Electronic Supplementary Material (ESI) for Dalton Transactions.

ELECTRONIC SUPPORTING INFORMATION (ESI)

for

A Stable Thiolato-Cu^{I}-Thiolato Triple Linkage That Bridges Two Cobalt(III) Centres

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General methods.

Λ-*fac*-$Na_3[Co(\text{D-pen})_3]\cdot 10H_2O$ was prepared according to a previously reported method.[S1] The IR spectra were measured with a JASCO FT/IR-4100 infrared spectrophotometer using KBr disks. The absorption spectra were measured with a JASCO V-660, V-670 spectrometer, and the CD spectra were measured with a JASCO J-820 spectropolarimeter at room temperature. Diffuse reflectance spectra were recorded with a JASCO V-570 UV/VIS/NIR spectrometer at room temperature. The ^1H NMR spectra were measured on JEOL RESONANCE ECS-400 and JEOL RESONANCE ECA-500 NMR spectrometers at room temperature in D_2O. Sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as the internal reference. Elemental analyses (C, H, N) were performed at Osaka University using a YANACO MT-5 instrument. The X-ray fluorescence analyses were conducted using a SHIMADZU Rayny EDX-720 spectrometer. The sorption isotherms of H_2, O_2 and CO_2 were measured with a BELSORP-mini II volumetric adsorption instrument. High-purity H_2, O_2 and CO_2 gases (99.9999%) were used. The obtained crystals of Na_3[**1**] and **2** were heated at 120°C or 90°C for 2 h under a reduced pressure before gas sorption measurements, respectively. The powder X-ray diffraction measurement of Na_3[**1**] was recorded at room temperature with a Bruker D2 PHASER instrument. The single-crystal X-ray diffraction measurement for Na[**1**] was performed on a RIGAKU FR-E Superbright rotating-anode X-ray source with a Mo target (λ = 0.71075 Å) equipped with a Rigaku RAXIS VII imaging plate as a detector at 200 K. The intensity data were collected by the ω-scan technique and empirically corrected for adsorption. The single-crystal synchrotron radiation X-ray diffraction measurement for **2** was carried out on BL02B1 at SPring-8 with a Rigaku Mercury 2 CCD detector. The structures of the complexes were solved by direct methods using SHELXS-2014.[S2] Structural refinements were carried out using the full matrix least-squares method (SHELXL-2014).[S2] Hydrogen atoms were placed at calculated positions. All of the structural parameters are summarized in Table S1. The calculation of **2** was carried out using intensity data corrected by SQUEEZE. The void space should be filled by the solvated water molecules and a part of $[Cr^{III}(H_2O)_6]^{3+}$ ions based on the elemental, fluorescence X-ray, and thermogravimetric analyses. However, they are severely disordered and only several solvated water molecules and a part of $[Cr^{III}(H_2O)_6]^{3+}$ ions could be modeled in the void space. After all the solvated water molecules were removed from the model, the crystal data were treated by the SQUEEZE in the PLATON package.

References.

S1. K. Okamoto, T. Yonemura, T. Konno and J. Hidaka, *Bull. Chem, Soc. Jpn.,* 1992, **65**, 794.

S2. G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.

Preparation of the complexes.

Preparation of ΛΛ-$Na_3[Co_2Cu_3(\text{D-pen})_6]$ ($Na_3[\mathbf{1}]$).

CuCl (0.02 g, 0.20 mmol) was added to a green solution containing 0.10 g (0.13 mmol) of Λ-*fac*-$Na_3[Co(\text{D-pen})_3]\cdot 10H_2O$ in 20 mL of water. The mixture was stirred at room temperature for 1.5 h. After removal of unreacted CuCl by filtration, the filtrate was evaporated to dryness. The dark-purple residue was dissolved in an aqueous NaCl solution (1.0 M, 3.0 mL) to give a dark-purple solution. Ethanol vapour was diffused in this solution at room temperature for several days, which gave dark-purple platelet crystals ($Na_3[\mathbf{1}]$) suitable for single-crystal X-ray analysis. Yield: 76 mg (74%). Anal. Calcd for $Na_3[Co_2Cu_3(\text{D-pen})_6]\cdot 6H_2O$ = $C_{30}H_{66}Na_3Co_2Cu_3N_6O_{18}S_6$: C, 26.33; H, 4.86; N, 6.14%. Found: C, 26.41; H, 4.97; N, 5.93%.

