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Tetrakis(μ-acetato-κ^2O:O')-bis[(3-pyridinecarboxaldehyde-$\kappa N'$)]-dicopper(II)(*Cu*—*Cu*)

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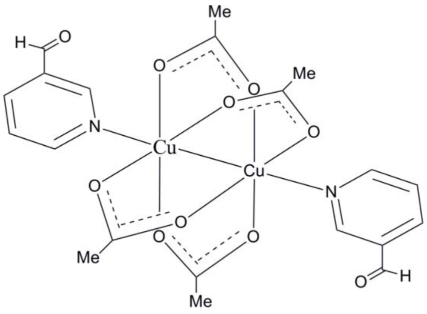
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.004 Å; R factor = 0.027; wR factor = 0.068; data-to-parameter ratio = 12.7.

The binuclear title compound, [$Cu_2(CH_3CO_2)_4(C_6H_5NO)$], is located about a center of inversion. The Cu^{II} atoms are connected [Cu—Cu = 2.6134 (5) Å] and bridged by four acetate ligands. Their distorted octahedral coordination geometry is completed by a terminal pyridine N atom of a 3-pyridincarboxaldehyde ligand. In the crystal, the complex molecules are linked by C—H⋯O hydrogen bonds, forming two-dimensional networks lying parallel to the *ab* plane. These networks are linked *via* C—H⋯O hydrogen bonds involving inversion-related 3-pyridinecarboxaldehyde ligands, forming a three dimensional supramolecular architecture.

Related literature

For related paddle-wheel structures, see: Aakeröy *et al.* (2003); Sieroń (2004); Fairuz *et al.* (2011); Trivedi *et al.* (2011). For Cu⋯Cu separations in related structures, see: Seco *et al.* (2004); Asem *et al.* (2011).



Experimental

Crystal data

[$Cu_2(C_2H_3O_2)_4(C_6H_5NO)$]
M_r = 577.48
Triclinic, $P\overline{1}$
a = 7.4099 (6) Å
b = 8.4298 (7) Å
c = 10.0254 (8) Å
α = 100.353 (1)°
β = 108.975 (1)°
γ = 98.679 (1)°
V = 567.61 (8) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.93 mm^{-1}
T = 100 K
0.48 × 0.21 × 0.17 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.448, $T_{\max}$ = 0.720
4118 measured reflections
1980 independent reflections
1921 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.018

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.068
S = 1.10
1980 reflections
156 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.41 e Å^{-3}
$\Delta\rho_{\min}$ = −0.36 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C3—H3⋯O1^{i}	0.93	2.43	3.262 (4)	148
C6—H6⋯O3^{ii}	0.93	2.56	3.449 (4)	159
C8—H8B⋯O3^{iii}	0.96	2.60	3.542 (3)	168
C10—H10C⋯O2^{iv}	0.96	2.48	3.420 (4)	167

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus-NT* (Bruker, 2001); data reduction: *SAINT-Plus-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 2012) and *Mercury* (Macrae *et al.* 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2505).

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Acta Cryst. (2012). E**68**, m1339–m1340   [doi:10.1107/S1600536812041074]

Tetrakis(μ-acetato-κ^2O:O')-bis[(3-pyridinecarboxaldehyde-$\kappa N'$)]dicopper(II)(*Cu*—*Cu*)

Adriana Cruz-Enriquez, Alberto Baez-Castro, Herbert Höpfl, Miguel Parra-Hake and Jose J. Campos-Gaxiola

S1. Comment

Bridged binuclear copper(II) complexes have been the subject of continuing interest because of their magneto-structural properties. Pyridine ligands have the potential to be used in the synthesis of supramolecular materials, particularly transition metal coordination polymers. Herein, we report on the synthesis and crystal structure of the new binuclear $Cu_2(OAc)_4L_2$ paddle-wheel complex with L = 3-pyridincarboxaldehyde.

The title complex (Fig. 1) is structurally similar to paddle-wheel structures of other $Cu_2(OAc)_4L_2$ complexes (Aakeröy *et al.*, 2003; Fairuz *et al.*, 2011; Seco *et al.*, 2004; Sieroń, 2004; Trivedi *et al.*, 2011). The binuclear molecule lies about an inversion center. Attached to the $Cu_2(OAc)_4$ core unit there are two apical pyridine groups from 3-pyridincarboxaldehyde ligands. The Cu—O distances [which vary from 1.9625 (19) - 1.9692 (17) Å], the Cu1—N1 distance [2.189 (2) Å], and the corresponding bond angles are consistent with the structurally similar Cu^{II}complexes mentioned above. Although the Cu1—Cu1^i separation of 2.6134 (6) Å [symmetry code: (i) -x+1, -y+1, -z+2] is towards the lower limit, it is within the range of values reported for other Cu^{II} paddle-wheel structures (Sieroń, 2004; Asem *et al.*, 2011).

