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A one-dimensional heterometallic coordination polymer with a three-dimensional supramolecular framework: poly[μ_2-aqua-diaqua(2,2′-bipyridyl)(μ_5-2-sulfonatobutanedioato)copper(II)sodium(I)]

Jiang-Hong Fu, Yu-Ling Wang,* Ying Chen, Chang-Hui Hu and Li Tang

College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang, Jiangxi 330022, People's Republic of China
Correspondence e-mail: ylwangchem@gmail.com

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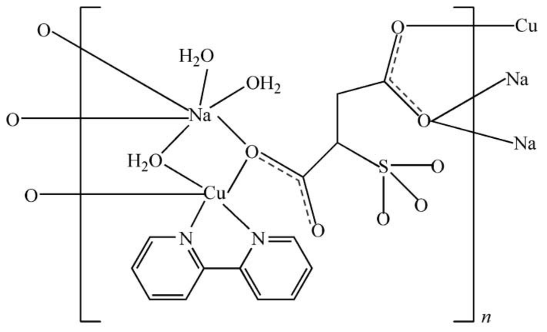
The title compound, $[\mathrm{CuNa}(\mathrm{C_4H_3O_7S})(\mathrm{C_{10}H_8N_2})(\mathrm{H_2O})_3]_n$, consists of one $\mathrm{Cu^{II}}$ cation, one $\mathrm{Na^I}$ cation, one 2-sulfonatobutanedioate trianion ($\mathrm{SSC^{3-}}$), one 2,2′-bipyridyl (bpy) ligand and three coordinated water molecules as the building unit. The coordination of the $\mathrm{Cu^{II}}$ cation is composed of two pyridyl N atoms, one water O atom and two carboxylate O atoms in a distorted square-pyramidal coordination geometry with an axial elongation. The $\mathrm{Na^I}$ cation is six-coordinated by three water molecules and three carboxylate O atoms from three $\mathrm{SSC^{3-}}$ ligands in a distorted octahedral geometry. Two $\mathrm{SSC^{3-}}$ ligands link two $\mathrm{Cu^{II}}$ cations to form a $\mathrm{Cu_2(SSC)_2(bpy)_2}$ macrocyclic unit lying across an inversion centre, which is further linked by $\mathrm{Na^I}$ cations *via* Na—O bonds to give a one-dimensional chain. Interchain hydrogen bonds link these chains to form a two-dimensional layer, which is further extended into a three-dimensional supramolecular framework through π–π stacking interactions. The thermal stability of the title compound has also been investigated.

Comment

Coordination polymers constructed from metal cations or metal clusters with multifunctional organic ligands have attracted much attention in recent decades, not only for their aesthetically pleasing structures but also for their potential applications in areas such as gas storage and separation, catalysis, photoluminescence, molecular magnetism and nonlinear optics (Eddaoudi *et al.*, 2001; Yoon *et al.*, 2012; Allendorf *et al.*, 2009; Wang *et al.*, 2008; Zhang *et al.*, 2009). Compared with the generally used carboxylate ligands, organosulfonate ligands have so far been less investigated. The sulfonate group has three potential O-atom coordination sites and is usually regarded as a weak ligating group with flexible coordination modes, which may form various coordination polymers or supramolecules with interesting structures through extensive hydrogen bonds (Xiao *et al.*, 2009; Mahmoudkhani & Shimizu, 2007; Cai, 2004). We are interested in bifunctional sulfonate–carboxylate ligands because they can exhibit discriminative coordination abilities. While some rigid sulfonate–carboxylate ligands, such as 5-sulfoisophthalic acid (Sun *et al.*, 2003; Liu *et al.*, 2010), 2-sulfoterephthalic acid (Horike *et al.* 2006), 4,8-disulfonylnaphthalene-2,6-dicarboxylic acid (Liu *et al.*, 2012) and 4-sulfobenzoic acid (Zhang & Zhu, 2006) and their metal complexes have been reported, only one flexible sulfonate–carboxylate ligand of 2-sulfobutanedioic acid ($\mathrm{H_3SSC}$) and two of its sodium–zinc heterometallic compounds have been reported, in which the $\mathrm{H_3SSC}$ ligand displays various coordination modes resulting in different frameworks (Liu *et al.*, 2011). Further research on the flexible $\mathrm{H_3SSC}$ ligand in other metal complexes is needed for a comprehensive understanding of $\mathrm{H_3SSC}$ coordination chemistry. We report herein the synthesis and crystal structure of the title heterometallic compound, (I), incorporating the $\mathrm{H_3SSC}$ ligand.



