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# *catena*-Poly[copper(II)-bis(μ-2-formyl-6-methoxyphenolato-$\kappa^4O^2,O^1:O^1,O^6$)-[(methanol-$\kappa O$)sodium]-μ-perchlorato-$\kappa^2O:O'$]

**Ting Gao,* Po Gao, Hong-Feng Li, Ju-Wen Zhang and Li-Li Xu**

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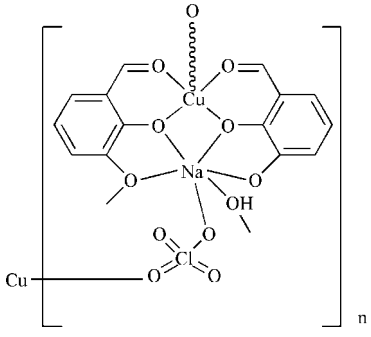
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.004 Å; disorder in main residue; $R$ factor = 0.034; $wR$ factor = 0.108; data-to-parameter ratio = 14.3.

In the title heterodinuclear complex, $[CuNa(C_8H_7O_3)_2(ClO_4)(CH_3OH)]_n$, the $Cu^{II}$ ion is five-coordinated by four O atoms from two 2-formyl-6-methoxyphenolate anions and one O atom from a perchlorate anion in a distorted square-pyramidal geometry. The $Na^+$ ion is six-coordinated by four O atoms from two 2-formyl-6-methoxyphenolate ligands, one O atom of a methanol molecule and one O atom of a perchlorate anion. The perchlorate anions link the $Na^+$ and $Cu^{II}$ ions, forming a chain along [010]. O—H···O hydrogen bonds connect the chains. $\pi$–$\pi$ interactions are present between the benzene rings [centroid–centroid distances = 3.566 (2) and 3.702 (2) Å]. The O atoms of the perchlorate anion are disordered over two sets of sites, with an occupancy ratio of 0.481 (8):0.519 (8).

## Related literature

For related structures, see: Gao *et al.* (2011); Lin & Zeng (2006); Yang *et al.* (2012).




## Experimental

### Crystal data

$[CuNa(C_8H_7O_3)_2(ClO_4)(CH_4O)]$
$M_r$ = 520.29
Triclinic, $P\overline{1}$
$a$ = 7.9552 (16) Å
$b$ = 8.9453 (18) Å
$c$ = 15.563 (3) Å
$\alpha$ = 81.27 (3)°
$\beta$ = 84.24 (3)°
$\gamma$ = 68.25 (3)°
$V$ = 1015.6 (4) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 1.29 mm$^{-1}$
$T$ = 293 K
0.43 × 0.28 × 0.28 mm

### Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min}$ = 0.610, $T_{max}$ = 0.714
9778 measured reflections
4591 independent reflections
3948 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.021

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.108
$S$ = 1.11
4591 reflections
321 parameters
48 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.58 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.59 e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O7—H71···O10$^{i}$ | 0.85 | 2.11 | 2.874 (7) | 149 |
| O7—H71···O11$'^{i}$ | 0.85 | 2.55 | 3.334 (13) | 154 |

Symmetry code: (i) $x-1, y, z$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

The authors gratefully acknowledge financial support from Heilongjiang Province (11551334) and Heilongjiang University.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2501).

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# supporting information

*Acta Cryst.* (2012). E**68**, m152 [doi:10.1107/S1600536812000876]

## *catena*-Poly[copper(II)-bis(*μ*-2-formyl-6-methoxyphenolato-$\kappa^4O^2,O^1:O^1,O^6$)-[(methanol-$\kappa O$)sodium]-*μ*-perchlorato-$\kappa^2O:O'$]

