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## Structure Reports

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Bis(*N*-nitroso-*N*-pentylhydroxylamino- $\kappa^2$ O, $O'$ )copper(II)Ali Sheikh Bostanabad,<sup>a\*</sup> Olga Kovalchukova,<sup>a</sup> Svetlana Strashnova,<sup>a</sup> Adam Stash<sup>b</sup> and Igor Zyuzin<sup>c</sup>

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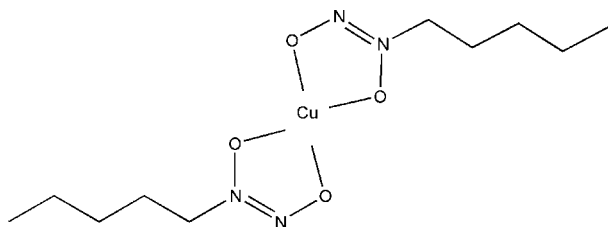
Received 13 February 2014; accepted 4 March 2014

Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å;  $R$  factor = 0.026;  $wR$  factor = 0.073; data-to-parameter ratio = 16.2.

In the centrosymmetric title compound,  $[\text{Cu}(\text{C}_5\text{H}_{11}\text{N}_2\text{O}_2)_2]$ , the  $\text{Cu}^{2+}$  ion, located on an inversion centre (Wyckoff position  $2b$ ), is in a square-planar environment, surrounded by four O atoms of the N—O groups of two *N*-nitroso-*N*-pentylhydroxylamine ligands [ $\text{Cu}-\text{O} = 1.9042$  (17) and  $1.9095$  (16) Å]. The hydroxylamine monoanions are bidentate chelating ligands. The  $\text{Cu}^{2+}$  cations form stacks along  $[010]$ , with intermolecular  $\text{Cu} \cdots \text{N}$  contacts of  $3.146$  (2) and  $3.653$  (2) Å.

## Related literature

The basic procedure for the synthesis of the reported complex is described by Zyuzin *et al.* (1997). For related structures of copper complexes with the *N*-nitrosohydroxylamine derivatives, see: Abraham *et al.* (1987); Kovalchukova *et al.* (2013, 2014). The synthesis and properties of other metal nitrosohydroxylamines are given in: Ahmed *et al.* (1988); Basson *et al.* (1992); Bolboaca *et al.* (2000); Kovalchukova *et al.* (2013); Najafi *et al.* (2011); Okabe & Tamaki (1995); Parkanyi *et al.* (1999); Pavel *et al.* (2000); Tamaki & Okabe (1998); Van der Helm *et al.* (1965). For applications of *N*-nitrosohydroxylamine derivatives see: Lundell & Knowles (1920); Buscarons & Canela (1974); Oztekin & Erim (2000); McGill *et al.* (2000).



## Experimental

## Crystal data

$[\text{Cu}(\text{C}_5\text{H}_{11}\text{N}_2\text{O}_2)_2]$   
 $M_r = 325.86$   
 Monoclinic,  $P2_1/c$   
 $a = 14.325$  (3) Å  
 $b = 4.776$  (1) Å  
 $c = 11.619$  (2) Å  
 $\beta = 103.82$  (3)°

$V = 771.9$  (3) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 1.43$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.80 \times 0.20 \times 0.03$  mm

## Data collection

Enraf–Nonius CAD-4 diffractometer  
 Absorption correction: part of the refinement model ( $\Delta F$ ) (Walker & Stuart, 1983)  
 $T_{\min} = 0.202$ ,  $T_{\max} = 0.670$

1509 measured reflections  
 1429 independent reflections  
 871 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.030$   
 3 standard reflections every 60 min  
 intensity decay: none

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$   
 $wR(F^2) = 0.073$   
 $S = 0.88$   
 1429 reflections

88 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.32$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.68$  e Å<sup>-3</sup>

Data collection: *CAD-4-PC* (Enraf–Nonius, 1993); cell refinement: *CAD-4-PC*; data reduction: *CAD-4-PC*; 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: *CIFTAB97* and *SHELXL97*.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: PJ2009).

