand.

Bridging carboxylate and sulfonate groups, along with the bridging hydroxide and bridging disordered water/hydroxide ligands produce asymmetric triangular [Cu₃(OCO)₂(OSO)(μ_3 -OH) (μ_2 -OH/H₂O)(pbn)] trinuclear units (Fig. 1), with a Cu1···Cu2 distance of 2.968(2) Å, a Cu2···Cu3 distance of 3.438(2) Å, and a Cu3···Cu1 distance of 3.465(2) Å. A pbn-A ligand in a curled conformation wraps around the periphery of the trinuclear unit, joining Cu1 and Cu2 atoms. The Cu4 atoms display either a {CuO₅} or a {CuO₄N} square pyramidal coordination environment ($\tau = 0.18$) depending on disorder component, with the latter shown in Fig. 2. In either case the apical position is taken up by an oxygen atom (O22) that represents either a carboxylate oxygen donor from a nic ligand or a carbonyl C=O donor atom from a pbn-B ligand. In

the basal plane at Cu4 are located two trans carboxylate oxygen donor atoms, one belonging to a sip-A ligand and the other belonging to a sip-B ligand. A third basal plane position at Cu4 is filled by a bound water molecule. The fourth position at Cu4 is taken up by either a pyridyl nitrogen donor atom from a pbn-B ligand or a second carbonyl C=O donor atom from a pbn-B ligand, depending on specific disordered ligand orientation (Fig. 3). The sulfonate groups of the sip-B ligands do not ligate to copper. Bond lengths and angles within the disparate copper coordination environments are listed in Table 2.

Adjacent $[Cu_3(OCO)_2(OSO)(\mu_2-OH)(\mu_3-OH/H_2O)(pbn)]$ trinuclear units are connected to each other by the full span of the sip-A and sip-B ligands through pairs of isolated Cu4 atoms, thereby constructing $[Cu_8(sip)_4(pbn)_2(nic)(\mu_2-OH)_2(\mu_3-OH)(\mu_3-H_2O)(H_2O)_4]$ thick ribbon motifs (Fig. 4) aligned along the *ab* crystal plane. In one of the disorder components, nic ligands generated

 Table 2

 Selected bond distance (Å) and angle (°) data for 1.

Cu1-01	1.933(6)	016-Cu1-N6	94.8(3)
Cu1-015	1.987(6)	N6-Cu1-O23	92.6(3)
Cu1-016	1.929(6)	09-Cu2-05 ^{#1}	91.2(2)
Cu1-023	2.276(7)	09-Cu2-015	95.5(2)
Cu1-N6	2.006(7)	09-Cu2-N1	89.4(3)
Cu2-05#1	2.286(6)	015-Cu2-05#1	95.1(2)
Cu2-09	1.955(6)	015-Cu2-N1	155.1(3)
Cu2-015	2.004(6)	016-Cu2-05 ^{#1}	91.4(3)
Cu2-016	1.906(6)	016-Cu2-09	175.9(3)
Cu2-N1	2.026(7)	016-Cu2-015	81.2(2)
Cu3-02	1.928(6)	016-Cu2-N1	92.7(3)
Cu3-06 ^{#1}	2.359(7)	N1-Cu2-05#1	109.2(3)
Cu3-08	1.939(7)	02-Cu3-06#1	89.1(3)
Cu3-015	1.929(6)	02-Cu3-08	168.4(3)
Cu3-N10 ^{#2}	1.960(12)	02-Cu3-N10 ^{#2}	84.9(4)
Cu4-04	1.927(6)	08-Cu3-06 ^{#1}	98.7(3)
Cu4-011 ^{#3}	1.958(6)	08-Cu3-N10 ^{#2}	85.7(4)
Cu4-017	1.961(7)	015-Cu3-02	95.9(3)
Cu4-N7	2.01(4)	015-Cu3-06#1	93.2(2)
01-Cu1-015	96.0(2)	015-Cu3-08	92.3(3)
01-Cu1-023	98.2(3)	015-Cu3-N10 ^{#2}	170.6(5)
01-Cu1-N6	88.9(3)	N10 ^{#2} -Cu3-O6 ^{#1}	96.2(4)
015-Cu1-023	82.5(3)	04-Cu4-011 ^{#3}	177.5(3)
015-Cu1-N6	173.5(3)	04-Cu4-017	89.5(3)
016-Cu1-01	169.9(3)	04-Cu4-N7	88.2(6)
016-Cu1-015	81.1(2)	011 ^{#3} -Cu4-017	89.9(3)
016-Cu1-023	90.9(3)	011 ^{#3} -Cu4-N7	92.9(6)
		017-Cu4-N7	166.6(7)

