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## Structure Reports

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catena-Poly[[bis( $\mu$ -2-formyl-6-methoxyphenolato)copper(II)sodium]- $\mu$ -nitrate]

Po Gao, Hai-Ge Hou, Ting Gao,\* Jing-Lin Yang and Yu Yang

School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, People's Republic of China

Correspondence e-mail: gaoting1218@yahoo.com.cn

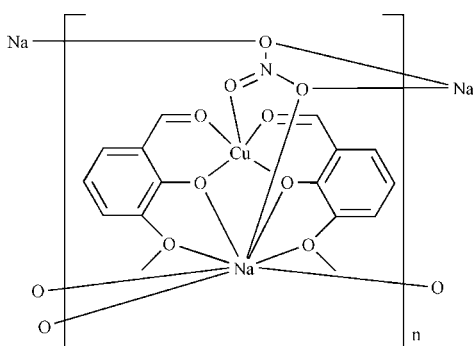
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.021;  $wR$  factor = 0.057; data-to-parameter ratio = 15.4.

In the title heterodinuclear complex,  $[\text{CuNa}(\text{C}_8\text{H}_7\text{O}_3)_2(\text{NO}_3)]_n$ , the  $\text{Cu}^{\text{II}}$  ion is five-coordinated in a square-pyramidal arrangement by four atoms of two different ligand molecules in equatorial positions and one remote nitrate O atom in the apical position. The  $\text{Na}^+$  ion is eight-coordinated by four ligand O atoms and four nitrate O atoms. The ligand links the  $\text{Cu}^{\text{II}}$  and Na ions, forming a layered arrangement extending parallel to (001).

## Related literature

For similar nickel–sodium complexes, see Costes *et al.* (1997*a,b*).



## Experimental

## Crystal data

 $[\text{CuNa}(\text{C}_8\text{H}_7\text{O}_3)_2(\text{NO}_3)]_n$   
 $M_r = 450.81$ 

 Orthorhombic,  $P2_12_12_1$   
 $a = 7.737$  (2) Å

 $b = 13.165$  (4) Å  
 $c = 16.889$  (6) Å  
 $V = 1720.2$  (9) Å<sup>3</sup>  
 $Z = 4$ 

 Mo  $K\alpha$  radiation  
 $\mu = 1.35$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.35 \times 0.33 \times 0.30$  mm

## Data collection

 Rigaku R-Axis RAPID  
 diffractometer  
 Absorption correction: multi-scan  
 (ABSCOR; Higashi, 1995)  
 $T_{\text{min}} = 0.648$ ,  $T_{\text{max}} = 0.691$ 

 16868 measured reflections  
 3926 independent reflections  
 3692 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.025$ 

## Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.021$   
 $wR(F^2) = 0.057$   
 $S = 1.03$   
 3926 reflections  
 255 parameters  
 H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.22$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.21$  e Å<sup>-3</sup>  
 Absolute structure: Flack (1983),  
 1671 Friedel pairs  
 Flack parameter: 0.007 (8)

Table 1

Selected bond lengths (Å).

|        |             |                      |             |
|--------|-------------|----------------------|-------------|
| Cu1—O5 | 1.8989 (12) | Na1—O8 <sup>i</sup>  | 2.4154 (17) |
| Cu1—O2 | 1.9074 (12) | Na1—O1               | 2.5249 (15) |
| Cu1—O6 | 1.9487 (12) | Na1—O4               | 2.6129 (16) |
| Cu1—O3 | 1.9608 (14) | Na1—O9 <sup>j</sup>  | 2.749 (2)   |
| Cu1—O7 | 2.3560 (14) | Na1—O9 <sup>ii</sup> | 2.755 (2)   |
| Na1—O2 | 2.3667 (16) | Na1—O8               | 2.937 (2)   |
| Na1—O5 | 2.3900 (14) |                      |             |

Symmetry codes: (i)  $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 1$ ; (ii)  $x - 1, y, z$ .

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

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG5236).