## References

- Abraham, M. H., Bullock, J. I., Garland, J. H. N., Golder, A. J., Harden, G. J., Larkworth-Iy, L. F., Povey, D. C., Riedl, M. J. & Smith, G. W. (1987). *Polyhedron*, **6**, 1375–1381.
- Ahmed, M., Edwards, A. J., Jones, C. J., McCleverty, J. A., Rothin, A. S. & Tate, J. P. (1988). *J. Chem. Soc. Dalton Trans.* pp. 257–263.
- Basson, S. S., Leipoldt, J. G., Purcell, W. & Venter, J. A. (1992). *Acta Cryst.* **C48**, 171–173.
- Bolboaca, M., Cinta, S., Venter, M., Deak, A., Haiduc, I., Cozar, O., Iliescu, T., Rosch, P. & Kiefer, W. (2000). *Spectrosc. Lett.* **33**, 857–862.
- Buscarons, F. & Canela, J. (1974). *Anal. Chim. Acta*, **70**, 113–120.
- Enraf–Nonius (1993). *CAD-4-PC*. Enraf–Nonius, Delft, The Netherlands.
- Kovalchukova, O., Bostanabad, A. S., Sergienko, V., Polyakova, I., Zyuzin, I. & Strashnova, S. (2013). *Open J. Inorg. Chem.* **3**, 1–6.
- Kovalchukova, O. V., Bostanabad, A. S., Stash, A. I., Strashnova, S. B. & Zyuzin, I. N. (2014). *Russ. J. Inorg. Chem.* **59**, 332–336.
- Lundell, G. E. F. & Knowles, H. B. (1920). *J. Ind. Eng. Chem.* **12**, 344–350.
- McGill, A. D., Zhang, W., Wittbrodt, J., Wang, J., Schlegel, H. B. & Wang, P. G. (2000). *Bioorg. Med. Chem.* **8**, 405–412.
- Najafi, E., Amini, M. M. & Ng, S. W. (2011). *Acta Cryst.* **E67**, m377.
- Okabe, N. & Tamaki, K. (1995). *Acta Cryst.* **C51**, 2004–2005.
- Oztekin, N. & Erim, F. B. (2000). *J. Chromatogr. A*, **895**, 263–268.
- Parkanyi, L., Kalman, A., Deak, A., Venter, M. & Haiduc, I. (1999). *Inorg. Chem. Commun.* **2**, 265–268.
- Pavel, I., Cinta, S., Venter, M., Deak, A., Haiduc, I., Rosch, P., Cozar, O. & Kiefer, W. (2000). *Vib. Spectrosc.* **23**, 71–76.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Tamaki, K. & Okabe, N. (1998). *Acta Cryst.* **C54**, 195–197.

## metal-organic compounds

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Van der Helm, D., Merritt, L. L., Degeilh, R. & MacGillavry, C. H. (1965). *Acta Cryst.* **18**, 355–362.  
Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

Zyuzin, I. N., Nechiporenko, G. N., Golovina, N. I., Trofimova, R. F. & Loginova, M. V. (1997). *Russ. Chem. Bull.* **46**, 1421–1429.

## supporting information

*Acta Cryst.* (2014). E70, m137–m138 [doi:10.1107/S1600536814004978]

**Bis(*N*-nitroso-*N*-pentylhydroxylaminato- $\kappa^2$ O,*O*')copper(II)**

Ali Sheikh Bostanabad, Olga Kovalchukova, Svetlana Strashnova, Adam Stash and Igor Zyuzin

**S1. Comment**

The chelate-forming derivatives of *N*-nitroso hydroxylamines form stable complexes with the metallic ions of various natures but only few of them have been structurally characterized (Abraham *et al.*, 1987; Ahmed *et al.*, 1988; Basson *et al.*, 1992; Bolboaca *et al.*, 2000; Kovalchukova *et al.*, 2013; Najafi *et al.*, 2011; Okabe & Tamaki, 1995; Parkanyi *et al.*, 1999; Pavel *et al.*, 2000; Tamaki & Okabe, 1998; Van der Helm *et al.*, 1965). Their ammonium and potassium salts are reported as good analytical reagents for different purposes (Lundell & Knowles, 1920; Buscarons & Canela, 1974; Oztekin & Erim, 2000). In addition, recently it was reported that many *o*-substituted *N*-nitroso-*N*-oxybenzenamines are good NO donors for both *in vitro* and *in vivo* assays (McGill *et al.*, 2000). The title compound C<sub>10</sub>H<sub>22</sub>CuN<sub>4</sub>O<sub>4</sub> (Fig. 1) is centrosymmetric with the Cu<sup>2+</sup> ion located on the inversion centre (Wyckoff position 2*b*) in square planar coordination, surrounded by four oxo O atoms of the N—O groups of two organic ligands [Cu—O = 1.9042 (17) and 1.90905 (16) Å]. The molecule of the metal complex is completed by the 1-*x*, 1-*y*, 1-*z* symmetry operation. The mean deviation from the plane is 0.0199 Å. The *N*-nitroso-*N*-(*n*-pentyl)hydroxylaminato anions are bidentate chelating ligands. The Cu cations in the columns form stacks in the columns along the [010] direction with intermolecular Cu—N contacts equal to 3.146 (2) and 3.653 (2) Å (Fig. 2). The described coordination type of the central atom correlates with those described previously for the bis(*N*-nitroso-*N*-benzyl-hydroxylaminato-*o,o*) copper(II) (Kovalchukova *et al.*, 2013) and bis(*N*-nitroso-*N*-ethyl-hydroxylaminato-*o,o*) copper(II) (Kovalchukova *et al.*, 2014).