Symmetry transformations: #1 x + 1, y, z. #2 -x, -y + 1, -z + 2. #3 x + 1, -y + 1, -z + 1.



Fig. 3. Disordered nic and pbn ligand components in 1.



Fig. 4. $[Cu_8(sip)_4(pbn)_2(nic)(\mu_2-OH)_2(\mu_3-OH)(\mu_3-H_2O)(H_2O)_4]$ thick ribbon motif in 1.



Fig. 5. $[Cu_8(sip)_4(pbn)_3(nic)(\mu_3-OH)_2(\mu_2-OH)(\mu_2-H_2O)(H_2O)_4]$ layer motif in 1.

in situ from amide hydrolysis of the pbn precursor bridge Cu3 and Cu4 atoms within the ribbon motif. In the other disorder component, exotetradentate pbn-B ligands conjoin Cu3 atoms and two Cu4 atoms within the ribbon, and another Cu4 atom within a neighboring ribbon motif. Thus, coordination polymer layer motifs with an overall stoichiometry of $[Cu_8(sip)_4(pbn)_3(nic)(\mu_3-OH)_2(\mu_2-$ OH)(μ_2 - H_2O)(H_2O)₄] are formed, and lay coincident with the *ac* crystal planes (Fig. 5). Hydrogen bonding pathways between the μ_2 -hydroxide/water molecule ligands within the trinuclear cluster units in one layer, and unligated sulfonate oxygen atoms in another, provide impetus for interlayer aggregation in an alternating ABAB fashion along the b axis (Fig. S1). Additional hydrogen bonding pathways involving pbn-A carbonyl groups, interlamellar water molecules of crystallization, and pbn-B carbonyl groups or nic carboxylate groups serve an ancillary structure directing role. Water molecules of crystallization are located in between the laver/ribbon motifs and occupy 3.5% of the unit cell volume according to PLATON [25].

4.3. Structural description of $\{[Cu_3(sip)_2(pbin)_4(H_2O)_4] \cdot 14H_2O\}_n$ (2)

The asymmetric unit of compound **2** contains a divalent copper atom on a general position (Cu1), a divalent copper atom on a crystallographic inversion center (Cu2), an sip ligand, two pbin ligands (pbin-A, pbin-B), two water molecules bound to Cu1, and net seven water molecules of crystallization located across multiple partially occupied positions. The Cu1 atom displays a slightly distorted {CuN₂O₃} square pyramidal coordination environment (τ = 0.05) with a bound water molecule filling the elongated apical position and one of the basal positions. Trans pyridyl nitrogen donor atoms from a pbin-A ligand and a pbin-B ligand occupy basal positions at Cu1, along with a carboxylate oxygen atom from an sip ligand. In contrast the Cu2 atoms display a square planar {CuN₂O₂} arrange-

Table 2				
Selected b	ond distance (A	Å) and	angle (°)	data for 2 .