(I)

The asymmetric unit of (I) consists of one $\mathrm{Na^I}$ cation, one $\mathrm{Cu^{II}}$ cation, one $\mathrm{SSC^{3-}}$ ligand, one 2,2′-bipyridyl (bpy) molecule and three aqua ligands. As depicted in Fig. 1, Cu1 is five-coordinated by two carboxylate O atoms [O1 and O3$^{\mathrm{i}}$; symmetry code: (i) $-x + 2$, $-y + 1$, $-z$] from two $\mathrm{SSC^{3-}}$ ligands and two N atoms from one bpy ligand in a distorted square-planar geometry, with a water molecule (O8) in the apical position. The apical Cu1—O8 distance is considerably longer than the equatorial ones (Table 1); such axial elongation can be attributed to the strong Jahn–Teller distortion of the $\mathrm{Cu^{II}}$ cation. As shown in Fig. 1, three O atoms from three $\mathrm{SSC^{3-}}$ ligands and three water molecules complete the distorted octahedral coordination environment for Na1. Two water molecules (O8 and O10) and two carboxylate O atoms [O1 and O4$^{\mathrm{ii}}$; symmetry code: (ii) $x - 1$, y, z] form the equatorial plane and the axial positions are occupied by one carboxylate O and one coordinating water molecule. The $\mathrm{NaO_6}$ octahedron is distorted, with O—Na—O angles varying from 74.09 (7) to 169.96 (9)° (Table 1). It is noted that one of the coordinating water molecules (O8) acts as a μ_2-bridging ligand between Cu1 and Na1, while the other two water molecules are terminal coordinating ligands. The $\mathrm{SSC^{3-}}$ ligand employs its two μ_2-carboxylate O atoms (O1 and O4) and one

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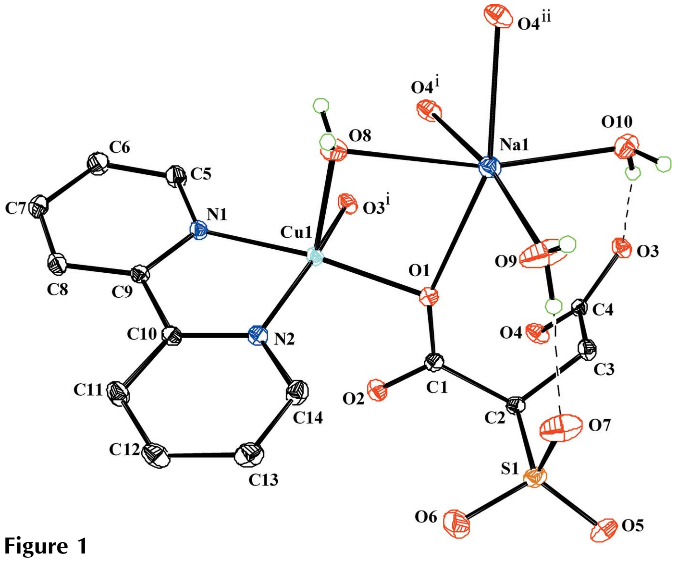

Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. All H atoms have been omitted for clarity, except for the water H atoms, which are shown as small spheres of arbitrary radii. Dashed lines indicate intramolecular hydrogen bonds. [Symmetry codes: (i) $-x + 2, -y + 1, -z$; (ii) $x - 1, y, z$.]

monodentate carboxylate O atom (O3) to bridge three Na^I and two Cu^{II} cations. Carboxylate atom O2 and the sulfonate O atoms are not involved in coordination but are engaged in hydrogen bonding.

As shown in Fig. 2, two symmetry-related SSC^{3-} ligands link two Cu1 cations (Cu1 and Cu1^i) to form a centrosymmetric $Cu_2(SSC)_2(bpy)_2$ macrocyclic unit with a 14-membered ring. These $Cu_2(SSC)_2(bpy)_2$ units are linked by Na1 cations through Na1—O1, Na1—O8, Na1—O4^i and Na1—O4^{ii} bonds to form a one-dimensional chain (Fig. 2), which is further reinforced by hydrogen bonds [O8···O10^{iii}, O8···O2^{ii}, O9···O5^{ii}, O9···O7 and O10···O3; symmetry code: (iii) $-x + 1, -y + 1, -z$] (Table 2). These one-dimensional chains are linked by an O10···O5^{iv} [symmetry code: (iv) $-x + 2, -y + 2, -z$] hydrogen bond to form a two-dimensional layer along the *ab* plane (Fig. 3). These two-dimensional layers are stacked along the *c* direction (Fig. 4). In the three-dimensional crystal packing, there are interlayer π–π stacking interactions between the pyridine rings, which are arranged in an offset fashion with a dihedral angle of 2.07 (12)°, a face-to-face distance of 3.4863 (10) Å and a centroid–centroid distance of 3.7775 (15) Å for the N1/C5–C9 and N2/C10–C14^v rings [symmetry code: (v) $-x + 2, -y + 1, -z + 1$]. The extensive

