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catena-Poly[[bis(nitrato- κ^2 O,O')-copper(II)]- μ -2,2'-(ethane-1,2-diylthio)-di-1,3,4-thiadiazole- κ^2 N⁴:N^{4'}]

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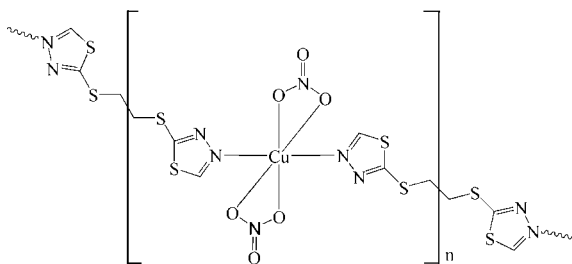
Received 20 November 2008; accepted 6 December 2008

Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{O}-\text{N}) = 0.006$ Å; disorder in main residue; R factor = 0.058; wR factor = 0.173; data-to-parameter ratio = 12.1.

In the title compound, $[\text{Cu}(\text{NO}_3)_2(\text{C}_6\text{H}_6\text{N}_4\text{S}_4)]_n$, the Cu^{II} atom, occupying a crystallographic inversion centre, is six-coordinated by two N atoms of two 2,2'-[1,2-ethanediybis(thio)]-bis[1,3,4-thiadiazole] ligands in *trans* positions, and four O atoms from two symmetry-related opposite nitrate anions, which are asymmetrically bonded, resulting in a strong distorted octahedral geometry of the central atom. The ethane group is equally disordered over two sites *via* another inversion centre. The bridging bidentate 2,2'-[1,2-ethanediybis(thio)]bis[1,3,4-thiadiazole] ligands link the Cu^{II} centres into a one-dimensional chain. The chains are interconnected *via* intermolecular $\text{S} \cdots \text{O}$ interactions [3.044 (4) and 3.084 (5) Å] and weak $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds, generating a three-dimensional supramolecular structure.

Related literature

For related *catena*-poly Cu(II) complexes, see, for example: Wang *et al.* (2008). For elongated Cu—O bonds see, for example: Lee & Barboiu (2004); Youngme *et al.* (2007). For $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds, see: Bhogala *et al.* (2005).



Experimental

Crystal data

$[\text{Cu}(\text{NO}_3)_2(\text{C}_6\text{H}_6\text{N}_4\text{S}_4)]$	$\gamma = 93.958$ (2)°
$M_r = 449.95$	$V = 367.88$ (9) Å ³
Triclinic, $P\bar{1}$	$Z = 1$
$a = 5.2143$ (8) Å	Mo $K\alpha$ radiation
$b = 7.0214$ (10) Å	$\mu = 2.09$ mm ⁻¹
$c = 10.6476$ (16) Å	$T = 296$ (2) K
$\alpha = 105.144$ (2)°	$0.48 \times 0.29 \times 0.04$ mm
$\beta = 100.000$ (2)°	

Data collection

Bruker SMART CCD area-detector diffractometer	1983 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 1997)	1336 independent reflections
$T_{\text{min}} = 0.432$, $T_{\text{max}} = 0.924$	1273 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.058$	1 restraint
$wR(F^2) = 0.173$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\text{max}} = 1.86$ e Å ⁻³
1336 reflections	$\Delta\rho_{\text{min}} = -0.50$ e Å ⁻³
110 parameters	

Table 1

Selected geometric parameters (Å, °).

Cu1—O1	2.588 (4)	Cu1—N2	2.007 (4)
Cu1—O3	1.971 (3)		
O1—Cu1—O3	54.74 (14)	O1—Cu1—O3 ⁱ	125.26 (14)
N2—Cu1—O3	89.02 (15)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{C1}-\text{H1A} \cdots \text{O1}^{\text{ii}}$	0.93	2.49	3.083 (6)	122

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

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); 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); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2137).

References

- Bhogala, B. R., Basavoju, S. & Nangia, A. (2005). *Cryst. Growth Des.* **5**, 1683–1686.
- Bruker (1997). SMART, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
- Lee, A. & Barboiu, M. (2004). *Acta Cryst.* **C60**, m156–m158.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

Wang, J. G., Qin, J. H., Hu, P. Z. & Zhao, B. T. (2008). *Z. Kristallogr. New Cryst. Struct.* **223**, 225–227.