Cu1-02	1.994(8)	016-Cu1-013	93.8(3)
Cu1-013	2.260(8)	O16-Cu1-N4 ^{#1}	88.0(4)
Cu1-016	1.996(9)	O16-Cu1-N5	93.3(3)
Cu1-N4 ^{#1}	2.019(9)	N4 ^{#1} -Cu1-O13	93.5(3)
Cu1-N5	2.013(9)	N5-Cu1-O13	93.3(3)
Cu2-04 ^{#2}	1.934(8)	N5-Cu1-N4 ^{#1}	173.0(4)
Cu2-04	1.934(8)	04 ^{#2} -Cu2-04	180.0
Cu2-N1	1.973(10)	04-Cu2-N1#2	89.8(4)
Cu2-N1#2	1.973(10)	04 ^{#2} -Cu2-N1 ^{#2}	90.2(4)
02-Cu1-013	95.4(3)	04-Cu2-N1	90.2(4)
02-Cu1-016	170.1(3)	04 ^{#2} -Cu2-N1	89.8(4)
02-Cu1-N4 ^{#1}	87.9(3)	N1 ^{#2} -Cu2-N1	180.0
02-Cu1-N5	89.7(3)		

Symmetry transformations: #1 - x, -y + 1, -z + 1; #2 - x, -y + 2, -z + 1.

ment with trans pyridyl nitrogen donor atoms from two pbin-A ligands, and trans carboxylate oxygen atoms from two sip ligands. Bond lengths and angles within the disparate coordination environments are listed in Table 3. A thermal ellipsoid plot of the coordination environments and ligand sets is depicted in Fig. 6.

Pairs of bis(monodentate) sip ligands connect Cu1 and Cu2 atoms at a distance of 9.49(2) Å to construct neutral linear trinuclear $\{Cu_3(sip)_2(H_2O)_4\}$ fragments (Fig. 7). The peripheral Cu1 atoms in one $\{Cu_3(sip)_2(H_2O)_4\}$ fragment are connected to central Cu2 atoms in a neighboring fragment by dipodal pbin-A ligands, which span a Cu···Cu distance of 5.88(1) Å. The central N–C–C–C torsion angles within the curled pbin-A ligands measure 63.0° and 93.2° indicating a gauche-gauche conformation. The pbin-B ligands, which also show a gauche-gauche conformation (N-C-C-C torsion angles = 72.1° and 73.4°), act only as monodentate donors to the Cu1 atom and dangle off of the sides of the $\{Cu_3(sip)_2(H_2O)_4\}$ fragments. The resulting 1D ribbon motifs (Fig. 8) have a stoichiometry of [Cu₃(sip)₂(pbin-A)₂(pbin-B)₂(H₂O)₄]_n, and are oriented parallel to the *b* crystal direction. Hydrogen bonding between the unligated pyridyl nitrogen atoms of the pbin-B ligands and water molecules bound to the Cu2 atoms (Table S1) serves an ancillary stabilization role within the ribbon motif, along with hydrogen bonding donation from the bound water molecules to pbin carbonyl oxygen atoms. Adjacent ribbon motifs aggregate by means of hydrogen bonding between the pbin N-H moieties and the sulfonate oxygen atoms belonging to the sip ligands, and also between other pbin N-H groups and the carbonyl groups within pbin ligands in other ribbons (Fig. S2). The disordered water molecules of crystallization in 2 occupy incipient voids between the ribbon motifs comprising 16.2% of the unit cell volume.

4.4. Structural description of $\{[Cu_4(\mu_3-OH)_2(sip)_2(hbin)]\cdot H_2O\}_n$ (3)

The asymmetric unit of compound 3 contains divalent copper atoms (Cu1, Cu2), a bridging hydroxide ion, a fully deprotonated sip ligand, half of an hbin ligand whose central C–C σ bond is located over a crystallographic inversion center, and a water molecule of crystallization refined best at half-occupancy. The Cu1 atom displays a {CuO₅} square pyramidal coordination geometry (τ = 0.07) with the elongated apical position filled by a sip sulfonate oxygen atom. Its basal plane contains two cis-disposed bridging hydroxide ions and carboxylate oxygen atoms from two different sip ligands also in cis positions. The Cu2 atom displays a much more distorted {CuNO₄} square pyramidal coordination geometry $(\tau = 0.41)$, also with a sip sulfonate oxygen atom in its apical site. In its basal plane, a pyridyl nitrogen donor atom from an hbin ligand and a bridging hydroxide ion occupy two trans positions, while carboxylate oxygen atoms from two different sip ligands occupy the other two trans positions. Bond lengths and angles



Fig. 6. Coordination environments in 2. Thermal ellipsoids are drawn at 50% probability.