Preparation of ΛΛ-$[Cr(H_2O)_6][Co_2Cu_3(\text{D-pen})_6]$ (2).

A dark purple solution containing 0.20 g (0.14 mmol) of $Na_3[\mathbf{1}]$ in 20 mL of water was layered under a blue solution containing 0.05 g (0.14 mmol) of $Cr(NO_3)_3\cdot 9H_2O$ in H_2O/EtOH (18 mL/2 mL). The layered solution was allowed to stand at room temperature for several days, which gave dark-blue-purple platelet crystals (**2**) suitable for single-crystal X-ray analysis. The crystals were collected by filtration and washed with water. Yield: 161 mg (82%). Anal. Calcd for $[Cr(H_2O)_6][Co_2Cu_3(\text{D-pen})_6]\cdot 6.5H_2O$ = $C_{30}H_{79}Co_2CrCu_3N_6O_{24.5}S_6$: C, 24.53; H, 5.42; N, 5.72%. Found: C, 24.47; H, 5.30; N, 5.70%.

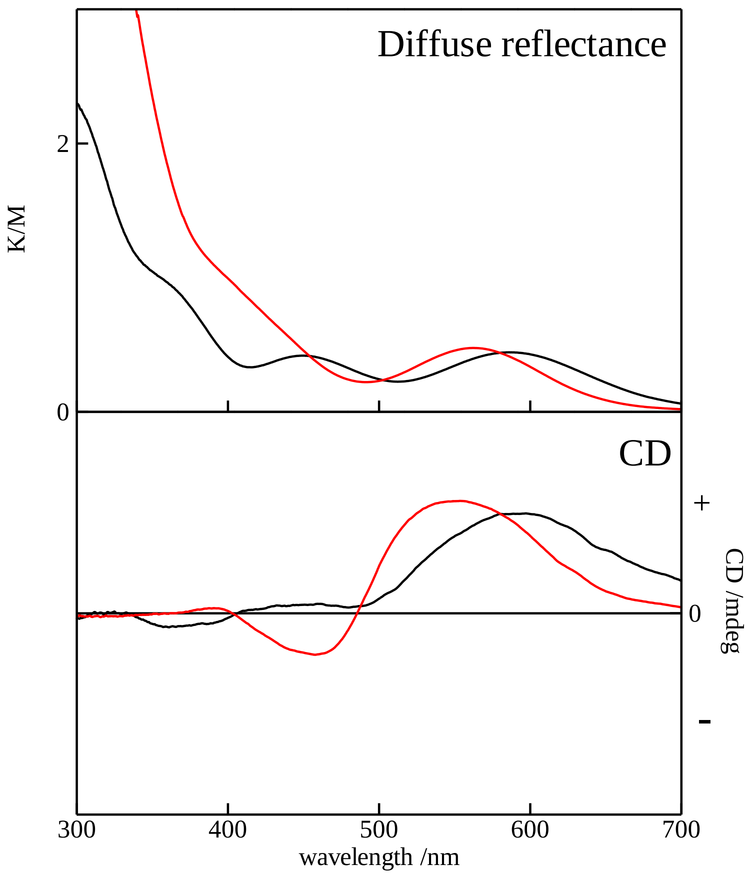


Figure S1. Diffuse reflectance and CD spectra of Λ-*fac*-Na_3[Co(D-pen-*N*,*S*)$_3$] (black) and Na_3[**1**] (red) in the solid state.