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### S1. Comment

Orthovanillin is a commercial ligand that is able to chelate 3d ions and several structure determinations are known, mainly with copper ions (Lin & Zeng, 2006). Recently, we were interested in the nature of the products obtained by reacting a 3d complex with alkali metal ions (Gao *et al.*, 2011; Yang *et al.*, 2012). In this paper we reacted a Cu complex with sodium perchlorate to yield a heterodinuclear complex. As shown in Fig. 1, the $Cu^{II}$ ion is five-coordinated by two aldehyde O atoms and two phenolate O atoms from two orthovanillin ligands and one O atom from a perchlorate anion in a distorted square-pyramidal geometry. The Cu atom is inserted into the inner cavity surrounded by four O atoms. The $Na^+$ ion is ligated by two phenolate O atoms, two methoxyl O atoms, one O atom from a methanol molecule and one O atom from a perchlorate anion. The Cu and Na atoms are bridged by the perchlorate anions, forming a one-dimensional structure along [0 1 0].

### S2. Experimental

To a solution of *o*-vanillin (0.046 g, 0.20 mmol) in dichloromethane (5 ml) was added a solution of copper(II) acetate monohydrate (0.040 g, 0.20 mmol) and sodium perchlorate (0.028 g, 0.20 mmol) in ethanol (5 ml). The mixture was stirred, heated under reflux (30 min) and then allowed to cool to room temperature (yield: 70%). Crystals suitable for X-ray determination were obtained by slow diffusion of diethylether into the solution for one week. Analysis, calculated for $C_{17}H_{18}ClCuNaO_{11}$: C 39.24, H 3.49%; found: C 39.38, H 3.48%.

### S3. Refinement

H atoms bound to C atoms were placed in calculated positions and treated as riding on their parent atoms, with C—H = 0.93 (aromatic and aldehyde) and 0.96 (methyl) Å and with $U_{iso}$(H) = 1.2(1.5 for methyl)$U_{eq}$(C). An O-bound H atom was initially located in a differece Fourier map and then treated as a riding atom, with O—H = 0.85 Å and with $U_{iso}$(H) = 1.5$U_{eq}$(O). The four O atoms of perchlorate anion were disordered over two sets of sites and refined with occupancy factors of 0.481 (8) for O8, O9, O10 and O11 and 0.519 (8) for O8′, O9′, O10′ and O11′ atoms. The command 'isor 0.01′ was used to restrict the ADP of the above eight O atoms.