Fig. 7. Linear trinuclear {Cu₃(sip)₂(H₂O)₄} fragment in 2.



Fig. 8. [Cu₃(sip)₂(pbin)₄(H₂O)₄]_n ribbon motif in **2**, showing bridging pbin-A ligands and dangling pbin-B ligands.

within the two different coordination environments in **3** are listed in Table 4, while a thermal ellipsoid plot showing the complete ligand set is shown in Fig. 9a.

Carboxylate and sulfonate termini belonging to sip ligands and the bridging hydroxide ions create $[Cu_4(\mu_3-OH)_2(OCO)_4(OSO)_2]$ "butterfly" tetranuclear clusters, as shown in Fig. 9b. Within the cluster, carboxylate groups from four sip ligands bridge Cu1 and Cu2 atoms via their basal plane positions, while two sip sulfonate

Selected bond distance (Å) and angle (°) data for ${f 3}$	j.,
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Cu1-01 ^{#1}	1.970(3)	02-Cu1-05#2	90.41(13)
Cu1-01	1.989(3)	02-Cu1-08	95.88(12)
Cu1-02	1.923(3)	05#2-Cu1-01	175.13(13)
Cu1-05 ^{#2}	1.950(3)	05 ^{#2} -Cu1-01 ^{#1}	96.06(12)
Cu1-08 ^{#3}	2.403(3)	05 ^{#2} -Cu1-08	82.21(12)
Cu2-01	1.948(3)	01-Cu2-O3	92.38(13)
Cu2-03	1.985(3)	01-Cu2-O4 ^{#4}	92.41(12)
Cu2-04#4	1.958(3)	01-Cu2-07#3	85.09(12)
Cu2-07#3	2.302(3)	01-Cu2-N1	175.21(15)
Cu2-N1	1.985(4)	03-Cu2-07#3	113.15(12)
01 ^{#1} -Cu1-O1	81.34(13)	03-Cu2-N1	91.01(14)
01-Cu1-08	101.89(12)	04 ^{#4} -Cu2-O3	150.37(13)
01 ^{#1} -Cu1-08	90.91(12)	04 ^{#4} -Cu2-07 ^{#3}	96.39(12)
02-Cu1-01#1	171.20(13)	04#4-Cu2-N1	86.30(14)
02-Cu1-01	91.76(13)	N1-Cu2-07#3	90.46(14)

Symmetry transformations: #1 - x + 1, -y + 2, -z + 1; #2 x + 1/2, -y + 3/2, z + 1/2; #3 - x, -y + 2, -z + 1; #4 - x + 1/2, y + 1/2, -z + 1/2.

groups bridge Cu1 and Cu2 atoms via apical positions and triply bridging hydroxide ions connect basal plane positions of two Cu1 atoms and a single Cu2 atom. The relevant internuclear distances between copper atoms within the tetranuclear clusters are as follows: 3.003(1)Å between hydroxide-bridged Cu1 atoms, and 3.279(2) and 3.272(1)Å between carboxylate-bridged and sulfonate-bridged Cu1 and Cu2 atoms.