In the crystal, the complex molecules are linked by C—H···O hydrogen bonds to form two-dimensional networks lying parallel to the ab plane (Table 1 and Fig. 2). These networks are linked via C-H···O hydrogen bonds involving inversion related 3-pyridincarboxaldehyde ligands forming a three dimensional supramolecular architecture (Table 1).

S2. Experimental

A mixture of 3-pyridincarboxaldehyde (0.05 g, 0.466 mmol) and $Cu(CH_3COO)_2H_2O$ (0.093 g, 0.466 mmol) dissolved in methanol (5 ml) was stirred for 2 h at room temperature to give a blue solution. After one week, blue crystals suitable for X-ray diffraction analysis had been formed, which were collected by filtration [Yield: 65%]. Spectroscopic and TGA data are given in the archived CIF.

S3. Refinement

The C-bound H-atoms were included in calculated positions and treated as riding atoms: C-H = 0.93 and 096 Å for CH and CH_3 H-atoms, respectively, with $U_{iso}(H) = k \times U_{eq}$(parent C-atom), where k = 1.5 for CH_3 H-atoms and = 1.2 for other H-atoms.

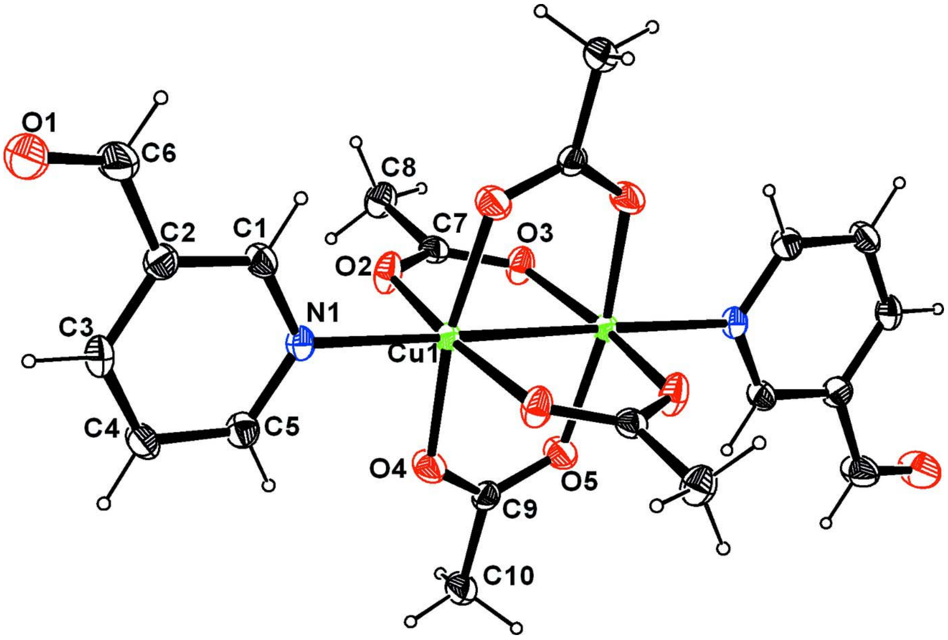

Figure 1

The molecular structure of the title complex, showing the atom-labelling scheme. The displacement ellipsoids are drawn at the 50% probability level. The unlabelled atoms are related by the symmetry code: -*x*+1, -*y*+1, -*z*+2.

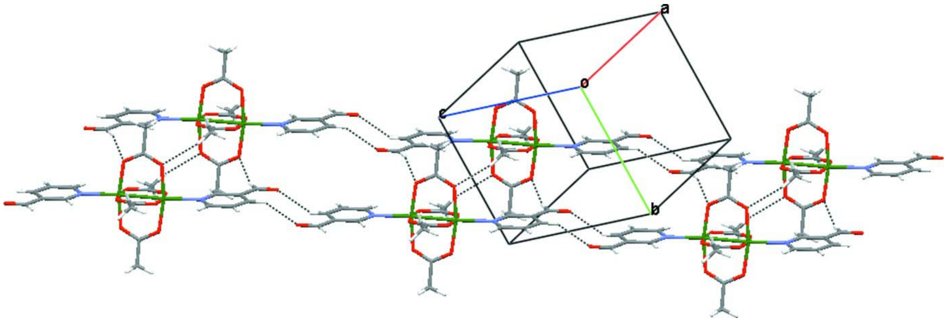

Figure 2

Perspective view of a fragment of the two-dimensional supramolecular network with the C—H···O hydrogen bonds shown as dashed lines.