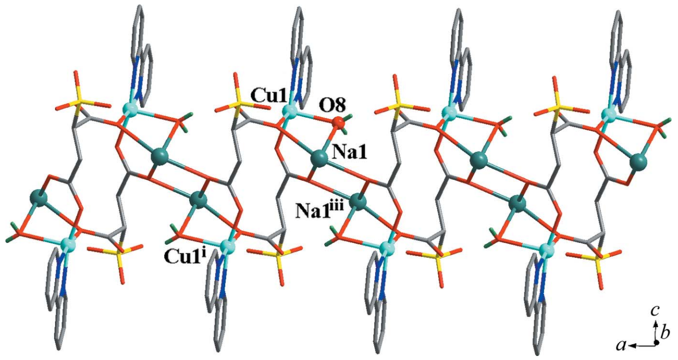

Figure 2
A perspective view of the macrocyclic $[Cu(SSC)_2(bpy)_2]^-$ unit of (I) and the one-dimensional chain. [Symmetry codes: (i) $-x + 2, -y + 1, -z$; (iii) $-x + 1, -y + 1, -z$.]

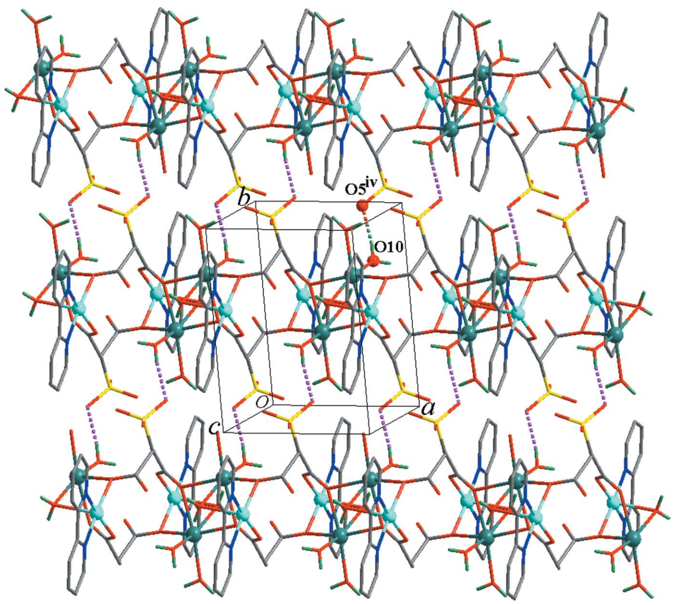

Figure 3
A perspective view of the two-dimensional layered structure of (I). Dashed lines indicate hydrogen bonds. [Symmetry code: (iv) $-x + 2, -y + 2, -z$.]

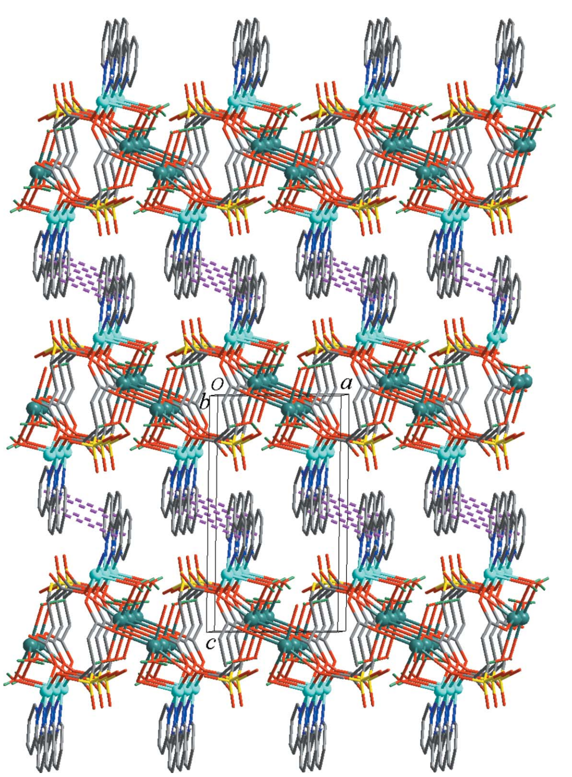

Figure 4
A view of the packing for (I), viewed along the *b* axis. Dotted lines between aromatic rings indicate π–π stacking interactions.

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hydrogen bonding and π–π stacking interactions are responsible for the final three-dimensional supramolecular architecture.