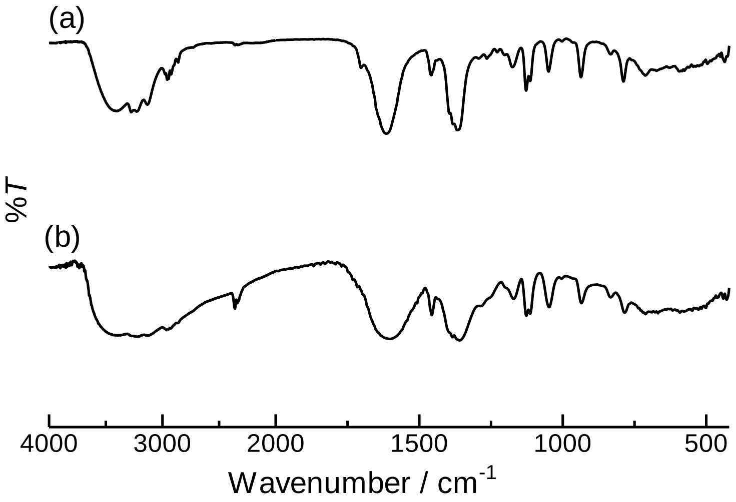


Figure S2. IR spectra of (a) Na_3[**1**] and (b) **2**.

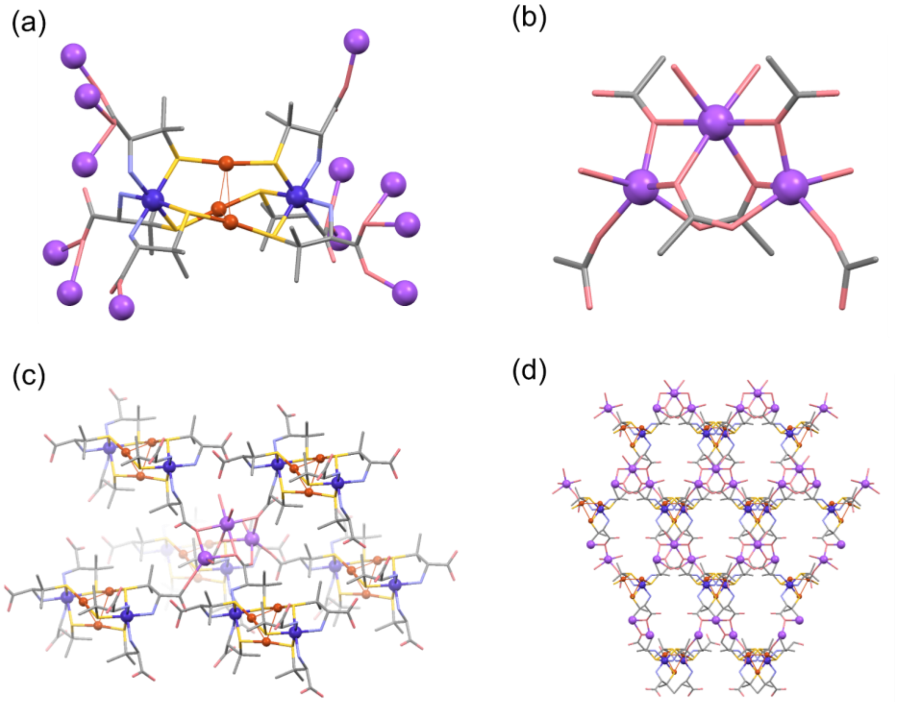


Figure S3. Perspective views of (a) the connectivity between $[\mathbf{1}]^{3-}$ and the Na^+ ions, (b) the $\{Na_3(H_2O)_4\}^{3+}$ cluster bound by six carboxylate groups, (c) the $\{Na_3(H_2O)_4\}^{3+}$ cluster surrounded by six $[\mathbf{1}]^{3-}$ anions, and (d) one sheet of the 3D coordination network in $Na_3[\mathbf{1}]$. Atom colours: grey = C, blue = N, red = O, purple = Na, yellow = S, navy = Co and orange = Cu.