Tetrakis(*μ*-acetato-κ^2*O*:*O*′)-bis[(3-pyridinecarboxaldehyde- *κN*′)]dicopper(II)(*Cu*—*Cu*)

Crystal data

$[Cu_2(C_2H_3O_2)_4(C_6H_5NO)]$
M_r = 577.48
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 7.4099 (6) Å
b = 8.4298 (7) Å
c = 10.0254 (8) Å
α = 100.353 (1)°
β = 108.975 (1)°
γ = 98.679 (1)°
V = 567.61 (8) Å^3

Z = 1
F(000) = 294
D_x = 1.689 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 3727 reflections
θ = 2.5–28.3°
μ = 1.93 mm^{-1}
T = 100 K
Rectangular prism, blue
0.48 × 0.21 × 0.17 mm

Data collection

Bruker SMART CCD area-detector diffractometer	4118 measured reflections
Radiation source: fine-focus sealed tube	1980 independent reflections
Graphite monochromator	1921 reflections with $I > 2\sigma(I)$
phi and ω scans	$R_{\text{int}} = 0.018$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{\text{max}} = 25.0°$, $\theta_{\text{min}} = 2.2°$
$T_{\text{min}} = 0.448$, $T_{\text{max}} = 0.720$	$h = -8 \rightarrow 8$
	$k = -8 \rightarrow 10$
	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.027$	H-atom parameters constrained
$wR(F^2) = 0.068$	$w = 1/[\sigma^2(F_o^2) + (0.0297P)^2 + 0.5378P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{\text{max}} = 0.001$
1980 reflections	$\Delta\rho_{\text{max}} = 0.41$ e Å^{-3}
156 parameters	$\Delta\rho_{\text{min}} = -0.36$ e Å^{-3}
0 restraints	
Primary atom site location: structure-invariant direct methods	

Special details

Experimental. Spectroscopic and TGA data for the title compound: IR (KBr, cm^{-1}): 3273, 3076, 2935, 2871, 1705, 1615, 1440, 1218, 1035, 690; TGA Calcd. for 2(C_6H_5NO): 37.07. Found: 37.53% (303 - 473 K).

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

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}
Cu1	0.56063 (4)	0.57222 (3)	0.91251 (3)	0.0137 (1)
O1	1.1945 (3)	0.9402 (3)	0.6523 (2)	0.0382 (7)
O2	0.6188 (3)	0.3569 (2)	0.85203 (19)	0.0232 (5)
O3	0.5192 (3)	0.2340 (2)	1.00330 (18)	0.0216 (5)
O4	0.2879 (2)	0.4870 (2)	0.77698 (18)	0.0235 (5)
O5	0.1855 (2)	0.3580 (2)	0.92442 (18)	0.0243 (5)
N1	0.6613 (3)	0.6761 (2)	0.7573 (2)	0.0155 (6)
C1	0.8501 (4)	0.7380 (3)	0.7858 (2)	0.0192 (7)
C2	0.9167 (4)	0.8063 (3)	0.6899 (3)	0.0203 (7)
C3	0.7811 (4)	0.8086 (3)	0.5568 (3)	0.0215 (8)
C4	0.5870 (4)	0.7427 (3)	0.5258 (3)	0.0223 (7)
C5	0.5325 (4)	0.6786 (3)	0.6284 (3)	0.0198 (7)
C6	1.1288 (4)	0.8746 (4)	0.7290 (3)	0.0306 (9)
C7	0.5933 (3)	0.2365 (3)	0.9070 (2)	0.0172 (7)
C8	0.6587 (4)	0.0847 (3)	0.8539 (3)	0.0230 (8)