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## supporting information

*Acta Cryst.* (2011). E67, m1522 [doi:10.1107/S1600536811040025]

**catena-Poly[[bis( $\mu$ -2-formyl-6-methoxyphenolato)copper(II)sodium]- $\mu$ -nitrate]**

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**S1. Comment**

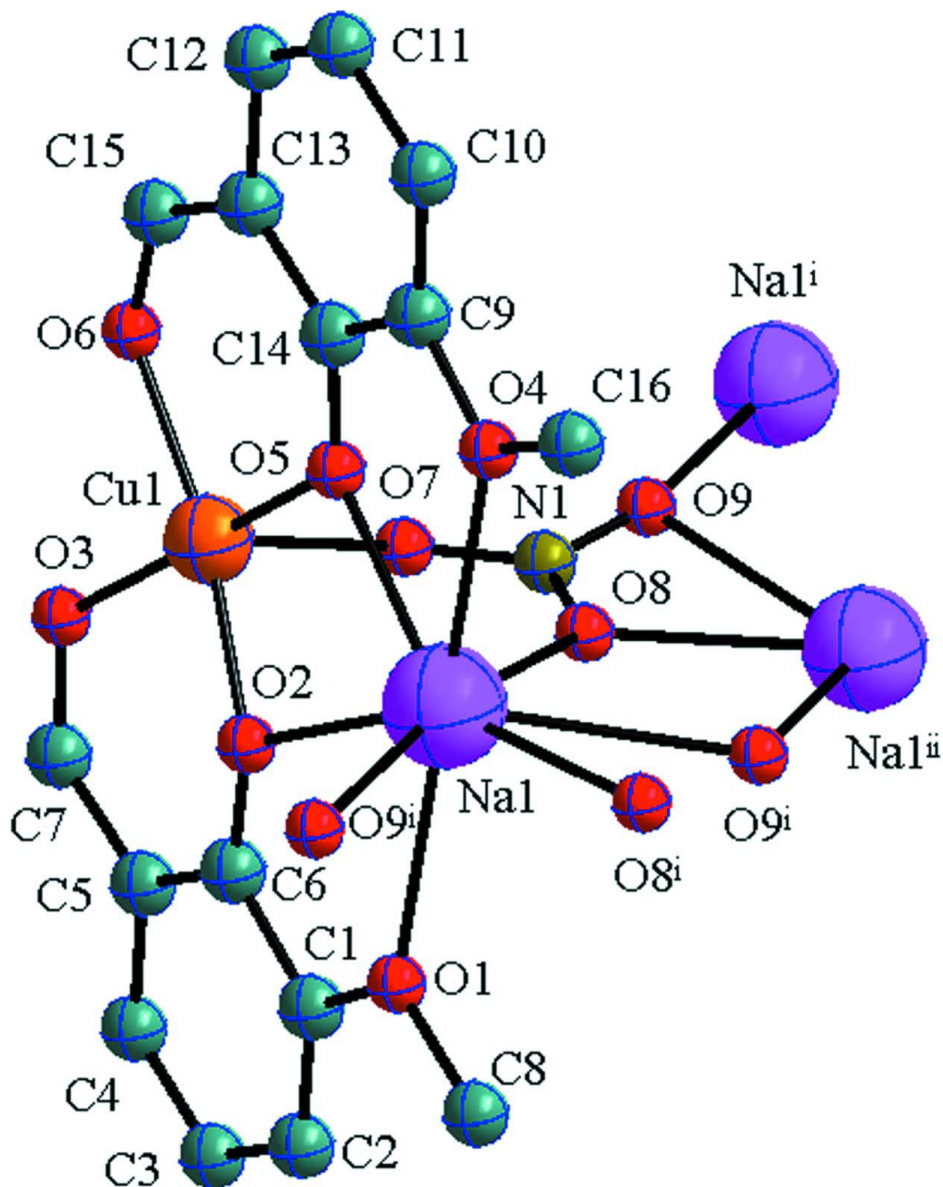
Orthovanillin is a commercial ligand that is able to chelate 3 d ions, mainly with copper ions. Furthermore, orthovanillin can also yield heterodinuclear 3 d-4f complexes and the first examples involve Cu—Ln complexes (Costes *et al.*, 1997*a,b*). We were interested in the nature of the products obtained by reacting a mononuclear 3 d complex with alkali metal ions. As shown in Fig. 1, The Cu<sup>II</sup> is four-coordinated by two aldehyde oxygen atoms and two phenol oxygen atoms from the two orthovanillin ligands. The copper atom centre is inserted into the inner cavity. The Na ion is ligated by two hydroxyl oxygen atoms, two methoxyl oxygen atoms, two oxygen atoms of one bidentate nitrate counterion and two oxygen atoms of two different monodentate nitrate counterion. The Cu<sup>II</sup> and Na are bridged by the phenolic oxygen atoms, layered arrangement extending parallel to (001).