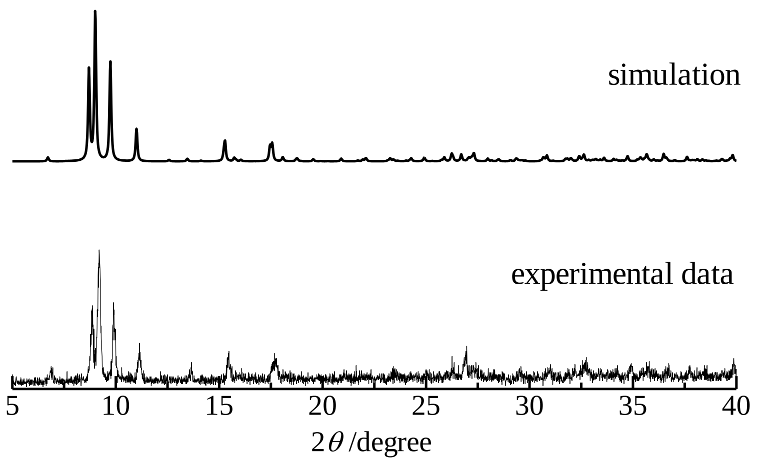


Figure S4. Powder X-ray diffraction patterns of Na_3[**1**].

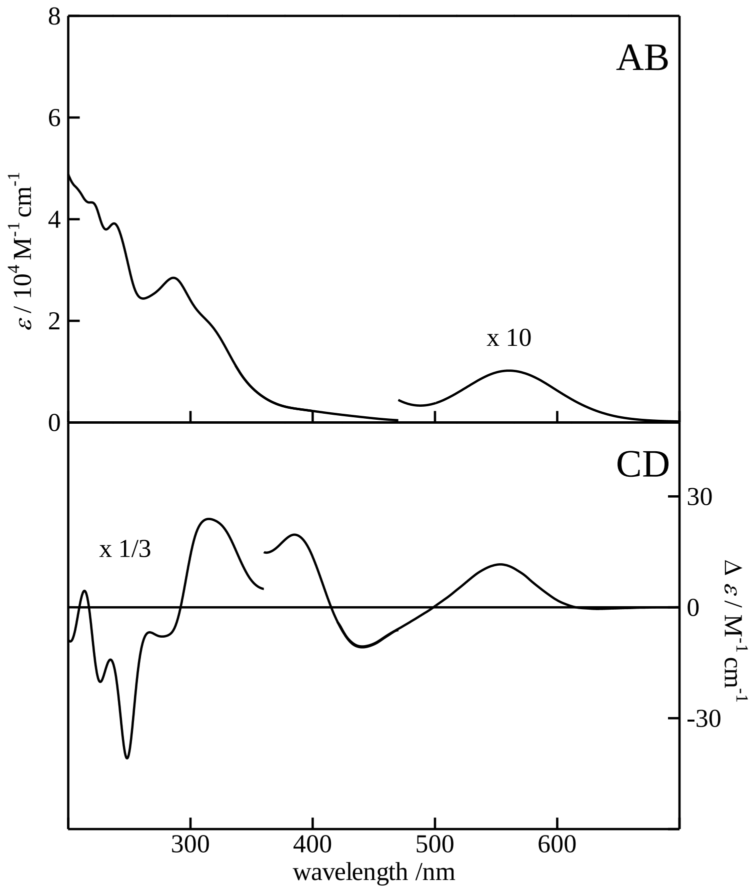


Figure S5. Absorption and CD spectra of Na_3[**1**] in H_2O.

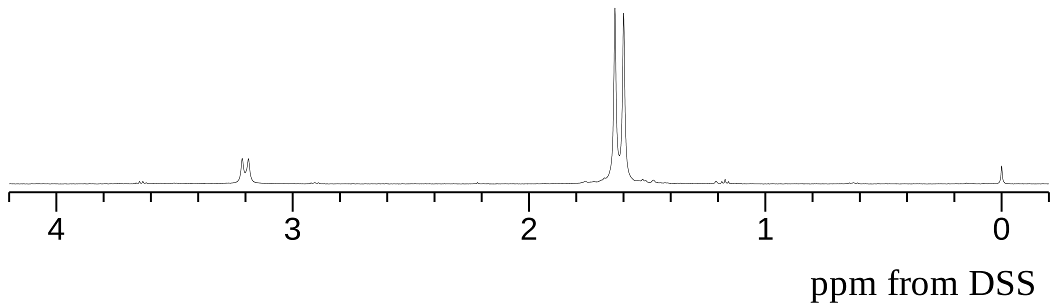


Figure S6. ^{1}H NMR spectrum of Na$_3$[**1**] in D$_2$O.