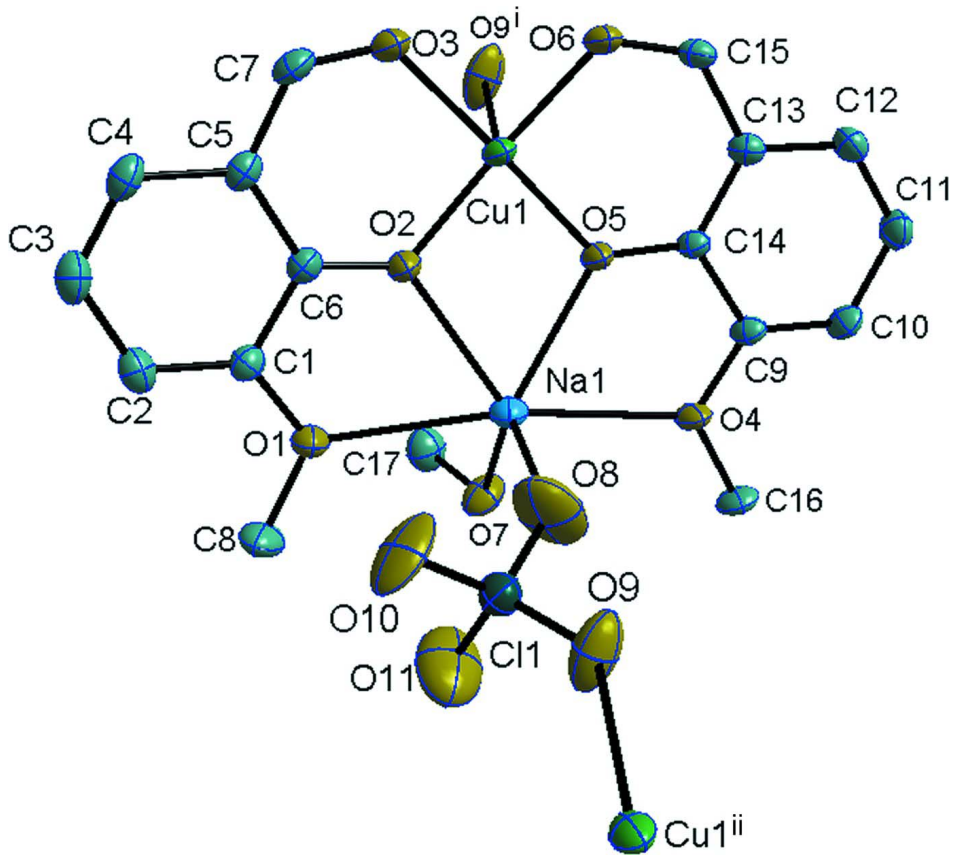


**Figure 1**

The asymmetric unit of the title compound, showing 30% probability displacement ellipsoids. H atoms and 0.519-occupied O atoms of the perchlorate anion are not shown. [Symmetry codes: (i) x, y-1, z; (ii) x, 1+y, z.]

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$\beta = 84.24$ (3)°
$\gamma = 68.25$ (3)°
$V = 1015.6$ (4) Å$^3$
$Z = 2$
$F(000) = 530$
$D_x = 1.701$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 8587 reflections
$\theta = 3.0$–$27.6$°
$\mu = 1.29$ mm$^{-1}$
$T = 293$ K
Block, green
0.43 × 0.28 × 0.28 mm

*Data collection*

Rigaku R-AXIS RAPID diffractometer
Radiation source: rotation anode
Graphite monochromator
$\omega$ scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.610$, $T_{max} = 0.714$
9778 measured reflections
4591 independent reflections

3948 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.0°$
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -20 \rightarrow 20$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.108$
$S = 1.11$
4591 reflections
321 parameters
48 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0586P)^2 + 0.4273P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.58$ e Å$^{-3}$
$\Delta\rho_{min} = -0.59$ e Å$^{-3}$
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.035 (3)

*Special details*

**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* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| C1 | 0.4762 (3) | 0.6763 (3) | 0.08377 (17) | 0.0364 (5) | |
| C2 | 0.5719 (4) | 0.6802 (4) | 0.00596 (19) | 0.0458 (6) | |
| H2 | 0.5263 | 0.7663 | −0.0374 | 0.055* | |
| C3 | 0.7386 (4) | 0.5555 (4) | −0.0092 (2) | 0.0537 (7) | |
| H3 | 0.8026 | 0.5604 | −0.0623 | 0.064* | |
| C4 | 0.8070 (4) | 0.4280 (4) | 0.0531 (2) | 0.0484 (7) | |
| H4 | 0.9171 | 0.3459 | 0.0424 | 0.058* | |
| C5 | 0.7105 (3) | 0.4198 (3) | 0.13468 (17) | 0.0374 (5) | |
| C6 | 0.5417 (3) | 0.5456 (3) | 0.15163 (16) | 0.0341 (5) | |
| C7 | 0.7836 (3) | 0.2828 (3) | 0.1967 (2) | 0.0433 (6) | |
| H7 | 0.8926 | 0.2054 | 0.1797 | 0.052* | |
| C8 | 0.2420 (5) | 0.9285 (4) | 0.0431 (2) | 0.0582 (8) | |
| H8A | 0.3249 | 0.9853 | 0.0322 | 0.087* | |
| H8B | 0.1275 | 0.9990 | 0.0651 | 0.087* | |
| H8C | 0.2256 | 0.8945 | −0.0100 | 0.087* | |
| C9 | 0.0881 (3) | 0.6812 (3) | 0.48246 (16) | 0.0332 (5) | |
| C10 | 0.0140 (3) | 0.6796 (3) | 0.56545 (18) | 0.0401 (6) | |
| H10 | −0.0893 | 0.7658 | 0.5797 | 0.048* | |
| C11 | 0.0922 (4) | 0.5491 (4) | 0.62961 (18) | 0.0451 (6) | |
| H11 | 0.0403 | 0.5495 | 0.6859 | 0.054* | |