**S2. Experimental**

To a solution of *o*-vanillin (0.046 g, 0.20 mmol) in dichloromethane (5 ml) was added to a solution of copper(II) acetate monohydrate (0.040 g, 0.20 mmol) and sodium nitrate (0.086 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%. The crystals suitable for X-ray determination were obtained by slow diffusion of diethylether into the solution for one week. Analysis calculated for C<sub>16</sub>H<sub>14</sub>NCuNaO<sub>9</sub>: C 42.63, H 3.13, N 3.11%; Found: C 42.29, H 3.17, N, 3.22%.

**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 Å (aromatic C), C—H = 0.97 Å (methylene C), and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or C—H = 0.96 Å (methly C) and with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ .



**Figure 1**

The molecular structure of the the title compound, showing 30% probability displacement ellipsoids.

**catena-Poly[[bis( $\mu$ -2-formyl-6-methoxyphenolato)copper(II)sodium]-  $\mu$ -nitrato]**

*Crystal data*

[CuNa(C<sub>8</sub>H<sub>7</sub>O<sub>3</sub>)<sub>2</sub>(NO<sub>3</sub>)]

$M_r = 450.81$

Orthorhombic,  $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 7.737$  (2) Å

$b = 13.165$  (4) Å

$c = 16.889$  (6) Å

$V = 1720.2$  (9) Å<sup>3</sup>

$Z = 4$

$F(000) = 916$

$D_x = 1.741$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 15663 reflections

$\theta = 3.1$ – $27.5^\circ$

$\mu = 1.35$  mm<sup>-1</sup>

$T = 293$  K

Block, brown

$0.35 \times 0.33 \times 0.30$  mm

Data collection

|   |  |
|---|--|
| Rigaku R-AXIS RAPID diffractometer                        | 16868 measured reflections   |
| Radiation source: fine-focus sealed tube                  | 3926 independent reflections   |
| Graphite monochromator                                    | 3692 reflections with $I > 2\sigma(I)$                                 |
| $\omega$ scans  | $R_{\text{int}} = 0.025$   |
| Absorption correction: multi-scan (ABSCOR; Higashi, 1995) | $\theta_{\text{max}} = 27.5^\circ$ , $\theta_{\text{min}} = 3.1^\circ$ |
| $T_{\text{min}} = 0.648$ , $T_{\text{max}} = 0.691$       | $h = -9 \rightarrow 10$  |
|   | $k = -17 \rightarrow 16$   |
|   | $l = -21 \rightarrow 21$   |

Refinement

|  |  |
|--|--|
| Refinement on $F^2$  | Hydrogen site location: inferred from neighbouring sites     |
| Least-squares matrix: full                                     | H-atom parameters constrained                                |
| $R[F^2 > 2\sigma(F^2)] = 0.021$                                | $w = 1/[\sigma^2(F_o^2) + (0.0375P)^2]$                      |
| $wR(F^2) = 0.057$  | where $P = (F_o^2 + 2F_c^2)/3$                               |
| $S = 1.03$   | $(\Delta/\sigma)_{\text{max}} = 0.001$                       |
| 3926 reflections   | $\Delta\rho_{\text{max}} = 0.22 \text{ e } \text{\AA}^{-3}$  |
| 255 parameters   | $\Delta\rho_{\text{min}} = -0.21 \text{ e } \text{\AA}^{-3}$ |
| 0 restraints   | Absolute structure: Flack (1983), 1671 Friedel pairs         |
| Primary atom site location: structure-invariant direct methods | Absolute structure parameter: 0.007 (8)                      |
| Secondary atom site location: difference Fourier map           |  |