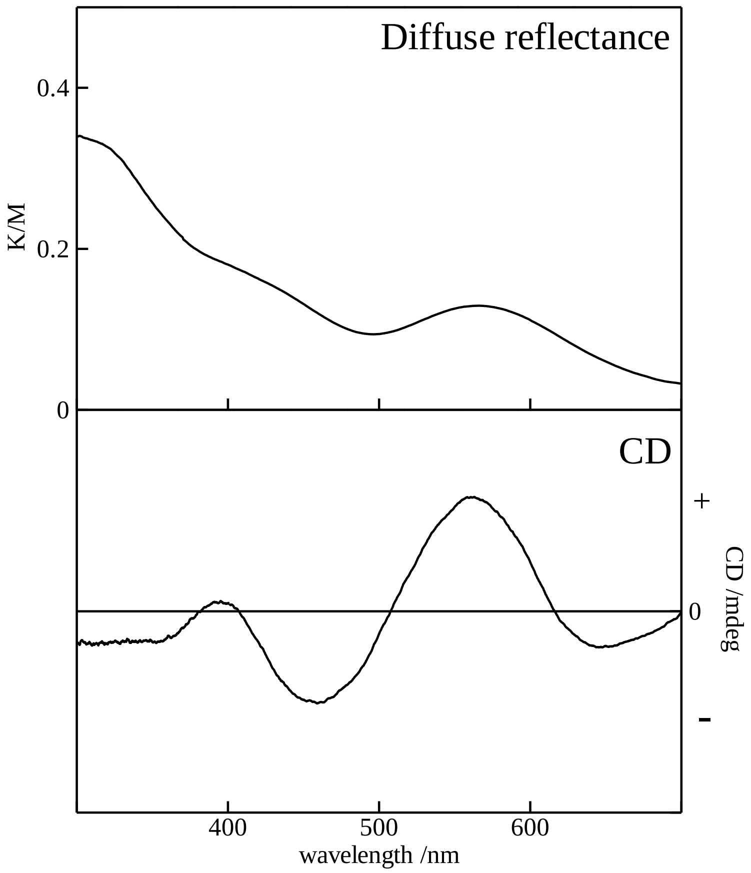
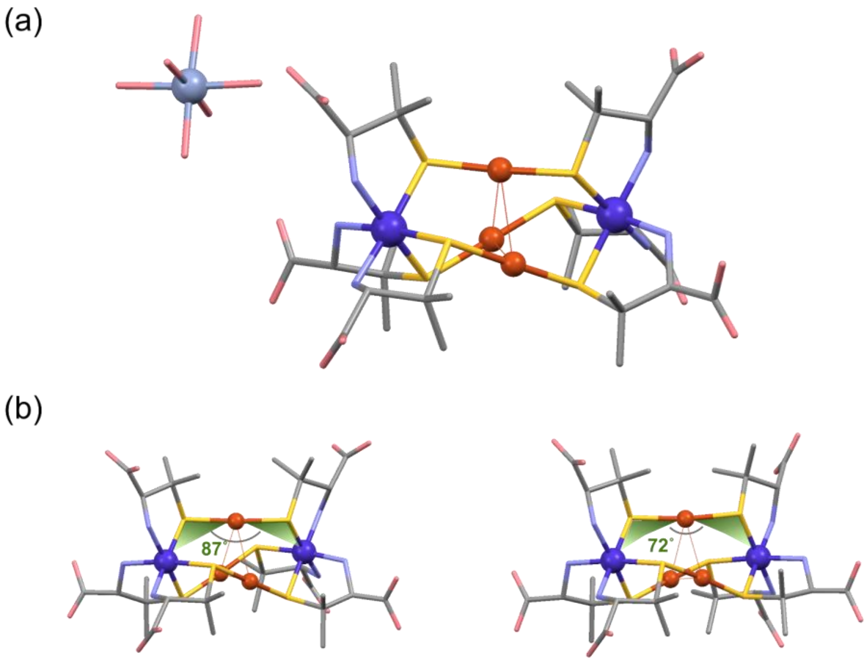


Figure S7. Diffuse reflectance and CD spectra of **2** in the solid state.