To the best of our knowledge, only two compounds, namely $[Na_2Zn_3(\mu_3\text{-}OH)_2(SSC)_2(H_2O)_4]_n$ and $[Na_4Zn(SSC)_2(H_2O)_{3.5}]_n$, based on the H_3SSC ligand have been reported to date (Liu *et al.*, 2011). In both compounds, the two-dimensional anionic layers constructed from the zinc cations and SSC^{3-} ligands are linked by sodium cations in various manners to generate quite different three-dimensional architectures, which are very different from the structure of (I). In addition, for the nonsulfonated analogue (succinate) of the H_3SSC ligand, three copper(II) compounds with succinate (SC) and bpy ligands have been reported. In the discrete dinuclear structure of $[Cu_2(SC)(bpy)_4]SC\cdot12H_2O$ (Lin & Xu, 2009) and the one-dimensional chain of $\{[Cu_2(SC)(\mu_2\text{-}H_2O)_2(bpy)_2]NO_3\}_n$ (Zhang *et al.*, 2004), the SC^{2-} ligand, in a bidentate bridging mode, bridges two metal cations, while the $\{[Cu_2(SC)(bpy)_2(H_2O)](ClO_4)_2\cdot0.5H_2O\}_n$ compound possesses a cationic two-dimensional layer charge-balanced by perchlorate anions (Ghoshal *et al.*, 2004), in which the SC^{2-} ligand binds to five metal cations. All are different from the corresponding sulfonated-analogue-based compound, which indicates that the sulfonate group has a significant influence on the structure of the final product, although the sulfonate group is uncoordinated in (I).

The results of thermal analysis are represented by the curves in Fig. S1 in the *Supplementary materials*. Compound (I) exhibits two main steps of weight loss. The first step (333–413 K) corresponds to release of the three coordinated water molecules (weight loss, measured = 12.02% and theoretical = 10.99%). A sharp continual weight loss then occurs at 518 K, which is attributed to decomposition of the organic ligands.

Experimental

An ethanol solution (5 ml) of 2,2′-bipyridyl (32.4 mg, 0.2 mmol) was carefully layered on top of a mixture of an aqueous solution (5 ml) of $Cu(CH_3CO_2)_2\cdot H_2O$ (49.9 mg, 0.25 mmol), a 2-sulfobutanedioic acid solution (141.6 mg, 0.5 mmol) and sodium hydroxide (20 mg, 0.5 mmol). Blue block-shaped crystals were obtained after a week. The crystalline product was filtered, washed with ethanol and dried at ambient temperature [yield: 43%, based on $Cu(CH_3CO_2)_2\cdot H_2O$].

Crystal data

$[CuNa(C_4H_3O_7S)(C_{10}H_8N_2)(H_2O)_3]$
$M_r = 491.89$
Triclinic, $P\overline{1}$
$a = 7.1560$ (5) Å
$b = 9.8692$ (6) Å
$c = 12.9585$ (8) Å
$\alpha = 95.853$ (1)°
$\beta = 90.544$ (1)°
$\gamma = 95.643$ (1)°
$V = 905.82$ (10) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 1.41$ mm^{-1}
$T = 296$ K
0.36 × 0.28 × 0.21 mm

Data collection

Bruker APEXII area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.632$, $T_{max} = 0.757$
8529 measured reflections
4360 independent reflections
3688 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$

Table 1
Selected geometric parameters (Å, °).

Na1—O9	2.342 (3)	Cu1—O3^{i}	1.9631 (15)
Na1—O4^{i}	2.4034 (19)	Cu1—O1	1.9820 (15)
Na1—O10	2.404 (2)	Cu1—N1	2.0035 (18)
Na1—O1	2.4174 (18)	Cu1—N2	2.0190 (18)
Na1—O4^{ii}	2.4306 (19)	Cu1—O8	2.2932 (17)
Na1—O8	2.474 (2)		
O9—Na1—O4^{i}	169.96 (9)	O1—Na1—O8	76.49 (6)
O9—Na1—O10	93.28 (11)	O4^{ii}—Na1—O8	82.81 (7)
O4^{i}—Na1—O10	90.46 (7)	O3^{i}—Cu1—O1	91.89 (7)
O9—Na1—O1	84.31 (9)	O3^{i}—Cu1—N1	90.71 (7)
O4^{i}—Na1—O1	85.65 (6)	O1—Cu1—N1	173.28 (7)
O10—Na1—O1	111.41 (7)	O3^{i}—Cu1—N2	164.01 (7)
O9—Na1—O4^{ii}	102.81 (8)	O1—Cu1—N2	95.24 (7)
O4^{i}—Na1—O4^{ii}	86.62 (7)	N1—Cu1—N2	80.75 (7)
O10—Na1—O4^{ii}	87.93 (7)	O3^{i}—Cu1—O8	101.93 (7)
O1—Na1—O4^{ii}	159.19 (7)	O1—Cu1—O8	89.89 (7)
O9—Na1—O8	103.37 (11)	N1—Cu1—O8	95.63 (7)
O4^{i}—Na1—O8	74.09 (7)	N2—Cu1—O8	92.40 (7)
O10—Na1—O8	162.37 (8)		