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 ( $\text{\AA}^2$ )

|     | $x$          | $y$          | $z$          | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| C1  | 0.0679 (2)   | 0.92359 (12) | 0.67688 (10) | 0.0321 (3)                       |
| C2  | 0.0859 (2)   | 1.02319 (13) | 0.70061 (11) | 0.0375 (4)                       |
| H2  | 0.0378       | 1.0749       | 0.6703       | 0.045*                           |
| C3  | 0.1765 (2)   | 1.04734 (13) | 0.77039 (12) | 0.0411 (4)                       |
| H3  | 0.1895       | 1.1148       | 0.7856       | 0.049*                           |
| C4  | 0.2450 (3)   | 0.97166 (13) | 0.81555 (10) | 0.0406 (4)                       |
| H4  | 0.3025       | 0.9878       | 0.8622       | 0.049*                           |
| C5  | 0.2298 (2)   | 0.86831 (12) | 0.79230 (10) | 0.0331 (3)                       |
| C6  | 0.14000 (19) | 0.84231 (11) | 0.72185 (10) | 0.0293 (3)                       |
| C7  | 0.3021 (2)   | 0.79245 (15) | 0.84132 (11) | 0.0401 (4)                       |
| H7  | 0.3452       | 0.8149       | 0.8897       | 0.048*                           |
| C8  | -0.0953 (3)  | 0.96653 (15) | 0.56154 (13) | 0.0484 (5)                       |
| H8A | -0.1781      | 1.0034       | 0.5926       | 0.073*                           |
| H8B | -0.1529      | 0.9341       | 0.5180       | 0.073*                           |
| H8C | -0.0095      | 1.0126       | 0.5416       | 0.073*                           |

|      |               |               |               |             |
|------|---------------|---------------|---------------|-------------|
| C9   | 0.0758 (2)    | 0.44760 (12)  | 0.54819 (9)   | 0.0309 (3)  |
| C10  | 0.0625 (3)    | 0.34687 (13)  | 0.52792 (12)  | 0.0421 (4)  |
| H10  | 0.0032        | 0.3281        | 0.4823        | 0.051*      |
| C11  | 0.1387 (3)    | 0.27166 (13)  | 0.57635 (13)  | 0.0495 (5)  |
| H11  | 0.1292        | 0.2036        | 0.5622        | 0.059*      |
| C12  | 0.2248 (3)    | 0.29714 (13)  | 0.64274 (12)  | 0.0446 (5)  |
| H12  | 0.2738        | 0.2466        | 0.6740        | 0.054*      |
| C13  | 0.2416 (3)    | 0.40139 (11)  | 0.66559 (10)  | 0.0337 (3)  |
| C14  | 0.1682 (2)    | 0.47851 (12)  | 0.61750 (9)   | 0.0287 (3)  |
| C15  | 0.3276 (2)    | 0.42379 (13)  | 0.73717 (11)  | 0.0379 (4)  |
| H15  | 0.3728        | 0.3688        | 0.7648        | 0.046*      |
| C16  | -0.0964 (3)   | 0.50378 (17)  | 0.43943 (13)  | 0.0513 (5)  |
| H16A | -0.0241       | 0.4728        | 0.4000        | 0.077*      |
| H16B | -0.1458       | 0.5650        | 0.4185        | 0.077*      |
| H16C | -0.1872       | 0.4577        | 0.4538        | 0.077*      |
| Cu1  | 0.25742 (3)   | 0.636953 (13) | 0.726538 (11) | 0.03049 (6) |
| N1   | 0.5362 (2)    | 0.72115 (11)  | 0.60308 (10)  | 0.0391 (3)  |
| Na1  | 0.03464 (14)  | 0.71081 (6)   | 0.56511 (5)   | 0.0556 (2)  |
| O1   | -0.01427 (18) | 0.89168 (9)   | 0.60950 (8)   | 0.0423 (3)  |
| O2   | 0.11760 (15)  | 0.74989 (9)   | 0.69651 (7)   | 0.0349 (3)  |
| O3   | 0.31612 (18)  | 0.69909 (10)  | 0.82857 (8)   | 0.0433 (3)  |
| O4   | 0.00468 (16)  | 0.52733 (9)   | 0.50775 (7)   | 0.0367 (3)  |
| O5   | 0.17851 (16)  | 0.57479 (8)   | 0.63174 (7)   | 0.0330 (2)  |
| O6   | 0.34982 (16)  | 0.50983 (9)   | 0.76779 (8)   | 0.0386 (3)  |
| O7   | 0.51745 (17)  | 0.70304 (11)  | 0.67537 (8)   | 0.0449 (3)  |
| O8   | 0.4100 (2)    | 0.74389 (12)  | 0.56117 (8)   | 0.0547 (4)  |
| O9   | 0.6790 (2)    | 0.7162 (2)    | 0.57232 (13)  | 0.0937 (7)  |