2

Na$_3$[**1**]

Figure S8. (a) Molecular structure of **2**. (b) Torsion angles between the two Λ-*fac*-[Co(D-pen-*N*,*S*)$_3$]$^{3-}$ units in **2** (left) and Na$_3$[**1**] (right). Atom colours: grey = C, blue = N, red = O, purple = Na, yellow = S, navy = Co, orange = Cu and pale blue = Cr.

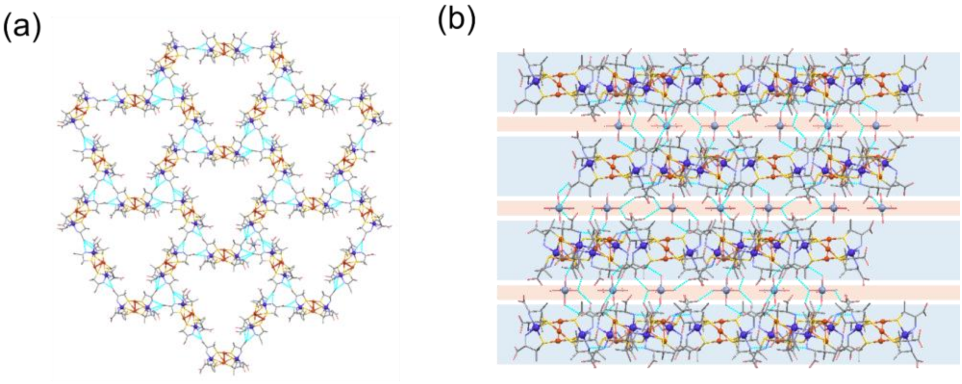


Figure S9. Perspective views of (a) the hexagonal sheet and (b) hexagonal sheets linked by $[Cr(H_2O)_6]^{3+}$ ions in **2**. Blue dashed lines represent hydrogen bonds. Atom colours: grey = C, blue = N, red = O, purple = Na, yellow = S, navy = Co, orange = Cu and pale blue = Cr.

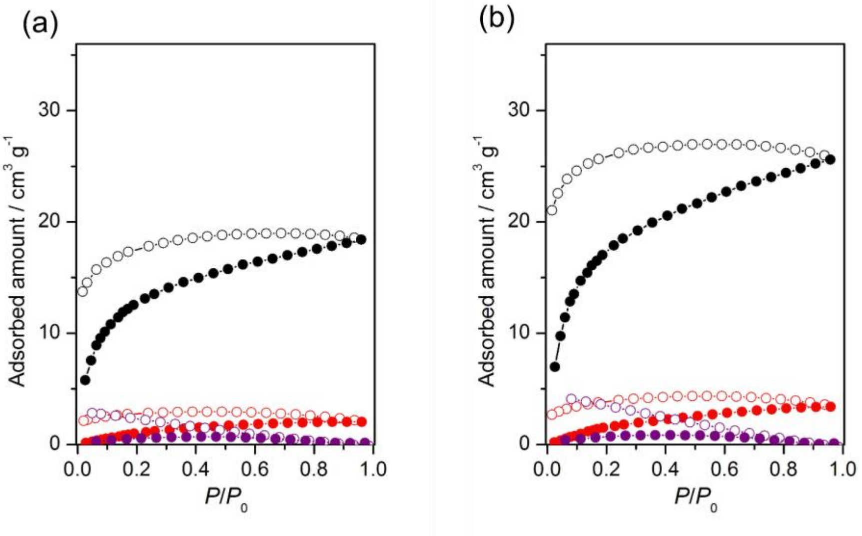


Figure S10. Comparison of the CO_2 (black), O_2 (red) and H_2 (purple) adsorption isotherms of (a) Na_3[**1**] and (b) **2**. The CO_2 and O_2 adsorption measurements were performed at 195 K, and the H_2 adsorption measurements were performed at 77 K.