Youngme, S., Chotkhun, T. & Chaichit, N. N. (2007). *Acta Cryst.* **C63**, m59–m61.

supporting information

Acta Cryst. (2009). E65, m80–m81 [doi:10.1107/S1600536808041202]

catena-Poly[[bis(nitrato- κ^2O,O')copper(II)]- μ -2,2'-(ethane-1,2-diyl-di-thio)di-1,3,4-thiadiazole- $\kappa^2N^4:N^{4'}$]

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S1. Comment

As shown in Fig. 1, the copper atom is coordinated by four O atoms from two chelating nitrate anions and two N atoms from two C; symmetry-related 2,2'-[1,2-ethanediybis(thio)]bis[1,3,4-thiadiazole] ligands. The geometry around the Cu(II) atom appears to be strong distorted octahedral, which is shown with the angle O1—Cu1—O3 = 54.74 (14) °. The nitrate anions are asymmetrically bonded, with Cu1—O3 = 1.971 (3) Å and Cu1—O1 = 2.588 (4) Å (Table 1). Two examples of asymmetrically bonded carboxylate groups show the wide range of short and long Cu(II)—O distances: 1.989 (2) Å and 2.339 (3) Å (Youngme *et al.*, 2007); 1.962 (3) Å and 2.706 Å were reported by Lee & Barboiu (2004).

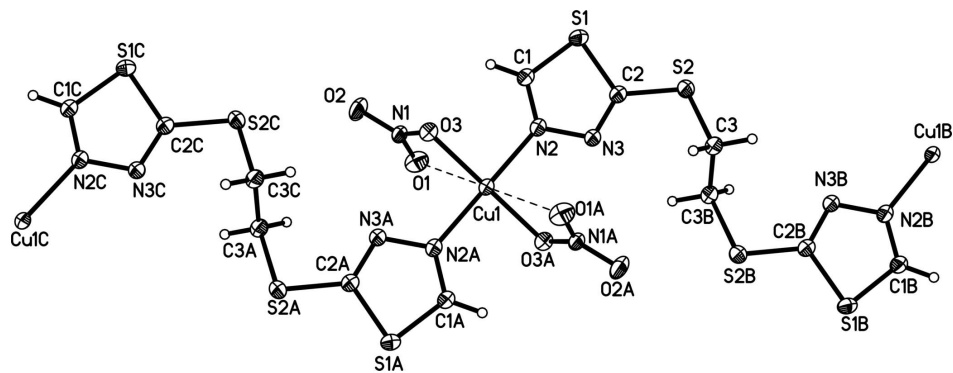
The ethane group was disordered and the C3 atom was refined on split positions with occupancy (50:50). The 2,2'-[1,2-ethanediybis(thio)]bis[1,3,4-thiadiazole] ligands adopt a N, N-bidentate bridging mode in *trans* configuration and bridge the copper atoms into one-dimensional infinite chains, with the bridged Cu-Cu distance of 11.2455 (12) Å (Fig. 2). The chains interact with neighboring molecules *via* intermolecular S...O interactions (the shortest distances found: O2...S1 = 3.084 (5) Å and O2...S2 = 3.044 (4) Å, with symmetry codes (1 - x, -1 - y, -z) and (1 - x, 1 - y, 1 - z), respectively, and weak intermolecular C—H...O hydrogen bonds (Bhogala *et al.* (2005), (Table 2). These chains are linked by the S...O interactions into two-dimensional layers (Fig. 3), which are further connected by weak intermolecular C—H...O hydrogen bonds to generate a three-dimensional supramolecular structure (Fig. 4).

S2. Experimental

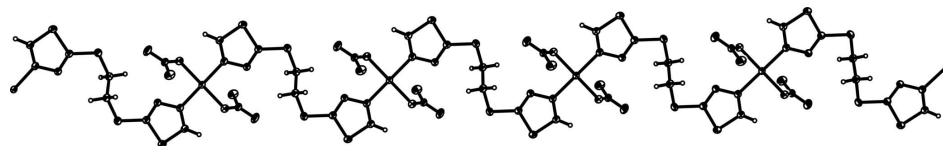
The reaction of 2,2'-[1,2-ethanediy-bis(thio)]bis(1,3,4- thiadiazole) (0.2 mmol) with Cu(NO₃)₂ (0.2 mmol) in MeOH(10 ml) for a few minutes afforded a light blue solid, which was filtered, washed with acetone, and dried on air. The single crystals suitable for X-ray analysis were obtained by slow diffusion of Et₂O into the acetonitrile solution of the solid.