*Atomic displacement parameters (Å<sup>2</sup>)*

|     | $U^{11}$     | $U^{22}$    | $U^{33}$     | $U^{12}$     | $U^{13}$     | $U^{23}$    |
|-----|--------------|-------------|--------------|--------------|--------------|-------------|
| C1  | 0.0297 (8)   | 0.0350 (8)  | 0.0315 (8)   | 0.0009 (7)   | 0.0035 (7)   | -0.0002 (7) |
| C2  | 0.0381 (9)   | 0.0324 (8)  | 0.0421 (10)  | 0.0028 (7)   | 0.0080 (7)   | 0.0033 (7)  |
| C3  | 0.0414 (9)   | 0.0336 (8)  | 0.0482 (10)  | -0.0039 (7)  | 0.0074 (9)   | -0.0076 (8) |
| C4  | 0.0388 (9)   | 0.0458 (9)  | 0.0373 (8)   | -0.0037 (10) | 0.0026 (9)   | -0.0099 (7) |
| C5  | 0.0318 (8)   | 0.0379 (8)  | 0.0296 (7)   | 0.0008 (8)   | 0.0032 (6)   | -0.0020 (6) |
| C6  | 0.0266 (7)   | 0.0320 (7)  | 0.0294 (7)   | 0.0012 (6)   | 0.0037 (6)   | -0.0007 (6) |
| C7  | 0.0437 (10)  | 0.0507 (9)  | 0.0258 (8)   | 0.0024 (8)   | -0.0044 (7)  | -0.0043 (7) |
| C8  | 0.0524 (12)  | 0.0468 (10) | 0.0461 (11)  | 0.0120 (10)  | -0.0117 (9)  | 0.0078 (9)  |
| C9  | 0.0315 (8)   | 0.0313 (7)  | 0.0299 (8)   | 0.0006 (7)   | 0.0048 (7)   | 0.0017 (6)  |
| C10 | 0.0514 (10)  | 0.0351 (8)  | 0.0399 (9)   | -0.0018 (8)  | 0.0041 (8)   | -0.0086 (8) |
| C11 | 0.0703 (14)  | 0.0269 (7)  | 0.0513 (12)  | 0.0020 (9)   | 0.0068 (11)  | -0.0041 (8) |
| C12 | 0.0541 (12)  | 0.0288 (7)  | 0.0508 (10)  | 0.0105 (9)   | 0.0092 (10)  | 0.0069 (7)  |
| C13 | 0.0352 (8)   | 0.0291 (6)  | 0.0367 (8)   | 0.0024 (8)   | 0.0045 (8)   | 0.0056 (6)  |
| C14 | 0.0289 (7)   | 0.0278 (7)  | 0.0293 (8)   | 0.0006 (6)   | 0.0053 (6)   | 0.0029 (6)  |
| C15 | 0.0399 (9)   | 0.0345 (8)  | 0.0394 (10)  | 0.0085 (8)   | 0.0024 (8)   | 0.0116 (7)  |
| C16 | 0.0540 (12)  | 0.0548 (11) | 0.0453 (11)  | -0.0040 (10) | -0.0180 (10) | -0.0021 (9) |
| Cu1 | 0.03520 (10) | 0.02981 (9) | 0.02645 (10) | 0.00292 (9)  | -0.00451 (9) | 0.00259 (7) |

|     |             |            |             |              |             |             |
|-----|-------------|------------|-------------|--------------|-------------|-------------|
| N1  | 0.0461 (9)  | 0.0354 (7) | 0.0357 (8)  | -0.0090 (7)  | 0.0044 (7)  | 0.0047 (6)  |
| Na1 | 0.0954 (7)  | 0.0374 (4) | 0.0340 (4)  | 0.0132 (4)   | -0.0188 (4) | 0.0012 (3)  |
| O1  | 0.0518 (7)  | 0.0344 (6) | 0.0407 (7)  | 0.0082 (6)   | -0.0130 (6) | 0.0016 (5)  |
| O2  | 0.0404 (6)  | 0.0302 (5) | 0.0340 (6)  | 0.0051 (5)   | -0.0081 (5) | -0.0019 (5) |
| O3  | 0.0581 (8)  | 0.0437 (6) | 0.0282 (6)  | 0.0092 (6)   | -0.0082 (6) | 0.0006 (5)  |
| O4  | 0.0423 (7)  | 0.0344 (6) | 0.0334 (6)  | 0.0006 (6)   | -0.0082 (5) | 0.0009 (5)  |
| O5  | 0.0434 (6)  | 0.0244 (5) | 0.0312 (6)  | -0.0007 (5)  | -0.0066 (5) | 0.0042 (4)  |
| O6  | 0.0415 (6)  | 0.0402 (6) | 0.0343 (6)  | 0.0054 (5)   | -0.0075 (6) | 0.0078 (5)  |
| O7  | 0.0448 (7)  | 0.0593 (8) | 0.0305 (6)  | -0.0087 (6)  | -0.0033 (6) | 0.0084 (6)  |
| O8  | 0.0627 (9)  | 0.0642 (9) | 0.0373 (8)  | -0.0019 (8)  | -0.0063 (7) | 0.0162 (7)  |
| O9  | 0.0520 (10) | 0.158 (2)  | 0.0716 (13) | -0.0040 (12) | 0.0224 (9)  | 0.0250 (14) |