| | | | | | |
|---|---|---|---|---|---|
| C12 | 0.2432 (4) | 0.4225 (3) | 0.60967 (17) | 0.0419 (6) | |
| H12 | 0.2955 | 0.3374 | 0.6526 | 0.050* | |
| C13 | 0.3218 (3) | 0.4197 (3) | 0.52328 (17) | 0.0344 (5) | |
| C14 | 0.2437 (3) | 0.5486 (3) | 0.45824 (15) | 0.0302 (5) | |
| C15 | 0.4787 (3) | 0.2836 (3) | 0.50530 (18) | 0.0379 (5) | |
| H15 | 0.5227 | 0.2051 | 0.5523 | 0.046* | |
| C16 | −0.1374 (4) | 0.9355 (3) | 0.4313 (2) | 0.0482 (7) | |
| H16A | −0.2361 | 0.8969 | 0.4426 | 0.072* | |
| H16B | −0.1606 | 1.0157 | 0.3810 | 0.072* | |
| H16C | −0.1257 | 0.9829 | 0.4807 | 0.072* | |
| C17 | −0.1080 (5) | 0.7533 (5) | 0.1549 (3) | 0.0673 (9) | |
| H17A | 0.0087 | 0.6922 | 0.1305 | 0.101* | |
| H17B | −0.1874 | 0.8128 | 0.1089 | 0.101* | |
| H17C | −0.1579 | 0.6806 | 0.1903 | 0.101* | |
| Cl1 | 0.36690 (9) | 1.08254 (8) | 0.25272 (5) | 0.04494 (18) | |
| Cu1 | 0.50540 (4) | 0.39856 (3) | 0.32609 (2) | 0.03585 (13) | |
| Na1 | 0.19514 (14) | 0.77412 (13) | 0.26850 (7) | 0.0424 (3) | |
| O1 | 0.3134 (3) | 0.7898 (2) | 0.10574 (13) | 0.0450 (4) | |
| O2 | 0.4454 (2) | 0.5493 (2) | 0.22418 (12) | 0.0426 (4) | |
| O3 | 0.7213 (3) | 0.2523 (2) | 0.27085 (13) | 0.0456 (5) | |
| O4 | 0.0270 (2) | 0.8028 (2) | 0.41576 (13) | 0.0429 (4) | |
| O5 | 0.3060 (2) | 0.5559 (2) | 0.37745 (11) | 0.0372 (4) | |
| O6 | 0.5644 (2) | 0.2566 (2) | 0.43425 (13) | 0.0424 (4) | |
| O7 | −0.0898 (3) | 0.8613 (3) | 0.20606 (16) | 0.0603 (6) | |
| H71 | −0.1953 | 0.9215 | 0.2223 | 0.090* | |
| O8 | 0.313 (2) | 0.9655 (12) | 0.2973 (6) | 0.134 (4) | 0.481 (8) |
| O9 | 0.3691 (13) | 1.1775 (13) | 0.3156 (6) | 0.090 (3) | 0.481 (8) |
| O10 | 0.5238 (9) | 1.0233 (14) | 0.2027 (7) | 0.104 (4) | 0.481 (8) |
| O11 | 0.2316 (12) | 1.1649 (14) | 0.1896 (6) | 0.134 (4) | 0.481 (8) |
| O8′ | 0.2175 (7) | 1.0358 (9) | 0.2565 (7) | 0.093 (3) | 0.519 (8) |
| O9′ | 0.3203 (10) | 1.2409 (8) | 0.2718 (7) | 0.086 (3) | 0.519 (8) |
| O10′ | 0.4646 (19) | 1.0763 (15) | 0.1746 (6) | 0.140 (4) | 0.519 (8) |