S3. Refinement

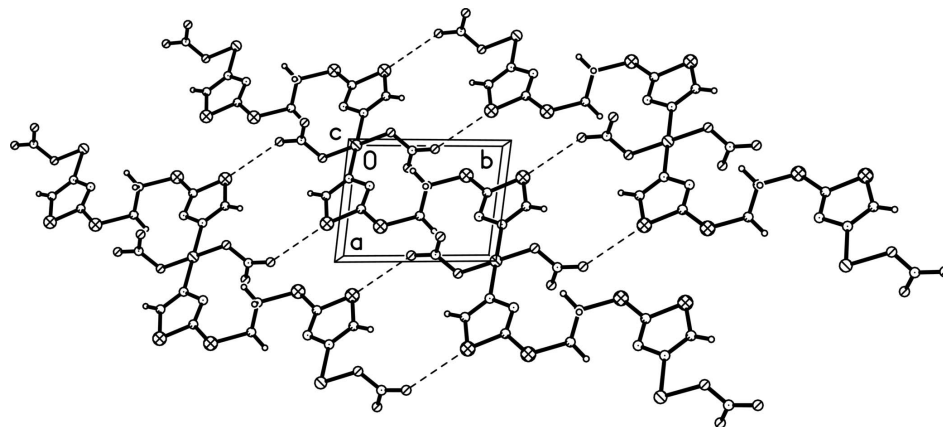
All hydrogen atoms were positioned geometrically and treated as riding, with C—H = 0.93 Å (CH) and $U_{iso}(H) = 1.2U_{eq}(C)$, with C—H = 0.97 Å (CH₂) and $U_{iso}(H) = 1.2U_{eq}(C)$,

**Figure 1**

A view of the local coordination of the Cu(II) cation in the title compound. Displacement ellipsoids are drawn at the 30% probability level. The disordered ethane group was omitted for clarity. Symmetry codes: (A) $(-x, -y, -z)$; (B) $(1 - x, 1 - y, 1 - z)$; (C) $(-1 + x, -1 + y, -1 + z)$.

**Figure 2**

A view of the polymeric chain in the title compound.

**Figure 3**

A view of the two-dimensional network, indicating the S...O interactions by dashed lines.

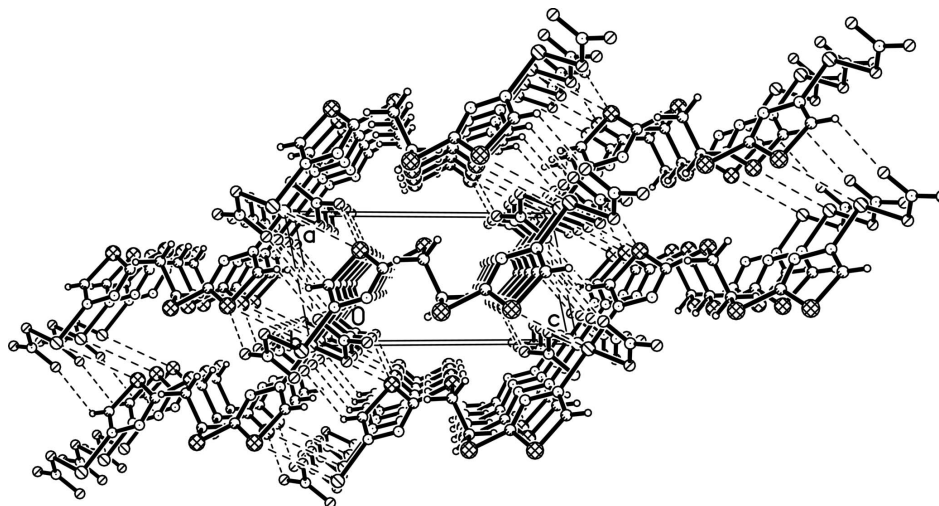


Figure 4

A view of the compound packing down the *b* axis.

catena-Poly[[bis(nitrato- κ^2O,O')copper(II)]- μ -2,2'-(ethane-1,2-diylidithio)di-1,3,4-thiadiazole- $\kappa^2N^4:N^4$]

Crystal data

[Cu(NO₃)₂(C₆H₆N₄S₄)]

$M_r = 449.95$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 5.2143$ (8) Å

$b = 7.0214$ (10) Å

$c = 10.6476$ (16) Å

$\alpha = 105.144$ (2)°

$\beta = 100.000$ (2)°

$\gamma = 93.958$ (2)°

$V = 367.88$ (9) Å³

$Z = 1$

$F(000) = 225$

$D_x = 2.031$ Mg m⁻³

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

Cell parameters from 1855 reflections

$\theta = 3.0$ – 29.2 °

$\mu = 2.09$ mm⁻¹

$T = 296$ K

Plate, colorless

$0.48 \times 0.29 \times 0.04$ mm

Data collection

Bruker SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

phi and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 1997)