*Geometric parameters (Å, °)*

|          |             |                        |             |
|----------|-------------|------------------------|-------------|
| C1—O1    | 1.370 (2)   | C14—O5                 | 1.2925 (19) |
| C1—C2    | 1.378 (2)   | C15—O6                 | 1.257 (2)   |
| C1—C6    | 1.426 (2)   | C15—H15                | 0.9300      |
| C2—C3    | 1.407 (3)   | C16—O4                 | 1.428 (2)   |
| C2—H2    | 0.9300      | C16—H16A               | 0.9600      |
| C3—C4    | 1.362 (3)   | C16—H16B               | 0.9600      |
| C3—H3    | 0.9300      | C16—H16C               | 0.9600      |
| C4—C5    | 1.421 (2)   | Cu1—O5                 | 1.8989 (12) |
| C4—H4    | 0.9300      | Cu1—O2                 | 1.9074 (12) |
| C5—C7    | 1.413 (2)   | Cu1—O6                 | 1.9487 (12) |
| C5—C6    | 1.420 (2)   | Cu1—O3                 | 1.9608 (14) |
| C6—O2    | 1.3013 (19) | Cu1—O7                 | 2.3560 (14) |
| C7—O3    | 1.252 (2)   | Cu1—Na1                | 3.3688 (11) |
| C7—H7    | 0.9300      | N1—O9                  | 1.223 (2)   |
| C8—O1    | 1.421 (2)   | N1—O8                  | 1.243 (2)   |
| C8—H8A   | 0.9600      | N1—O7                  | 1.252 (2)   |
| C8—H8B   | 0.9600      | N1—Na1 <sup>i</sup>    | 2.978 (2)   |
| C8—H8C   | 0.9600      | Na1—O2                 | 2.3667 (16) |
| C9—O4    | 1.368 (2)   | Na1—O5                 | 2.3900 (14) |
| C9—C10   | 1.373 (2)   | Na1—O8 <sup>ii</sup>   | 2.4154 (17) |
| C9—C14   | 1.431 (2)   | Na1—O1                 | 2.5249 (15) |
| C10—C11  | 1.413 (3)   | Na1—O4                 | 2.6129 (16) |
| C10—H10  | 0.9300      | Na1—O9 <sup>ii</sup>   | 2.749 (2)   |
| C11—C12  | 1.347 (3)   | Na1—O9 <sup>iii</sup>  | 2.755 (2)   |
| C11—H11  | 0.9300      | Na1—O8                 | 2.937 (2)   |
| C12—C13  | 1.431 (2)   | Na1—N1 <sup>ii</sup>   | 2.978 (2)   |
| C12—H12  | 0.9300      | O8—Na1 <sup>i</sup>    | 2.4154 (17) |
| C13—C15  | 1.411 (3)   | O9—Na1 <sup>i</sup>    | 2.749 (2)   |
| C13—C14  | 1.419 (2)   | O9—Na1 <sup>iv</sup>   | 2.755 (2)   |
| O1—C1—C2 | 125.48 (15) | O8—N1—O7               | 120.68 (16) |
| O1—C1—C6 | 113.20 (14) | O9—N1—Na1 <sup>i</sup> | 67.31 (13)  |
| C2—C1—C6 | 121.31 (16) | O8—N1—Na1 <sup>i</sup> | 51.77 (9)   |
| C1—C2—C3 | 120.59 (16) | O7—N1—Na1 <sup>i</sup> | 170.58 (13) |