C9	0.1593 (3)	0.3988 (3)	0.8058 (2)	0.0168 (7)
C10	−0.0418 (4)	0.3371 (3)	0.6896 (3)	0.0242 (8)
H1	0.94130	0.73520	0.87420	0.0230*
H3	0.82120	0.85370	0.49020	0.0260*
H4	0.49320	0.74120	0.43710	0.0270*
H5	0.40040	0.63520	0.60690	0.0240*
H6	1.21540	0.86630	0.81720	0.0370*
H8A	0.58970	0.04310	0.75100	0.0340*
H8B	0.63120	0.00150	0.90290	0.0340*
H8C	0.79690	0.11290	0.87380	0.0340*
H10A	−0.06390	0.22020	0.65090	0.0360*
H10B	−0.05110	0.39310	0.61300	0.0360*
H10C	−0.13850	0.35880	0.73070	0.0360*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0144 (2)	0.0153 (2)	0.0134 (2)	0.0035 (1)	0.0066 (1)	0.0051 (1)
O1	0.0245 (10)	0.0576 (14)	0.0370 (11)	0.0009 (9)	0.0121 (9)	0.0276 (10)
O2	0.0356 (10)	0.0191 (9)	0.0269 (9)	0.0118 (8)	0.0217 (8)	0.0106 (7)
O3	0.0309 (10)	0.0186 (9)	0.0244 (9)	0.0100 (7)	0.0174 (8)	0.0096 (7)
O4	0.0165 (9)	0.0326 (10)	0.0188 (8)	−0.0007 (8)	0.0039 (7)	0.0096 (7)
O5	0.0168 (9)	0.0343 (10)	0.0200 (9)	0.0000 (7)	0.0050 (7)	0.0103 (8)
N1	0.0195 (10)	0.0129 (10)	0.0157 (9)	0.0028 (8)	0.0083 (8)	0.0042 (8)
C1	0.0222 (13)	0.0214 (12)	0.0162 (11)	0.0070 (10)	0.0069 (10)	0.0085 (9)
C2	0.0211 (13)	0.0213 (13)	0.0226 (12)	0.0068 (10)	0.0102 (10)	0.0096 (10)
C3	0.0266 (14)	0.0243 (13)	0.0180 (12)	0.0052 (11)	0.0125 (11)	0.0079 (10)
C4	0.0231 (13)	0.0276 (14)	0.0146 (11)	0.0042 (11)	0.0042 (10)	0.0072 (10)
C5	0.0194 (12)	0.0199 (12)	0.0190 (12)	0.0018 (10)	0.0072 (10)	0.0042 (10)
C6	0.0220 (14)	0.0439 (17)	0.0291 (14)	0.0053 (12)	0.0082 (12)	0.0202 (13)
C7	0.0139 (11)	0.0195 (12)	0.0154 (11)	0.0018 (9)	0.0029 (9)	0.0033 (9)
C8	0.0263 (14)	0.0195 (13)	0.0260 (13)	0.0067 (10)	0.0128 (11)	0.0051 (10)
C9	0.0161 (12)	0.0176 (12)	0.0166 (11)	0.0048 (10)	0.0068 (10)	0.0018 (9)
C10	0.0187 (13)	0.0334 (15)	0.0181 (12)	0.0028 (11)	0.0053 (10)	0.0053 (10)

Geometric parameters (Å, º)

Cu1—O2	1.9643 (19)	C3—C4	1.371 (4)
Cu1—O4	1.9677 (17)	C4—C5	1.385 (4)
Cu1—N1	2.189 (2)	C7—C8	1.505 (4)
Cu1—O3^{i}	1.9625 (19)	C9—C10	1.506 (4)
Cu1—O5^{i}	1.9692 (17)	C1—H1	0.9300
O1—C6	1.204 (4)	C3—H3	0.9300
O2—C7	1.257 (3)	C4—H4	0.9300
O3—C7	1.258 (3)	C5—H5	0.9300
O4—C9	1.260 (3)	C6—H6	0.9300
O5—C9	1.260 (3)	C8—H8A	0.9600
N1—C1	1.333 (4)	C8—H8B	0.9600

N1—C5	1.340 (3)	C8—H8C	0.9600
C1—C2	1.386 (4)	C10—H10A	0.9600
C2—C3	1.391 (4)	C10—H10B	0.9600
C2—C6	1.483 (4)	C10—H10C	0.9600