| O11′ | 0.5004 (15) | 0.9750 (12) | 0.3065 (8) | 0.164 (5) | 0.519 (8) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0334 (11) | 0.0377 (12) | 0.0389 (13) | −0.0130 (10) | −0.0007 (10) | −0.0073 (10) |
| C2 | 0.0491 (15) | 0.0542 (16) | 0.0385 (14) | −0.0258 (13) | 0.0003 (12) | −0.0023 (12) |
| C3 | 0.0503 (16) | 0.070 (2) | 0.0445 (15) | −0.0287 (15) | 0.0133 (13) | −0.0103 (14) |
| C4 | 0.0365 (13) | 0.0568 (17) | 0.0508 (16) | −0.0156 (12) | 0.0138 (12) | −0.0175 (13) |
| C5 | 0.0322 (11) | 0.0395 (13) | 0.0410 (14) | −0.0121 (10) | 0.0045 (10) | −0.0126 (10) |
| C6 | 0.0318 (11) | 0.0336 (12) | 0.0370 (12) | −0.0113 (10) | 0.0014 (10) | −0.0087 (10) |
| C7 | 0.0299 (11) | 0.0374 (13) | 0.0552 (16) | −0.0022 (10) | 0.0055 (11) | −0.0140 (12) |
| C8 | 0.0620 (19) | 0.0440 (16) | 0.0535 (18) | −0.0038 (14) | −0.0136 (15) | 0.0062 (13) |
| C9 | 0.0264 (10) | 0.0290 (11) | 0.0407 (13) | −0.0062 (9) | 0.0004 (9) | −0.0047 (9) |
| C10 | 0.0316 (11) | 0.0404 (13) | 0.0439 (14) | −0.0077 (10) | 0.0057 (10) | −0.0111 (11) |
| C11 | 0.0447 (14) | 0.0531 (16) | 0.0359 (13) | −0.0170 (12) | 0.0050 (11) | −0.0076 (11) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C12 | 0.0482 (14) | 0.0424 (14) | 0.0327 (12) | −0.0156 (12) | −0.0048 (11) | 0.0017 (10) |
| C13 | 0.0321 (11) | 0.0312 (11) | 0.0384 (13) | −0.0103 (9) | −0.0040 (10) | −0.0015 (9) |
| C14 | 0.0259 (10) | 0.0265 (10) | 0.0351 (12) | −0.0063 (9) | −0.0003 (9) | −0.0037 (9) |
| C15 | 0.0342 (12) | 0.0293 (11) | 0.0428 (13) | −0.0052 (10) | −0.0073 (10) | 0.0053 (10) |
| C16 | 0.0365 (13) | 0.0316 (13) | 0.0631 (18) | 0.0043 (11) | −0.0030 (12) | −0.0086 (12) |
| C17 | 0.074 (2) | 0.075 (2) | 0.060 (2) | −0.033 (2) | −0.0058 (18) | −0.0119 (18) |
| Cl1 | 0.0447 (3) | 0.0444 (4) | 0.0470 (4) | −0.0179 (3) | 0.0014 (3) | −0.0071 (3) |
| Cu1 | 0.03095 (18) | 0.02748 (18) | 0.0382 (2) | 0.00017 (12) | 0.00257 (12) | −0.00201 (12) |
| Na1 | 0.0378 (5) | 0.0354 (5) | 0.0444 (6) | −0.0028 (4) | −0.0055 (4) | −0.0013 (4) |
| O1 | 0.0428 (10) | 0.0383 (10) | 0.0424 (10) | −0.0039 (8) | −0.0028 (8) | 0.0017 (8) |
| O2 | 0.0382 (9) | 0.0373 (9) | 0.0375 (9) | 0.0003 (7) | 0.0040 (8) | −0.0005 (7) |