Each sip ligand in **3** adopts an exohexadentate μ_6 - κ^6 -0:0':0": O"':O""':O""' binding mode, bridging two copper ions within three different $[Cu_4(\mu_3-OH)_2(OCO)_4(OSO)_2]$ clusters, and thereby forms a neutral 3D $[Cu_4(\mu-OH)_2(sip)_2]$ coordination polymer network (Fig. 10a). Treating the sip ligands as 3-connected nodes and the tetranuclear clusters as 6-connected nodes reveals a 3,6-connected binodal net with rtl (4.6²)₂(4²6¹⁰8³) rutile topology (Fig. 10b) according to a calculation with TOPOS [26]. Each $[Cu_4(\mu_3-OH)_2]$ $(OCO)_4(OSO)_2$ cluster connects to two others by means of pillaring hbin ligands that span a Cu2...Cu2 distance of 20.440(5) Å. The central hexamethylene tethers within the hbin ligands show an anti-anti conformation (C–C–C torsion angles = 177.7°, 180°, 177.7°). Including the hbin connections results in a 3D $[Cu_4(\mu-OH)_2(sip)_2(hbin)]_n$ coordination polymer net (Fig. 11). Now with the tetranuclear clusters acting as 8-connected nodes, the resulting 3,8-connected network possesses a unique $(4.6^2)_2(4^26^{18}7^{4}8^4)$ topology (Fig. 12). The water molecules of crystallization in 3 occupy incipient pockets comprising 9.5% of the unit cell volume.



Fig. 9. a) Coordination environments in 3. Thermal ellipsoids are drawn at 50% probability. b) [Cu₄(µ₃-OH)₂(OCO)₄(OSO)₂] "butterfly" cluster in 3.



Fig. 10. a) Neutral 3D $[Cu_4(\mu-OH)_2(sip)_2]$ coordination polymer network in 3. b) 3,6-connected binodal net with rtl $(4.6^2)_2(4^{26}1^{0}8^3)$ topology in 3.

4.5. Structural description of $\{[Cu(Hsip)(hbn)(H_2O)] \cdot 2H_2O\}_n$ (4)

The asymmetric unit of compound **4** contains a divalent copper atom, a Hsip ligand protonated at one of its carboxylate groups, an hbn ligand, a bound water molecule and two water molecules of crystallization. The copper atom displays a highly distorted {CuN₂-O₃} square pyramidal coordination environment ($\tau = 0.37$, Fig. 13), with the elongated apical position filled by a sulfonate oxygen atom donor of a Hsip ligand. Its basal plane contains trans pyridyl nitrogen donor atoms from two hbn ligands along with a carboxylate oxygen atom from another Hsip ligand and the bound water molecule. Bond lengths and angles within the coordination sphere are listed in Table 5.

Adjacent copper atoms are bridged by bis(monodentate) Hsip ligands, which connect to the metal ions through their deprotonated carboxylate and sulfonate groups, thereby forming [Cu (Hsip)(H₂O)]_n coordination polymer chain motifs arranged parallel to the *a* crystal direction. The Cu \cdots Cu through ligand distance is

9.2962(12) Å, which represents the *a* lattice parameter. The protonated Hsip carboxylate group does not bind to copper. [Cu(Hsip) $(H_2O)]_n$ chains are pillared into sinusoidal $[Cu(Hsip)(hbn)(H_2O)]_n$ layer motifs (Fig. 14) by hbn ligands that show an anti-anti-anti conformation of their central hexamethylene tethers (torsion angles = 172.0°, 177.3°, 176.9°) and bridge a Cu…Cu distance of 18.91(4) Å. The overall topology of the layer motif is that of a 4connected (4,4) grid, in contrast to the 3,4-connected topology seen in $\{[Cu_3(sip)_2(hbn)_3(H_2O)_4] \cdot 11.5H_2O\}_n$ [15]. Additionally, the layer motifs in 4 simply interdigitate as they stack along the c crystal direction (Fig. S3) as opposed to the more complicated 2D + 2D \rightarrow 3D parallel interpenetration of $(4.6^2)_2(4^26^28^2)$ topology layers observed in $\{[Cu_3(sip)_2(hbn)_3(H_2O)_4] \cdot 11.5H_2O\}_n$ [15]. The co-crystallized water molecules in 4 occupy 3.0% of the unit cell volume and play a key role in interlayer aggregation via hydrogen bonding acceptance (Table S1) from protonated Hsip carboxylate groups and hbn N-H groups, and hydrogen bonding donation to hbn C=O carbonyl groups.



Fig. 11. 3D $[Cu_4(\mu-OH)_2(sip)_2(hbin)]_n$ full coordination polymer net in **3**.