|               |             |   |             |
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| C1—C2—H2      | 119.7       | O2—Na1—O5                               | 66.12 (4)   |
| C3—C2—H2      | 119.7       | O2—Na1—O8 <sup>ii</sup>                 | 151.95 (6)  |
| C4—C3—C2      | 119.82 (16) | O5—Na1—O8 <sup>ii</sup>                 | 141.87 (6)  |
| C4—C3—H3      | 120.1       | O2—Na1—O1                               | 63.72 (4)   |
| C2—C3—H3      | 120.1       | O5—Na1—O1                               | 129.54 (5)  |
| C3—C4—C5      | 120.89 (17) | O8 <sup>ii</sup> —Na1—O1                | 88.25 (6)   |
| C3—C4—H4      | 119.6       | O2—Na1—O4                               | 124.94 (5)  |
| C5—C4—H4      | 119.6       | O5—Na1—O4                               | 61.52 (4)   |
| C7—C5—C6      | 120.96 (15) | O8 <sup>ii</sup> —Na1—O4                | 82.27 (5)   |
| C7—C5—C4      | 118.82 (16) | O1—Na1—O4                               | 165.61 (6)  |
| C6—C5—C4      | 120.21 (15) | O2—Na1—O9 <sup>ii</sup>                 | 127.27 (7)  |
| O2—C6—C5      | 124.49 (14) | O5—Na1—O9 <sup>ii</sup>                 | 118.04 (7)  |
| O2—C6—C1      | 118.32 (15) | O8 <sup>ii</sup> —Na1—O9 <sup>ii</sup>  | 47.97 (5)   |
| C5—C6—C1      | 117.18 (14) | O1—Na1—O9 <sup>ii</sup>                 | 88.98 (7)   |
| O3—C7—C5      | 128.84 (17) | O4—Na1—O9 <sup>ii</sup>                 | 92.63 (7)   |
| O3—C7—H7      | 115.6       | O2—Na1—O9 <sup>iii</sup>                | 102.93 (7)  |
| C5—C7—H7      | 115.6       | O5—Na1—O9 <sup>iii</sup>                | 117.63 (7)  |
| O1—C8—H8A     | 109.5       | O8 <sup>ii</sup> —Na1—O9 <sup>iii</sup> | 68.52 (6)   |
| O1—C8—H8B     | 109.5       | O1—Na1—O9 <sup>iii</sup>                | 79.21 (7)   |
| H8A—C8—H8B    | 109.5       | O4—Na1—O9 <sup>iii</sup>                | 87.24 (7)   |
| O1—C8—H8C     | 109.5       | O9 <sup>ii</sup> —Na1—O9 <sup>iii</sup> | 115.72 (6)  |
| H8A—C8—H8C    | 109.5       | O2—Na1—O8                               | 73.79 (5)   |
| H8B—C8—H8C    | 109.5       | O5—Na1—O8                               | 70.20 (5)   |
| O4—C9—C10     | 125.88 (16) | O8 <sup>ii</sup> —Na1—O8                | 109.77 (5)  |
| O4—C9—C14     | 113.03 (14) | O1—Na1—O8                               | 90.86 (5)   |
| C10—C9—C14    | 121.08 (16) | O4—Na1—O8                               | 102.50 (6)  |
| C9—C10—C11    | 120.06 (18) | O9 <sup>ii</sup> —Na1—O8                | 61.80 (5)   |
| C9—C10—H10    | 120.0       | O9 <sup>iii</sup> —Na1—O8               | 169.91 (7)  |
| C11—C10—H10   | 120.0       | O2—Na1—N1 <sup>ii</sup>                 | 145.87 (6)  |
| C12—C11—C10   | 120.92 (16) | O5—Na1—N1 <sup>ii</sup>                 | 132.26 (6)  |
| C12—C11—H11   | 119.5       | O8 <sup>ii</sup> —Na1—N1 <sup>ii</sup>  | 23.83 (5)   |
| C10—C11—H11   | 119.5       | O1—Na1—N1 <sup>ii</sup>                 | 90.01 (5)   |
| C11—C12—C13   | 120.54 (17) | O4—Na1—N1 <sup>ii</sup>                 | 85.69 (5)   |
| C11—C12—H12   | 119.7       | O9 <sup>ii</sup> —Na1—N1 <sup>ii</sup>  | 24.23 (5)   |
| C13—C12—H12   | 119.7       | O9 <sup>iii</sup> —Na1—N1 <sup>ii</sup> | 92.20 (6)   |
| C15—C13—C14   | 121.97 (15) | O8—Na1—N1 <sup>ii</sup>                 | 85.98 (5)   |
| C15—C13—C12   | 118.31 (16) | O2—Na1—Cu1                              | 33.40 (3)   |
| C14—C13—C12   | 119.70 (16) | O5—Na1—Cu1                              | 33.32 (3)   |
| O5—C14—C13    | 124.79 (15) | O8 <sup>ii</sup> —Na1—Cu1               | 171.94 (5)  |
| O5—C14—C9     | 117.52 (14) | O1—Na1—Cu1                              | 96.23 (4)   |
| C13—C14—C9    | 117.69 (15) | O4—Na1—Cu1                              | 94.51 (4)   |
| O6—C15—C13    | 127.26 (15) | O9 <sup>ii</sup> —Na1—Cu1               | 125.19 (5)  |
| O6—C15—H15    | 116.4       | O9 <sup>iii</sup> —Na1—Cu1              | 118.86 (6)  |
| C13—C15—H15   | 116.4       | O8—Na1—Cu1                              | 63.60 (3)   |
| O4—C16—H16A   | 109.5       | N1 <sup>ii</sup> —Na1—Cu1               | 148.94 (5)  |
| O4—C16—H16B   | 109.5       | C1—O1—C8                                | 117.75 (14) |
| H16A—C16—H16B | 109.5       | C1—O1—Na1                               | 117.80 (10) |
| O4—C16—H16C   | 109.5       | C8—O1—Na1                               | 123.41 (12) |