| O3 | 0.0391 (9) | 0.0340 (9) | 0.0501 (11) | 0.0003 (8) | 0.0036 (8) | −0.0033 (8) |
| O4 | 0.0375 (9) | 0.0287 (8) | 0.0461 (10) | 0.0041 (7) | 0.0032 (8) | −0.0005 (7) |
| O5 | 0.0335 (8) | 0.0295 (8) | 0.0352 (9) | 0.0016 (7) | 0.0038 (7) | −0.0006 (7) |
| O6 | 0.0392 (9) | 0.0285 (9) | 0.0461 (10) | 0.0017 (7) | −0.0020 (8) | −0.0006 (7) |
| O7 | 0.0401 (10) | 0.0648 (14) | 0.0727 (15) | −0.0083 (10) | −0.0068 (10) | −0.0239 (12) |
| O8 | 0.216 (9) | 0.107 (6) | 0.119 (6) | −0.117 (6) | −0.013 (6) | 0.018 (5) |
| O9 | 0.090 (5) | 0.121 (7) | 0.091 (5) | −0.064 (5) | 0.026 (4) | −0.064 (5) |
| O10 | 0.035 (3) | 0.137 (7) | 0.124 (7) | 0.007 (3) | 0.012 (3) | −0.073 (6) |
| O11 | 0.100 (5) | 0.169 (8) | 0.097 (5) | −0.007 (5) | −0.034 (4) | −0.001 (5) |
| O8′ | 0.046 (3) | 0.078 (4) | 0.174 (7) | −0.031 (3) | 0.009 (3) | −0.059 (5) |
| O9′ | 0.059 (3) | 0.049 (3) | 0.157 (7) | −0.021 (3) | 0.013 (4) | −0.038 (4) |
| O10′ | 0.193 (10) | 0.154 (8) | 0.071 (5) | −0.077 (7) | 0.044 (6) | −0.005 (5) |
| O11′ | 0.165 (7) | 0.126 (6) | 0.171 (7) | −0.033 (5) | −0.086 (6) | 0.073 (6) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—O1 | 1.367 (3) | C16—O4 | 1.432 (3) |
| C1—C2 | 1.367 (4) | C16—H16A | 0.9600 |
| C1—C6 | 1.427 (4) | C16—H16B | 0.9600 |
| C2—C3 | 1.407 (4) | C16—H16C | 0.9600 |
| C2—H2 | 0.9300 | C17—O7 | 1.396 (4) |
| C3—C4 | 1.360 (5) | C17—H17A | 0.9600 |
| C3—H3 | 0.9300 | C17—H17B | 0.9600 |
| C4—C5 | 1.422 (4) | C17—H17C | 0.9600 |
| C4—H4 | 0.9300 | Cl1—O8 | 1.347 (7) |
| C5—C7 | 1.413 (4) | Cl1—O10 | 1.373 (7) |
| C5—C6 | 1.428 (3) | Cl1—O10′ | 1.373 (9) |
| C6—O2 | 1.297 (3) | Cl1—O11′ | 1.390 (8) |
| C7—O3 | 1.242 (3) | Cl1—O8′ | 1.392 (5) |
| C7—H7 | 0.9300 | Cl1—O9 | 1.395 (8) |
| C8—O1 | 1.426 (3) | Cl1—O9′ | 1.396 (7) |
| C8—H8A | 0.9600 | Cl1—O11 | 1.439 (8) |
| C8—H8B | 0.9600 | Cu1—O5 | 1.8890 (18) |
| C8—H8C | 0.9600 | Cu1—O2 | 1.8941 (19) |
| C9—C10 | 1.365 (4) | Cu1—O6 | 1.932 (2) |
| C9—O4 | 1.365 (3) | Cu1—O3 | 1.944 (2) |
| C9—C14 | 1.426 (3) | Cu1—O9$^{i}$ | 2.614 (11) |