Symmetry codes: (i) $-x+2, -y+1, -z$; (ii) $x-1, y, z$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O8—H8A···O10^{iii}	0.81 (2)	2.01 (2)	2.801 (3)	166 (3)
O8—H8B···O2^{ii}	0.79 (2)	1.98 (2)	2.720 (2)	156 (3)
O9—H9A···O5^{ii}	0.83 (2)	2.13 (3)	2.920 (3)	159 (5)
O9—H9B···O7	0.83 (2)	1.94 (2)	2.756 (3)	170 (5)
O10—H10A···O5^{iv}	0.82 (2)	2.03 (2)	2.818 (3)	162 (4)
O10—H10B···O3	0.81 (2)	2.11 (2)	2.903 (3)	166 (4)

Symmetry codes: (ii) $x-1, y, z$; (iii) $-x+1, -y+1, -z$; (iv) $-x+2, -y+2, -z$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.086$
$S = 1.01$
4360 reflections
280 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

H atoms bonded to C atoms were placed in calculated positions and treated using a riding-model approximation, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic H atoms, C—H = 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for methylene H atoms, and C—H = 0.98 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for the methylidyne H atom. Water H atoms were located in a difference Fourier map and refined with a restraint of O—H = 0.82 (2) Å and with $U_{iso}(H) = 1.5U_{eq}(O)$.

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LG3089). Services for accessing these data are described at the back of the journal.

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supplementary materials

Acta Cryst. (2012). C**68**, m209–m212 [doi:10.1107/S0108270112030909]

A one-dimensional heterometallic coordination polymer with a three-dimensional supramolecular framework: poly[μ_2-aqua-diaqua(2,2′-bipyridyl)(μ_5-2-sulfonatobutanedioato)copper(II)sodium(I)]

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poly[μ_2-aqua-diaqua(2,2′-bipyridyl)(μ_5- 2-sulfonatobutanedioato)copper(II)sodium(I)]

Crystal data

[NaCu($C_4H_3O_7S$)($C_{10}H_8N_2$)(H_2O)$_3$]
M_r = 491.89
Triclinic, $P\overline{1}$
a = 7.1560 (5) Å
b = 9.8692 (6) Å
c = 12.9585 (8) Å
α = 95.853 (1)°
β = 90.544 (1)°
γ = 95.643 (1)°
V = 905.82 (10) Å^3
Z = 2
F(000) = 502
D_x = 1.803 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4042 reflections
θ = 2.5–28.2°
μ = 1.41 mm^{-1}
T = 296 K
Block, blue
0.36 × 0.28 × 0.21 mm

Data collection

Bruker APEXII area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.632, $T_{\max}$ = 0.757
8529 measured reflections
4360 independent reflections
3688 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
$\theta_{\max}$ = 28.3°, $\theta_{\min}$ = 2.5°
$h = -9\rightarrow 9$
$k = -13\rightarrow 13$
$l = -16\rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.086
S = 1.01
4360 reflections
280 parameters
6 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.6176P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.56 e Å^{-3}
$\Delta\rho_{\min}$ = −0.30 e Å^{-3}

Special details

Experimental. Spectroscopic analysis: IR (KBr pellet, *v*, cm^{-1}): 3428, 2926, 1608, 1495, 1473, 1445, 1400, 1323, 1283, 1213, 1151, 1080, 949, 859, 766, 730, 594, 546, 523.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
Na1	0.63906 (13)	0.64665 (10)	0.05549 (7)	0.0304 (2)
Cu1	0.81668 (4)	0.49559 (2)	0.246359 (19)	0.02049 (8)
S1	1.17897 (8)	0.95225 (6)	0.20643 (5)	0.02834 (14)
O1	0.9098 (2)	0.65127 (15)	0.16923 (12)	0.0242 (3)
O2	1.1698 (2)	0.60962 (17)	0.24859 (13)	0.0295 (4)
O3	1.1190 (2)	0.63830 (16)	−0.13295 (12)	0.0265 (3)
O4	1.3196 (2)	0.59098 (17)	−0.01191 (13)	0.0331 (4)
O5	1.3305 (3)	1.04046 (17)	0.16576 (16)	0.0395 (4)
O6	1.2095 (4)	0.9343 (2)	0.31395 (15)	0.0579 (6)
O7	0.9968 (3)	0.9934 (2)	0.1843 (2)	0.0581 (6)
O8	0.5138 (2)	0.52714 (19)	0.20275 (14)	0.0323 (4)
H8A	0.460 (4)	0.455 (2)	0.178 (2)	0.048*
H8B	0.433 (4)	0.570 (3)	0.226 (2)	0.048*
O9	0.6444 (3)	0.8784 (3)	0.1173 (3)	0.0762 (9)
H9A	0.569 (6)	0.937 (4)	0.120 (4)	0.114*
H9B	0.755 (4)	0.909 (5)	0.130 (4)	0.114*
O10	0.7298 (3)	0.6957 (2)	−0.11602 (16)	0.0372 (4)
H10A	0.728 (5)	0.778 (2)	−0.119 (3)	0.056*
H10B	0.837 (3)	0.683 (4)	−0.131 (3)	0.056*
N1	0.7477 (3)	0.34523 (18)	0.33602 (14)	0.0239 (4)
N2	0.8048 (3)	0.60898 (18)	0.38449 (14)	0.0229 (4)
C1	1.0864 (3)	0.6747 (2)	0.18858 (16)	0.0220 (4)
C2	1.1978 (3)	0.7868 (2)	0.13611 (16)	0.0230 (4)
H2	1.3302	0.7697	0.1403	0.028*
C3	1.1499 (3)	0.7881 (2)	0.02207 (17)	0.0257 (4)
H3A	1.2155	0.8688	−0.0029	0.031*
H3B	1.0161	0.7942	0.0141	0.031*
C4	1.2026 (3)	0.6609 (2)	−0.04387 (16)	0.0215 (4)
C5	0.7137 (4)	0.2119 (2)	0.30334 (19)	0.0343 (6)
H5	0.7210	0.1840	0.2329	0.041*
C6	0.6680 (4)	0.1145 (3)	0.3707 (2)	0.0375 (6)
H6	0.6426	0.0227	0.3459	0.045*
C7	0.6608 (4)	0.1556 (2)	0.4745 (2)	0.0340 (5)
H7	0.6325	0.0915	0.5213	0.041*
C8	0.6959 (3)	0.2932 (2)	0.50965 (18)	0.0300 (5)