Fig. 12. 3,8-Connected network with unique $(4.6^2)_2(4^26^{18}7^48^4)$ topology in **3**. The green and blue spheres represent the 8-connected tetramers and 3-connected sip ligand nodes, respectively. The red and blue rods represent connections mediated by the sip and hbin ligands, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4.6. Thermal properties of 1-4

Compound **1** underwent dehydration between 25 and 60 °C, with a 3.9% mass loss corresponding to elimination of five molar equivalents of co-crystallized water (3.4% calc'd). An additional mass loss of 5.8% between 60 and 125 °C corresponded to elimination of the bridging water molecules/hydroxide ions (2.7% calc'd) along with elimination of SO₃ (3.0% calc'd). Ligand combustion occurred above 245 °C. Compound **2** underwent elimination of its co-crystallized water in a multi-step process between

20 and 115 °C, as evidenced by a mass of 12.7% with the calculated value for 14 molar equivalents of water being 11.8%. The total mass loss of 15.2% between 20 and 265 °C matches the exact value predicted for ejection of all bound and free water molecules in **2**. Ligand combustion occurred above 265 °C. Compound **3** underwent elimination of its co-crystallized water and bridging hydroxide ions between 25 and 55 °C, with a mass loss of 4.6% corresponding closely with the expected value of 4.8%. Ligand combustion occurred above 255 °C. Compound **4** underwent dehydration between 25 and 260 °C, with a 5.6% mass loss



Fig. 13. Coordination environment in 4. Thermal ellipsoids are drawn at 50% probability.

Table 5 Selected bond distance (Å) and angle (°) data for 4.

Cu1-01	1.927(4)	01-Cu1-N4#2	90.9(3)
Cu1-07 ^{#1}	2.163(4)	08-Cu1-07 ^{#1}	85.74(17)
Cu1-08	1.986(4)	08-Cu1-N1	88.1(3)
Cu1-N1	2.003(7)	08-Cu1-N4 ^{#2}	89.7(3)
Cu1-N4#2	2.019(7)	N1-Cu1-07#1	101.6(3)
01-Cu1-07	90.74(17)	N1-Cu1-N4 ^{#2}	154.0(2)
01-Cu1-08	176.48(18)	N4-Cu1-07#1	104.0(3)
01-Cu1-N1	92.8(3)		

Symmetry transformations: #1 x - 1, y, z; #2 -x + 1, y - 1/2, -z.

corresponding to the predicted value of 5.2% for two molar equivalents of water. Ligand combustion occurred above 260 °C. TGA traces for **1–4** are shown in Figs. S4–S7.

4.7. Magnetic properties of 1 and 3

The variable temperature magnetic properties of compounds **1** and **3** were probed in order to investigate possible magnetic superexchange within the $[Cu_3(OCO)_2(OSO)(\mu_2-OH)(\mu_3-OH/H_2O)$ (pbn)] trinuclear units in **1** and within the $[Cu_4(\mu_3-OH)_2(OCO)_4$ (OSO)₂] tetrameric clusters in **3**. For compound **1**, the $\chi_m T \text{ vs } T$ plot (Fig. 15) shows a $\chi_m T$ value of 2.94 cm³-K mol⁻¹ at 300 K, consistent with the idealized value for eight uncoupled S = 1/2 spins (3.00 cm³-K mol⁻¹) in the formula unit. The $\chi_m T$ value then decreased to 2.69 cm³-K mol⁻¹ upon cooling to 50 K, and then to 2.10 cm³-K mol⁻¹ at 15 K, with a final value of 0.98 cm³-K mol⁻¹ at 2 K. The shape of the $\chi_m T$ vs T curve for **1** portends some level of antiferromagnetic coupling within the trimer units, although total spin cancellation is not possible due to the spin frustration



Fig. 14. $[Cu(Hsip)(hbn)(H_2O)]_n$ layer motif in 4.



Fig. 15. Variable temperature magnetic susceptibility plot for **1**. The best fit to Eq. (1) is shown as a thin line.