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| C10—C11 | 1.407 (4) | Cu1—O9′$^{i}$ | 2.650 (8) |
| C10—H10 | 0.9300 | Cu1—Na1 | 3.4010 (17) |
| C11—C12 | 1.358 (4) | Na1—O5 | 2.342 (2) |
| C11—H11 | 0.9300 | Na1—O8 | 2.349 (9) |
| C12—C13 | 1.424 (4) | Na1—O7 | 2.365 (2) |
| C12—H12 | 0.9300 | Na1—O2 | 2.379 (2) |
| C13—C14 | 1.408 (3) | Na1—O8′ | 2.390 (7) |
| C13—C15 | 1.423 (3) | Na1—O4 | 2.533 (2) |
| C14—O5 | 1.306 (3) | Na1—O1 | 2.614 (2) |
| C15—O6 | 1.246 (3) | O7—H71 | 0.8500 |
| C15—H15 | 0.9300 | | |

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|---|---|---|---|
| O1—C1—C2 | 125.9 (3) | O11′—Cl1—O8′ | 111.4 (6) |
| O1—C1—C6 | 113.0 (2) | O8—Cl1—O9 | 104.4 (6) |
| C2—C1—C6 | 121.1 (2) | O10—Cl1—O9 | 116.6 (6) |
| C1—C2—C3 | 120.7 (3) | O10′—Cl1—O9′ | 105.4 (7) |
| C1—C2—H2 | 119.6 | O11′—Cl1—O9′ | 110.6 (6) |
| C3—C2—H2 | 119.6 | O8′—Cl1—O9′ | 112.5 (4) |
| C4—C3—C2 | 120.5 (3) | O8—Cl1—O11 | 104.6 (7) |
| C4—C3—H3 | 119.7 | O10—Cl1—O11 | 103.6 (6) |
| C2—C3—H3 | 119.7 | O9—Cl1—O11 | 113.9 (6) |
| C3—C4—C5 | 120.1 (3) | O5—Cu1—O2 | 83.82 (8) |
| C3—C4—H4 | 119.9 | O5—Cu1—O6 | 93.45 (8) |
| C5—C4—H4 | 119.9 | O2—Cu1—O6 | 176.21 (8) |
| C7—C5—C4 | 118.3 (2) | O5—Cu1—O3 | 174.49 (8) |
| C7—C5—C6 | 121.4 (2) | O2—Cu1—O3 | 93.50 (9) |
| C4—C5—C6 | 120.2 (3) | O6—Cu1—O3 | 89.00 (8) |
| O2—C6—C1 | 118.2 (2) | O2—Cu1—O9$^{i}$ | 107.1 (2) |
| O2—C6—C5 | 124.5 (2) | O3—Cu1—O9$^{i}$ | 84.5 (2) |
| C1—C6—C5 | 117.2 (2) | O5—Cu1—O9$^{i}$ | 100.9 (2) |
| O3—C7—C5 | 128.4 (2) | O6—Cu1—O9$^{i}$ | 75.9 (2) |
| O3—C7—H7 | 115.8 | O2—Cu1—O9′$^{i}$ | 88.9 (2) |
| C5—C7—H7 | 115.8 | O3—Cu1—O9′$^{i}$ | 87.86 (19) |
| O1—C8—H8A | 109.5 | O5—Cu1—O9′$^{i}$ | 96.87 (19) |
| O1—C8—H8B | 109.5 | O6—Cu1—O9′$^{i}$ | 94.0 (2) |
| H8A—C8—H8B | 109.5 | O5—Na1—O8 | 104.4 (3) |
| O1—C8—H8C | 109.5 | O5—Na1—O7 | 126.05 (9) |
| H8A—C8—H8C | 109.5 | O8—Na1—O7 | 120.1 (3) |
| H8B—C8—H8C | 109.5 | O5—Na1—O2 | 64.72 (7) |
| C10—C9—O4 | 125.8 (2) | O8—Na1—O2 | 106.8 (4) |
| C10—C9—C14 | 120.8 (2) | O7—Na1—O2 | 121.84 (9) |
| O4—C9—C14 | 113.4 (2) | O5—Na1—O8′ | 127.7 (2) |
| C9—C10—C11 | 120.7 (2) | O8—Na1—O8′ | 24.3 (3) |
| C9—C10—H10 | 119.6 | O7—Na1—O8′ | 96.63 (19) |
| C11—C10—H10 | 119.6 | O2—Na1—O8′ | 120.27 (15) |
| C12—C11—C10 | 120.3 (2) | O5—Na1—O4 | 63.79 (7) |
| C12—C11—H11 | 119.9 | O8—Na1—O4 | 87.9 (3) |
| C10—C11—H11 | 119.9 | O7—Na1—O4 | 87.65 (8) |