|               |             |  |             |
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| H16A—C16—H16C | 109.5       | C6—O2—Cu1                              | 124.46 (10) |
| H16B—C16—H16C | 109.5       | C6—O2—Na1                              | 123.21 (11) |
| O5—Cu1—O2     | 85.95 (5)   | Cu1—O2—Na1                             | 103.51 (5)  |
| O5—Cu1—O6     | 92.82 (5)   | C7—O3—Cu1                              | 122.72 (12) |
| O2—Cu1—O6     | 166.56 (5)  | C9—O4—C16                              | 117.21 (14) |
| O5—Cu1—O3     | 174.40 (6)  | C9—O4—Na1                              | 119.25 (10) |
| O2—Cu1—O3     | 92.28 (5)   | C16—O4—Na1                             | 123.29 (11) |
| O6—Cu1—O3     | 87.66 (6)   | C14—O5—Cu1                             | 126.82 (10) |
| O5—Cu1—O7     | 97.15 (5)   | C14—O5—Na1                             | 128.20 (11) |
| O2—Cu1—O7     | 95.67 (5)   | Cu1—O5—Na1                             | 102.93 (5)  |
| O6—Cu1—O7     | 97.76 (5)   | C15—O6—Cu1                             | 125.21 (11) |
| O3—Cu1—O7     | 88.31 (6)   | N1—O7—Cu1                              | 121.78 (11) |
| O5—Cu1—Na1    | 43.75 (4)   | N1—O8—Na1 <sup>i</sup>                 | 104.40 (12) |
| O2—Cu1—Na1    | 43.08 (4)   | N1—O8—Na1                              | 136.74 (11) |
| O6—Cu1—Na1    | 136.46 (4)  | Na1 <sup>i</sup> —O8—Na1               | 116.83 (6)  |
| O3—Cu1—Na1    | 135.18 (4)  | N1—O9—Na1 <sup>i</sup>                 | 88.46 (14)  |
| O7—Cu1—Na1    | 91.92 (4)   | N1—O9—Na1 <sup>iv</sup>                | 157.32 (17) |
| O9—N1—O8      | 118.74 (18) | Na1 <sup>i</sup> —O9—Na1 <sup>iv</sup> | 112.18 (7)  |
| O9—N1—O7      | 120.58 (18) |  |             |

Symmetry codes: (i)  $x+1/2, -y+3/2, -z+1$ ; (ii)  $x-1/2, -y+3/2, -z+1$ ; (iii)  $x-1, y, z$ ; (iv)  $x+1, y, z$ .