Table S1. Crystallographic data for Na_3[**1**] and **2**.

	Na_3[**1**]	**2**
Formula	$C_{34}H_{84}Co_2Cu_3N_6Na_3O_{23}S_6$	$C_{30}H_{67}Co_2Cr_{0.33}Cu_3N_6O_{20.5}S_6$
Colour, shape	Dark purple, plate	Dark blue-purple, plate
M	1514.88	1358.07
Crystal system	Monoclinic	Trigonal
Space group	$C2$	$R32$
a /Å	11.7354(7)	24.812(5)
b /Å	20.308(3)	24.812(5)
c /Å	13.771(3)	67.434(7)
β /°	107.289(11)	
V /Å^3	3133.7(8)	35952(16)
Z	2	18
T /K	200(2)	100(2)
$F(000)$	1568	12564
ρ_{calcd} /g cm^{-3}	1.605	1.129
μ(Mo Kα) /mm^{-1}	1.813	1.334
Crystal size /mm^3	0.10 × 0.10 × 0.02	0.10 × 0.08 × 0.03
Limiting indices	$-15 \leq h \leq 15$	$-32 \leq h \leq 32$
	$-24 \leq k \leq 26$	$-31 \leq k \leq 32$
	$-17 \leq l \leq 17$	$-87 \leq l \leq 87$
R_1[a] ($I > 2\sigma(I)$)	0.0507	0.0760
wR_2[b] (all data)	0.0795	0.2217
GOF	1.035	0.834
Flack parameter	0.053(9)	0.032(16)
CCDC number	1581365	1581366

[a] $R_1 = \Sigma |(|Fo| - |Fc|)| / \Sigma (|Fo|)$.

[b] $wR_2 = [\Sigma w(Fo^2 - Fc^2)^2 / \Sigma w (Fo^2)^2]^{1/2}$.

Table S2. Selected bond distances (Å) and angles (˚) for Na$_3$[**1**] and **2**.

Na$_3$[**1**]

Distances (Å)

Cu(1)-S(1)	2.1722(17)	Co(1)-S(1)	2.2634(17)
Cu(1)-S(2)	2.1701(16)	Co(1)-S(2)	2.2498(17)
Cu(1)-Cu(2)	2.7033(12)	Na(1)-O(2)	2.220(5)
Cu(1)-Cu(1)	2.7140(14)	Na(1)-O(4)	2.537(5)
Cu(2)-S(3)	2.1474(16)	Na(1)-O(6)	2.569(5)
Cu(2)-Cu(1)	2.7033(12)	Na(2)-O(6)	2.209(5)
Co(1)-N(1)	1.979(4)	Na(2)-O(3)	2.343(5)
Co(1)-N(2)	2.009(5)	Na(2)-O(4)	2.340(5)
Co(1)-N(3)	1.999(5)	Na(2)-O(1)	2.433(6)
Co(1)-S(3)	2.2641(17)		

Angles (˚)

S(1)-Cu(1)-S(2)	172.88(7)	S(2)-Co(1)-S(1)	93.49(6)
S(3)-Cu(2)-S(3)	172.31(10)	N(1)-Co(1)-S(3)	89.59(18)
N(1)-Co(1)-N(3)	90.1(2)	N(3)-Co(1)-S(3)	85.09(14)
N(1)-Co(1)-N(2)	92.8(2)	N(2)-Co(1)-S(3)	179.97(14)
N(3)-Co(1)-N(2)	89.38(18)	S(2)-Co(1)-S(3)	92.56(6)
N(1)-Co(1)-S(2)	177.27(16)	S(1)-Co(1)-S(3)	91.77(6)
N(3)-Co(1)-S(2)	91.74(14)	Cu(1)-S(1)-Co(1)	107.96(7)
N(2)-Co(1)-S(2)	85.18(15)	Cu(1)-S(2)-Co(1)	110.14(7)
N(1)-Co(1)-S(1)	84.76(15)	Cu(2)-S(3)-Co(1)	108.58(7)
N(3)-Co(1)-S(1)	174.02(15)	Na(2)-O(4)-Na(1)	82.62(14)
N(2)-Co(1)-S(1)	93.94(14)	Na(2)-O(6)-Na(1)	84.45(17)