H8	0.6925	0.3224	0.5801	0.036*
C9	0.7361 (3)	0.3862 (2)	0.43834 (16)	0.0223 (4)
C10	0.7706 (3)	0.5357 (2)	0.46573 (16)	0.0221 (4)
C11	0.7681 (4)	0.5981 (2)	0.56641 (18)	0.0322 (5)
H11	0.7450	0.5460	0.6217	0.039*
C12	0.8005 (4)	0.7388 (3)	0.5832 (2)	0.0359 (6)
H12	0.7988	0.7828	0.6501	0.043*
C13	0.8352 (4)	0.8131 (3)	0.5005 (2)	0.0347 (5)
H13	0.8579	0.9080	0.5107	0.042*
C14	0.8359 (3)	0.7459 (2)	0.40237 (19)	0.0306 (5)
H14	0.8587	0.7969	0.3465	0.037*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Na1	0.0299 (5)	0.0307 (5)	0.0310 (5)	0.0046 (4)	−0.0034 (4)	0.0035 (4)
Cu1	0.02715 (15)	0.01869 (14)	0.01526 (13)	0.00161 (10)	0.00060 (9)	0.00058 (9)
S1	0.0349 (3)	0.0203 (3)	0.0273 (3)	−0.0012 (2)	0.0037 (2)	−0.0063 (2)
O1	0.0249 (8)	0.0236 (8)	0.0237 (8)	−0.0001 (6)	−0.0012 (6)	0.0033 (6)
O2	0.0292 (8)	0.0333 (9)	0.0269 (8)	0.0060 (7)	−0.0006 (7)	0.0052 (7)
O3	0.0347 (9)	0.0259 (8)	0.0186 (8)	0.0072 (6)	−0.0008 (6)	−0.0020 (6)
O4	0.0369 (9)	0.0328 (9)	0.0291 (9)	0.0123 (7)	−0.0065 (7)	−0.0063 (7)
O5	0.0413 (10)	0.0233 (8)	0.0521 (12)	−0.0041 (7)	0.0041 (8)	0.0014 (8)
O6	0.1062 (19)	0.0370 (11)	0.0264 (10)	−0.0022 (11)	−0.0031 (11)	−0.0074 (8)
O7	0.0384 (11)	0.0394 (11)	0.0920 (18)	0.0112 (9)	−0.0033 (11)	−0.0222 (11)
O8	0.0243 (9)	0.0373 (10)	0.0349 (10)	0.0073 (7)	−0.0004 (7)	−0.0023 (8)
O9	0.0345 (12)	0.0430 (13)	0.144 (3)	0.0030 (10)	−0.0047 (15)	−0.0234 (15)
O10	0.0336 (9)	0.0334 (9)	0.0452 (11)	0.0032 (8)	0.0021 (8)	0.0073 (8)
N1	0.0319 (10)	0.0200 (9)	0.0193 (9)	0.0012 (7)	−0.0001 (7)	0.0006 (7)
N2	0.0257 (9)	0.0210 (9)	0.0213 (9)	0.0028 (7)	0.0026 (7)	−0.0016 (7)
C1	0.0290 (11)	0.0180 (10)	0.0173 (10)	−0.0002 (8)	0.0051 (8)	−0.0051 (7)
C2	0.0279 (11)	0.0200 (10)	0.0201 (10)	0.0004 (8)	0.0013 (8)	−0.0011 (8)
C3	0.0372 (12)	0.0212 (10)	0.0190 (10)	0.0068 (9)	0.0012 (9)	0.0001 (8)
C4	0.0259 (11)	0.0212 (10)	0.0166 (10)	−0.0009 (8)	0.0031 (8)	0.0011 (8)
C5	0.0541 (16)	0.0234 (11)	0.0234 (12)	−0.0015 (10)	−0.0010 (10)	−0.0024 (9)
C6	0.0539 (16)	0.0211 (11)	0.0361 (14)	−0.0027 (11)	−0.0027 (12)	0.0026 (10)
C7	0.0410 (14)	0.0279 (12)	0.0332 (13)	−0.0027 (10)	0.0002 (10)	0.0106 (10)
C8	0.0369 (13)	0.0313 (12)	0.0216 (11)	0.0009 (10)	0.0003 (9)	0.0037 (9)
C9	0.0226 (10)	0.0238 (10)	0.0199 (10)	0.0012 (8)	−0.0003 (8)	0.0006 (8)
C10	0.0221 (10)	0.0231 (10)	0.0211 (10)	0.0036 (8)	0.0003 (8)	0.0010 (8)
C11	0.0441 (14)	0.0312 (12)	0.0208 (11)	0.0055 (10)	0.0017 (10)	−0.0011 (9)
C12	0.0457 (15)	0.0348 (13)	0.0252 (12)	0.0074 (11)	−0.0003 (10)	−0.0093 (10)
C13	0.0406 (14)	0.0224 (11)	0.0389 (14)	0.0034 (10)	0.0030 (11)	−0.0078 (10)
C14	0.0365 (13)	0.0239 (11)	0.0312 (13)	0.0022 (9)	0.0069 (10)	0.0017 (9)