$T_{\min} = 0.432$, $T_{\max} = 0.924$

1983 measured reflections

1336 independent reflections

1273 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.020$

$\theta_{\max} = 25.5$ °, $\theta_{\min} = 3.0$ °

$h = -6 \rightarrow 3$

$k = -8 \rightarrow 8$

$l = -11 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.058$

$wR(F^2) = 0.173$

$S = 1.05$

1336 reflections

110 parameters

1 restraint

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

$$w = 1/[\sigma^2(F_o^2) + (0.1363P)^2 + 0.4692P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 1.86 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.50 \text{ e } \text{\AA}^{-3}$$

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C3	0.6301 (17)	0.4878 (11)	0.4823 (9)	0.0366 (14)	0.499 (9)
H3A	0.7602	0.5921	0.5422	0.044*	0.499 (9)
H3B	0.6243	0.4972	0.3926	0.044*	0.499 (9)
C3'	0.4746 (17)	0.4163 (12)	0.5298 (9)	0.0366 (14)	0.501 (9)
H3B'	0.2988	0.3485	0.4917	0.044*	0.501 (9)
H3A'	0.4890	0.4680	0.6249	0.044*	0.501 (9)
Cu1	0.0000	0.0000	0.0000	0.0312 (3)	
S1	0.6997 (3)	-0.12017 (17)	0.26648 (12)	0.0406 (4)	
S2	0.7207 (3)	0.23982 (18)	0.49437 (12)	0.0455 (4)	
O1	-0.2024 (8)	-0.3668 (6)	-0.0576 (4)	0.0546 (10)	
O2	-0.0393 (10)	-0.5352 (6)	-0.2188 (4)	0.0650 (12)	
O3	0.1101 (7)	-0.2255 (5)	-0.1244 (3)	0.0417 (8)	
N1	-0.0491 (8)	-0.3829 (5)	-0.1353 (4)	0.0385 (9)	
N2	0.3011 (8)	-0.0167 (6)	0.1409 (4)	0.0345 (8)	
N3	0.3672 (7)	0.1312 (5)	0.2605 (4)	0.0370 (9)	
C1	0.4554 (9)	-0.1563 (6)	0.1321 (4)	0.0355 (10)	
H1A	0.4330	-0.2663	0.0583	0.043*	
C2	0.5716 (9)	0.0958 (6)	0.3353 (4)	0.0347 (10)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C3	0.036 (4)	0.032 (3)	0.038 (3)	0.005 (2)	0.007 (3)	0.004 (3)
C3'	0.036 (4)	0.032 (3)	0.038 (3)	0.005 (2)	0.007 (3)	0.004 (3)
Cu1	0.0330 (5)	0.0269 (5)	0.0289 (5)	0.0069 (3)	0.0028 (3)	0.0009 (3)
S1	0.0423 (7)	0.0364 (7)	0.0419 (7)	0.0170 (5)	0.0040 (5)	0.0086 (5)
S2	0.0479 (8)	0.0415 (7)	0.0367 (7)	0.0153 (5)	-0.0092 (5)	0.0016 (5)
O1	0.062 (2)	0.049 (2)	0.059 (2)	0.0151 (17)	0.020 (2)	0.0183 (17)
O2	0.088 (3)	0.0380 (19)	0.053 (2)	0.024 (2)	-0.002 (2)	-0.0102 (17)
O3	0.0405 (18)	0.0406 (17)	0.0388 (17)	0.0109 (14)	0.0058 (14)	0.0017 (14)
N1	0.049 (2)	0.0291 (17)	0.0304 (18)	0.0149 (16)	-0.0031 (17)	0.0004 (14)
N2	0.0384 (19)	0.0289 (17)	0.0321 (19)	0.0068 (15)	0.0039 (15)	0.0025 (14)
N3	0.039 (2)	0.0306 (19)	0.035 (2)	0.0102 (17)	-0.0015 (17)	0.0016 (16)
C1	0.039 (2)	0.032 (2)	0.033 (2)	0.0098 (18)	0.0062 (18)	0.0034 (17)
C2	0.037 (2)	0.0291 (19)	0.035 (2)	0.0078 (18)	0.0048 (19)	0.0054 (17)