Fig. 16. Variable temperature magnetic susceptibility plot for **3**. The best fit to Eq. (2) is shown as a thin line.

inherent in a trimeric unit. The best fit to Eq. (1) [10] for a pair of trimeric units and two isolated divalent copper atoms reveals g = 2.079(6) and J = -5.7(2) cm⁻¹ with $R = \{\sum [(\chi_m T)_{obs} - (\chi_m T)_{calc}]^2\}^{1/2} = 7.81 \times 10^{-3}$. The sign and magnitude of the *J* value corroborate the presence of weak antiferromagnetic coupling within the trimeric cluster units of **1**.

$$\chi_m T = \frac{Ng^2 \beta^2}{3k} \left(\frac{A}{B}\right) + \frac{2Ng^2 \beta^2}{3k} \tag{1}$$

where $A = 15 \exp(J/kT) + 1.5 \exp(-2J/kT) + 1.5$ and $B = 4 \exp(J/kT) + 2 \exp(-2J/kT) + 2$

For compound **3**, the $\chi_m T$ vs *T* plot (Fig. 16) shows a $\chi_m T$ value of 1.69 cm³-K mol⁻¹ at 300 K, roughly consistent with the idealized value for four uncoupled S = 1/2 spins (1.50 cm³-K mol⁻¹) in the formula unit. The $\chi_m T$ product decreased more rapidly than seen in **1**, with values of 1.31 cm³-K mol⁻¹ at 150 K, 0.90 cm³-K mol⁻¹ at 70 K, 0.57 cm³-K mol⁻¹ at 25 K, and 0.25 cm³-K mol⁻¹ at 2 K. The best fit to Eq. (2) [10] gave g = 2.14(2), $J_1 = -19(1)$ cm⁻¹,

 $J_2 = -35(2) \text{ cm}^{-1}$ with $R = 9.34 \times 10^{-3}$, indicating moderately strong antiferromagnetic coupling within the tetrameric cluster units. The J_1 exchange integral marks superexchange mediated by the carboxylate bridges, while the J_2 exchange integral denotes superexchange mediated by the hydroxyl groups.

$$\chi_m T = \frac{Ng^2 \beta^2}{3k} \left(\frac{A}{B}\right) \tag{2}$$

where $A = 30 \exp((2J_1 + 0.5J_2)/kT) + 6 \exp((-2J_1 + 0.5J_2)/kT) + 6 \exp((0.5J_2/kT) + 6 \exp(-1.5J_2/kT))$ and $B = 5 \exp((2J_1 + 0.5J_2)/kT) + 3 \exp((-2J_1 + 0.5J_2)/kT) + \exp((-4J_1 + 0.5J_2)/kT) + 3 \exp(0.5J_2/kT) + 4 \exp(-1.5J_2/kT)$

5. Conclusions

A wide variety of structural diversity has been achieved in a series of copper 5-sulfoisophthalate coordination polymers featuring conformationally flexible dipyridylamide ligands. In the cases of the shorter tethering ligands pbn and pbin, slab and ribbon motifs were observed, respectively. The slab motifs in the pbn containing phase **1** were generated by wide ribbon motifs linked through crystallographically disordered dipyridylamide coligands. The ribbon motifs in the pbin containing phase **2** propagate by means of curled conformation pbin ligands that prevent connection into higher dimensionality. In the cases of the longer tethering ligands hbin and hbn, a novel 3D cage and common layer topologies were observed, respectively. The protonation of the sip ligands in **4** prevent aggregation into higher dimensionality. Compounds **1** and **3** contained ligand-bridged multi-nuclear copper ion aggregations that revealed antiferromagnetic behavior.

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Appendix A. Supplementary data

Additional molecular graphics and thermogravimetric analysis plots. Crystallographic data (excluding structure factors) for **1–4** have been deposited with the Cambridge Crystallographic Data Centre with Nos. 1577133, 1577134, 1577135, and 1577136, respectively. Copies of the data can be obtained free of charge via the Internet at <<u>https://summary.ccdc.cam.ac.uk/structure-summary-form</u>>. Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.ica. 2017.11.062.

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