Geometric parameters (Å, º)

Na1—O9	2.342 (3)	N1—C5	1.338 (3)
Na1—O4^{i}	2.4034 (19)	N1—C9	1.352 (3)
Na1—O10	2.404 (2)	N2—C14	1.344 (3)

Na1—O1	2.4174 (18)	N2—C10	1.348 (3)
Na1—O4^{ii}	2.4306 (19)	C1—C2	1.521 (3)
Na1—O8	2.474 (2)	C2—C3	1.516 (3)
Cu1—O3^{i}	1.9631 (15)	C2—H2	0.9800
Cu1—O1	1.9820 (15)	C3—C4	1.526 (3)
Cu1—N1	2.0035 (18)	C3—H3A	0.9700
Cu1—N2	2.0190 (18)	C3—H3B	0.9700
Cu1—O8	2.2932 (17)	C5—C6	1.381 (3)
S1—O7	1.438 (2)	C5—H5	0.9300
S1—O6	1.440 (2)	C6—C7	1.369 (4)
S1—O5	1.4594 (18)	C6—H6	0.9300
S1—C2	1.805 (2)	C7—C8	1.385 (3)
O1—C1	1.280 (3)	C7—H7	0.9300
O2—C1	1.241 (3)	C8—C9	1.380 (3)
O3—C4	1.284 (3)	C8—H8	0.9300
O3—Cu1^{i}	1.9631 (15)	C9—C10	1.477 (3)
O4—C4	1.231 (3)	C10—C11	1.386 (3)
O4—Na1^{i}	2.4034 (19)	C11—C12	1.379 (4)
O4—Na1^{iii}	2.4306 (19)	C11—H11	0.9300
O8—H8A	0.810 (18)	C12—C13	1.371 (4)
O8—H8B	0.791 (18)	C12—H12	0.9300
O9—H9A	0.827 (19)	C13—C14	1.373 (3)
O9—H9B	0.827 (19)	C13—H13	0.9300
O10—H10A	0.816 (18)	C14—H14	0.9300
O10—H10B	0.813 (18)		