Geometric parameters (\AA , $^\circ$)

C3—C3 ⁱ	1.479 (17)	Cu1—N2 ⁱⁱ	2.007 (4)
C3—S2	1.866 (7)	S1—C1	1.693 (5)
C3—H3A	0.9700	S1—C2	1.735 (4)

C3—H3B	0.9700	S2—C2	1.743 (4)
C3'—C3 ⁱⁱ	1.504 (17)	O1—N1	1.237 (6)
C3'—S2	1.863 (7)	O2—N1	1.209 (5)
C3'—H3B'	0.9700	O3—N1	1.303 (5)
C3'—H3A'	0.9700	N2—C1	1.305 (6)
Cu1—O1	2.588 (4)	N2—N3	1.389 (5)
Cu1—O3 ⁱⁱ	1.971 (3)	N3—C2	1.295 (6)
Cu1—O3	1.971 (3)	C1—H1A	0.9300
Cu1—N2	2.007 (4)		
C3 ⁱ —C3—S2	108.9 (7)	C2—S2—C3'	100.6 (3)
C3 ⁱ —C3—H3A	109.9	C2—S2—C3	99.5 (3)
S2—C3—H3A	109.9	N1—O3—Cu1	107.4 (2)
C3 ⁱ —C3—H3B	109.9	O2—N1—O1	123.7 (5)
S2—C3—H3B	109.9	O2—N1—O3	119.2 (4)
H3A—C3—H3B	108.3	O1—N1—O3	117.1 (4)
C3 ⁱⁱ —C3'—S2	108.5 (7)	O1—Cu1—O3	54.74 (14)
C3 ⁱⁱ —C3'—H3B'	110.0	N2—Cu1—O3	89.02 (15)
S2—C3'—H3B'	110.0	O1—Cu1—O3 ⁱⁱ	125.26 (14)
C3 ⁱⁱ —C3'—H3A'	110.0	C1—N2—N3	113.3 (4)
S2—C3'—H3A'	110.0	C1—N2—Cu1	126.2 (3)
H3B'—C3'—H3A'	108.4	N3—N2—Cu1	120.5 (3)
O3 ⁱⁱ —Cu1—O3	180.0	C2—N3—N2	110.7 (4)
O3 ⁱⁱ —Cu1—N2	90.98 (15)	N2—C1—S1	114.2 (3)
O3—Cu1—N2	89.02 (15)	N2—C1—H1A	122.9
O3 ⁱⁱ —Cu1—N2 ⁱⁱ	89.02 (15)	S1—C1—H1A	122.9
O3—Cu1—N2 ⁱⁱ	90.98 (15)	N3—C2—S1	114.8 (3)
N2—Cu1—N2 ⁱⁱ	180.0	N3—C2—S2	126.5 (3)
C1—S1—C2	87.1 (2)	S1—C2—S2	118.7 (3)
C3 ⁱⁱ —C3'—S2—C2	-83.9 (9)	Cu1—N2—N3—C2	-177.8 (3)
C3 ⁱⁱ —C3'—S2—C3	7.8 (7)	N3—N2—C1—S1	-1.2 (5)
C3 ⁱ —C3—S2—C2	87.1 (9)	Cu1—N2—C1—S1	177.3 (2)
C3 ⁱ —C3—S2—C3'	-7.9 (7)	C2—S1—C1—N2	0.9 (4)
N2—Cu1—O3—N1	103.2 (3)	N2—N3—C2—S1	-0.1 (5)
N2 ⁱⁱ —Cu1—O3—N1	-76.8 (3)	N2—N3—C2—S2	-179.2 (3)
Cu1—O3—N1—O2	171.2 (4)	C1—S1—C2—N3	-0.4 (4)
Cu1—O3—N1—O1	-9.2 (4)	C1—S1—C2—S2	178.7 (3)
O3 ⁱⁱ —Cu1—N2—C1	171.9 (4)	C3'—S2—C2—N3	9.6 (5)
O3—Cu1—N2—C1	-8.1 (4)	C3—S2—C2—N3	-27.8 (5)
O3 ⁱⁱ —Cu1—N2—N3	-9.7 (3)	C3'—S2—C2—S1	-169.5 (4)
O3—Cu1—N2—N3	170.3 (3)	C3—S2—C2—S1	153.1 (3)
C1—N2—N3—C2	0.8 (6)		

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

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C1—H1A \cdots O1 ⁱⁱⁱ	0.93	2.49	3.083 (6)	122

Symmetry code: (iii) $x+1, y, z$.