2

Distances (Å)

Cu(1)-S(1)	2.151(4)	Cu(1)-Cu(3)	2.664(3)
Cu(1)-S(4)	2.125(4)	Cu(2)-Cu(3)	2.641(3)
Cu(2)-S(5)	2.143(4)	Co(1)-N(2)	1.952(11)
Cu(2)-S(2)	2.152(4)	Co(1)-N(3)	1.990(11)
Cu(3)-S(6)	2.132(4)	Co(1)-N(1)	1.952(11)
Cu(3)-S(3)	2.162(4)	Co(1)-S(2)	2.230(4)
Cu(1)-Cu(2)	2.666(3)	Co(1)-S(3)	2.229(4)

Co(1)-S(1)	2.263(4)	Co(2)-S(4)	2.242(5)
Co(2)-N(5)	1.902(13)	Co(2)-S(5)	2.261(5)
Co(2)-N(6)	1.973(13)	Cr(1)-O(1 W)	1.966(9)
Co(2)-N(4)	2.011(11)	Cr(1)-O(2 W)	2.006(10)
Co(2)-S(6)	2.237(4)		
Angles (˚)			
S(4)-Cu(1)-S(1)	176.49(19)	S(2)-Co(1)-S(3)	91.26(16)
S(5) -Cu(2)-S(2)	179.5(2)	S(2)-Co(1)-S(1)	92.16(15)
S(6) -Cu(3)-S(3)	176.91(19)	S(3)-Co(1)-S(1)	93.71(16)
Cu(2)-Cu(1)-Cu(3)	59.42(7)	N(5)-Co(2)-N(6)	89.7(5)
Cu(3)-Cu(2)-Cu(1)	60.25(7)	N(5)-Co(2)-N(4)	91.2(5)
Cu(2)-Cu(3)-Cu(1)	60.33(7)	N(6)-Co(2)-N(4)	89.5(5)
N(2)-Co(1)-N(3)	90.5(5)	N(5)-Co(2)-S(6)	91.3(4)
N(2)-Co(1)-N(1)	92.2(4)	N(6)-Co(2)-S(6)	86.0(4)
N(3)-Co(1)-N(1)	90.5(5)	N(4)-Co(2)-S(6)	174.9(4)
N(2)-Co(1)-S(2)	84.1(3)	N(5)-Co(2)-S(4)	175.1(4)
N(3)-Co(1)-S(2)	93.4(4)	N(6)-Co(2)-S(4)	93.6(4)
N(1)-Co(1)-S(2)	174.7(3)	N(4)-Co(2)-S(4)	85.2(4)
N(2)-Co(1)-S(3)	173.9(3)	N(5)-Co(2)-S(5)	84.0(4)
N(3)-Co(1)-S(3)	84.7(3)	N(6)-Co(2)-S(5)	173.2(4)
N(1)-Co(1)-S(3)	92.7(3)	N(4)-Co(2)-S(5)	93.2(4)
N(2)-Co(1)-S(1)	90.4(3)	S(6)-Co(2)-S(4)	92.52(16)
N(3)-Co(1)-S(1)	174.3(4)	S(6)-Co(2)-S(5)	91.51(16)
N(1)-Co(1)-S(1)	84.1(3)	S(4)-Co(2)-S(5)	92.81(17)

Table S3. Absorption and CD spectral data of $Na_3[\mathbf{1}]$ in water.

Absorption maxima: λ / nm ($\log \varepsilon$)	CD extrema: λ / nm ($\Delta\varepsilon$ / mol^{-1} dm^3 cm^{-1})
562 (3.01)	553 (+11.62)
286 (4.45)	441 (–10.58)
238 (4.59)	385 (+19.65)
	315 (+71.73)
	248 (–122.5)
	225 (–42.45)
	213 (+13.38)