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| C11—C12—C13 | 120.2 (2) | O2—Na1—O4 | 128.46 (8) |
| C11—C12—H12 | 119.9 | O8′—Na1—O4 | 93.2 (2) |
| C13—C12—H12 | 119.9 | O5—Na1—O1 | 126.62 (8) |
| C14—C13—C15 | 121.7 (2) | O8—Na1—O1 | 92.0 (3) |
| C14—C13—C12 | 120.1 (2) | O7—Na1—O1 | 82.97 (9) |
| C15—C13—C12 | 118.2 (2) | O2—Na1—O1 | 61.92 (7) |
| O5—C14—C13 | 124.3 (2) | O8′—Na1—O1 | 82.4 (2) |
| O5—C14—C9 | 117.9 (2) | O4—Na1—O1 | 169.07 (7) |
| C13—C14—C9 | 117.9 (2) | C1—O1—C8 | 116.7 (2) |
| O6—C15—C13 | 128.0 (2) | C1—O1—Na1 | 118.00 (15) |
| O6—C15—H15 | 116.0 | C8—O1—Na1 | 123.66 (18) |
| C13—C15—H15 | 116.0 | C6—O2—Cu1 | 127.00 (16) |
| O4—C16—H16A | 109.5 | C6—O2—Na1 | 126.71 (16) |
| O4—C16—H16B | 109.5 | Cu1—O2—Na1 | 104.90 (9) |
| H16A—C16—H16B | 109.5 | C7—O3—Cu1 | 124.61 (17) |
| O4—C16—H16C | 109.5 | C9—O4—C16 | 117.8 (2) |
| H16A—C16—H16C | 109.5 | C9—O4—Na1 | 118.86 (14) |
| H16B—C16—H16C | 109.5 | C16—O4—Na1 | 123.15 (17) |
| O7—C17—H17A | 109.5 | C14—O5—Cu1 | 127.46 (15) |
| O7—C17—H17B | 109.5 | C14—O5—Na1 | 125.99 (14) |
| H17A—C17—H17B | 109.5 | Cu1—O5—Na1 | 106.52 (8) |
| O7—C17—H17C | 109.5 | C15—O6—Cu1 | 125.08 (16) |
| H17A—C17—H17C | 109.5 | C17—O7—Na1 | 114.4 (2) |
| H17B—C17—H17C | 109.5 | C17—O7—H71 | 108.0 |
| O8—Cl1—O10 | 113.3 (8) | Na1—O7—H71 | 132.5 |
| O10′—Cl1—O11′ | 100.0 (8) | Cl1—O8—Na1 | 138.4 (7) |
| O10′—Cl1—O8′ | 116.1 (7) | Cl1—O8′—Na1 | 131.5 (4) |

Symmetry code: (i) $x, y-1, z$.

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O7—H71···O10$^{ii}$ | 0.85 | 2.11 | 2.874 (7) | 149 |
| O7—H71···O11′$^{ii}$ | 0.85 | 2.55 | 3.334 (13) | 154 |

Symmetry code: (ii) $x-1, y, z$.