O9—Na1—O4^{i}	169.96 (9)	C9—N1—Cu1	115.09 (14)
O9—Na1—O10	93.28 (11)	C14—N2—C10	118.68 (19)
O4^{i}—Na1—O10	90.46 (7)	C14—N2—Cu1	126.62 (16)
O9—Na1—O1	84.31 (9)	C10—N2—Cu1	114.61 (14)
O4^{i}—Na1—O1	85.65 (6)	O2—C1—O1	122.52 (19)
O10—Na1—O1	111.41 (7)	O2—C1—C2	118.90 (19)
O9—Na1—O4^{ii}	102.81 (8)	O1—C1—C2	118.59 (19)
O4^{i}—Na1—O4^{ii}	86.62 (7)	C3—C2—C1	114.58 (18)
O10—Na1—O4^{ii}	87.93 (7)	C3—C2—S1	110.92 (15)
O1—Na1—O4^{ii}	159.19 (7)	C1—C2—S1	110.67 (14)
O9—Na1—O8	103.37 (11)	C3—C2—H2	106.7
O4^{i}—Na1—O8	74.09 (7)	C1—C2—H2	106.7
O10—Na1—O8	162.37 (8)	S1—C2—H2	106.7
O1—Na1—O8	76.49 (6)	C2—C3—C4	112.57 (18)
O4^{ii}—Na1—O8	82.81 (7)	C2—C3—H3A	109.1
O3^{i}—Cu1—O1	91.89 (7)	C4—C3—H3A	109.1
O3^{i}—Cu1—N1	90.71 (7)	C2—C3—H3B	109.1
O1—Cu1—N1	173.28 (7)	C4—C3—H3B	109.1
O3^{i}—Cu1—N2	164.01 (7)	H3A—C3—H3B	107.8
O1—Cu1—N2	95.24 (7)	O4—C4—O3	125.1 (2)
N1—Cu1—N2	80.75 (7)	O4—C4—C3	120.59 (19)
O3^{i}—Cu1—O8	101.93 (7)	O3—C4—C3	114.34 (19)
O1—Cu1—O8	89.89 (7)	N1—C5—C6	122.2 (2)

N1—Cu1—O8	95.63 (7)	N1—C5—H5	118.9
N2—Cu1—O8	92.40 (7)	C6—C5—H5	118.9
O3^{i}—Cu1—Na1	83.56 (5)	C7—C6—C5	118.8 (2)
O7—S1—O6	113.75 (16)	C7—C6—H6	120.6
O7—S1—O5	112.31 (13)	C5—C6—H6	120.6
O6—S1—O5	112.33 (14)	C6—C7—C8	119.7 (2)
O7—S1—C2	108.26 (11)	C6—C7—H7	120.2
O6—S1—C2	105.56 (11)	C8—C7—H7	120.2
O5—S1—C2	103.82 (11)	C9—C8—C7	118.9 (2)
C1—O1—Cu1	106.85 (13)	C9—C8—H8	120.6
C1—O1—Na1	151.58 (14)	C7—C8—H8	120.6
Cu1—O1—Na1	97.49 (6)	N1—C9—C8	121.4 (2)
C4—O3—Cu1^{i}	125.31 (14)	N1—C9—C10	114.62 (18)
C4—O4—Na1^{i}	130.17 (14)	C8—C9—C10	124.0 (2)
C4—O4—Na1^{iii}	132.73 (15)	N2—C10—C11	121.6 (2)
Na1^{i}—O4—Na1^{iii}	93.38 (7)	N2—C10—C9	114.78 (18)
Cu1—O8—Na1	88.20 (6)	C11—C10—C9	123.6 (2)
Cu1—O8—H8A	109 (2)	C12—C11—C10	118.9 (2)
Na1—O8—H8A	106 (2)	C12—C11—H11	120.6
Cu1—O8—H8B	138 (2)	C10—C11—H11	120.6
Na1—O8—H8B	106 (2)	C13—C12—C11	119.4 (2)
H8A—O8—H8B	104 (3)	C13—C12—H12	120.3
Na1—O9—H9A	136 (4)	C11—C12—H12	120.3
Na1—O9—H9B	109 (4)	C12—C13—C14	119.2 (2)
H9A—O9—H9B	114 (5)	C12—C13—H13	120.4
Na1—O10—H10A	108 (3)	C14—C13—H13	120.4
Na1—O10—H10B	116 (3)	N2—C14—C13	122.2 (2)
H10A—O10—H10B	103 (3)	N2—C14—H14	118.9
C5—N1—C9	118.98 (19)	C13—C14—H14	118.9
C5—N1—Cu1	125.93 (16)		

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*; (ii) *x*−1, *y*, *z*; (iii) *x*+1, *y*, *z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O8—H8*A*···O10^{iv}	0.81 (2)	2.01 (2)	2.801 (3)	166 (3)
O8—H8*B*···O2^{ii}	0.79 (2)	1.98 (2)	2.720 (2)	156 (3)
O9—H9*A*···O5^{ii}	0.83 (2)	2.13 (3)	2.920 (3)	159 (5)
O9—H9*B*···O7	0.83 (2)	1.94 (2)	2.756 (3)	170 (5)
O10—H10*A*···O5^{v}	0.82 (2)	2.03 (2)	2.818 (3)	162 (4)
O10—H10*B*···O3	0.81 (2)	2.11 (2)	2.903 (3)	166 (4)

Symmetry codes: (ii) *x*−1, *y*, *z*; (iv) −*x*+1, −*y*+1, −*z*; (v) −*x*+2, −*y*+2, −*z*.