O2—Cu1—O4	89.70 (8)	O3—C7—C8	117.9 (2)
O2—Cu1—N1	92.99 (8)	O4—C9—O5	125.2 (2)
O2—Cu1—O3^{i}	168.80 (8)	O4—C9—C10	117.59 (19)
O2—Cu1—O5^{i}	90.47 (8)	O5—C9—C10	117.3 (2)
O4—Cu1—N1	94.72 (7)	N1—C1—H1	118.00
O3^{i}—Cu1—O4	88.36 (8)	C2—C1—H1	119.00
O4—Cu1—O5^{i}	168.89 (7)	C2—C3—H3	121.00
O3^{i}—Cu1—N1	98.16 (7)	C4—C3—H3	121.00
O5^{i}—Cu1—N1	96.36 (7)	C3—C4—H4	120.00
O3^{i}—Cu1—O5^{i}	89.32 (8)	C5—C4—H4	120.00
Cu1—O2—C7	124.41 (17)	N1—C5—H5	118.00
Cu1^{i}—O3—C7	121.63 (16)	C4—C5—H5	119.00
Cu1—O4—C9	123.33 (14)	O1—C6—H6	118.00
Cu1^{i}—O5—C9	122.48 (15)	C2—C6—H6	118.00
Cu1—N1—C1	122.12 (14)	C7—C8—H8A	109.00
Cu1—N1—C5	120.33 (19)	C7—C8—H8B	110.00
C1—N1—C5	117.6 (2)	C7—C8—H8C	109.00
N1—C1—C2	123.1 (2)	H8A—C8—H8B	109.00
C1—C2—C3	118.7 (3)	H8A—C8—H8C	109.00
C1—C2—C6	120.3 (3)	H8B—C8—H8C	110.00
C3—C2—C6	121.0 (3)	C9—C10—H10A	109.00
C2—C3—C4	118.6 (3)	C9—C10—H10B	109.00
C3—C4—C5	119.1 (3)	C9—C10—H10C	110.00
N1—C5—C4	123.1 (3)	H10A—C10—H10B	109.00
O1—C6—C2	123.3 (3)	H10A—C10—H10C	110.00
O2—C7—O3	125.1 (2)	H10B—C10—H10C	109.00
O2—C7—C8	117.1 (2)		

O2—Cu1—N1—C1	−82.47 (19)	Cu1—O2—C7—C8	−176.00 (17)
O2—Cu1—N1—C5	97.24 (19)	Cu1—O2—C7—O3	3.4 (3)
O4—Cu1—N1—C1	−172.41 (18)	Cu1^{i}—O3—C7—O2	−2.2 (3)
O4—Cu1—N1—C5	7.30 (19)	Cu1^{i}—O3—C7—C8	177.20 (17)
O3^{i}—Cu1—N1—C1	98.57 (19)	Cu1—O4—C9—O5	2.2 (3)
O3^{i}—Cu1—N1—C5	−81.72 (19)	Cu1—O4—C9—C10	−177.83 (16)
O5^{i}—Cu1—N1—C1	8.34 (19)	Cu1^{i}—O5—C9—O4	−0.1 (3)
O5^{i}—Cu1—N1—C5	−171.95 (18)	Cu1^{i}—O5—C9—C10	179.91 (17)
O4—Cu1—O2—C7	−86.4 (2)	Cu1—N1—C1—C2	−179.13 (19)
N1—Cu1—O2—C7	178.9 (2)	C5—N1—C1—C2	1.2 (4)
O5^{i}—Cu1—O2—C7	82.5 (2)	Cu1—N1—C5—C4	179.93 (19)
O5—Cu1^{i}—O3—C7	85.16 (19)	C1—N1—C5—C4	−0.4 (4)
O4^{i}—Cu1^{i}—O3—C7	−83.97 (19)	N1—C1—C2—C6	179.4 (2)
N1^{i}—Cu1^{i}—O3—C7	−178.51 (18)	N1—C1—C2—C3	−0.9 (4)
O2—Cu1—O4—C9	80.85 (19)	C1—C2—C6—O1	−177.5 (3)

N1—Cu1—O4—C9	173.83 (18)	C6—C2—C3—C4	179.5 (3)
O3^{i}—Cu1—O4—C9	−88.12 (19)	C1—C2—C3—C4	−0.2 (4)
O3—Cu1^{i}—O5—C9	−86.94 (19)	C3—C2—C6—O1	2.8 (5)
O2^{i}—Cu1^{i}—O5—C9	81.86 (19)	C2—C3—C4—C5	0.9 (4)
N1^{i}—Cu1^{i}—O5—C9	174.92 (18)	C3—C4—C5—N1	−0.7 (4)

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···O1^{ii}	0.93	2.43	3.262 (4)	148
C6—H6···O3^{iii}	0.93	2.56	3.449 (4)	159
C8—H8*B*···O3^{iv}	0.96	2.60	3.542 (3)	168
C10—H10*C*···O2^{v}	0.96	2.48	3.420 (4)	167

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