**S2. Experimental**

The title compound was obtained in accordance with the previously published procedure (Zyuzin *et al.*, 1997) with some modifications. A solution of *n*-pentylmagnesium chloride was prepared from magnesium (12.2 g, 0.5 mol) and 1-bromopentane (75.5 g, 0.5 mol) in the dry Et<sub>2</sub>O (0.5 L). The NO gas was bubbled through the solution under vigorous stirring and cooling at such a rate that NO was almost entirely absorbed. The reaction mixture temperature was maintained in the range 248 to 243 K. After the period of a rapid NO absorption (1 h), stirring was continued in an NO atmosphere for 0.5 h until the NO absorption was completed, with a gradual increase in temperature to 263 K. The reaction mixture was purged with Ar, treated with MeOH (100 mL), poured into ice (300 g) and acidified with 2 M H<sub>2</sub>SO<sub>4</sub>. The organic layer was separated, and the aqueous layer was extracted with Et<sub>2</sub>O (100 mL × 3). The combined extracts were washed with 50 mL 1 M NaOH and 50 mL H<sub>2</sub>O. The aqueous layer was neutralized with 2 M H<sub>2</sub>SO<sub>4</sub> until pH 4 and treated with 20 per cent CuSO<sub>4</sub> solution (120 g, 0.2 mol). The blue precipitate was washed with water, dried and crystallized from EtOH. Yield 42.3 g (52 per cent), blue crystals, m.p. 355–356 K. Analysis calculated for C<sub>10</sub>H<sub>22</sub>CuN<sub>4</sub>O<sub>4</sub>: Cu 19.50; found: Cu 18.83. Single crystals of C<sub>10</sub>H<sub>22</sub>CuN<sub>4</sub>O<sub>4</sub> were grown by the slow evaporation of the ethanol solution of the bis[*N*-nitroso-*N*-(*n*-pentyl)hydroxylaminato] copper(II) powdered sample.

## S3. Refinement

The structure of  $C_{10}H_{22}CuN_4O_4$  was solved by direct method and all non-hydrogen atoms were located and refined anisotropically. All the hydrogen atoms added using a riding model.

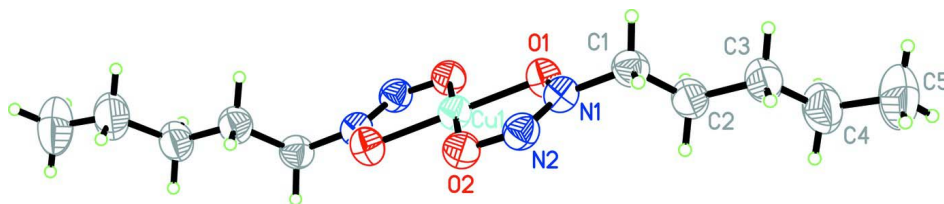


Figure 1

ORTEP view of  $C_{10}H_{22}CuN_4O_4$  with atom labeling scheme (displacement ellipsoids are drawn at the 50% probability level for non-hydrogen atoms). The second half of the molecule is generated by the symmetry operator  $1-x, 1-y, 1-z$ .

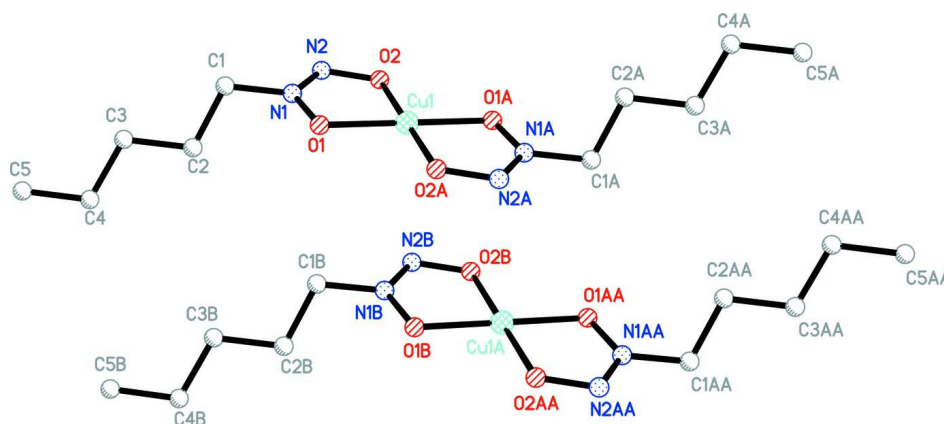


Figure 2

Mutual arrangement of neighboring complexes in a stack.

Bis(*N*-nitroso-*N*-pentylhydroxylaminate- $\kappa^2O,O'$ )copper(II)

## Crystal data

$[Cu(C_5H_{11}N_2O_2)_2]$

$M_r = 325.86$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P\ 2ybc$

$a = 14.325\ (3)\ \text{\AA}$

$b = 4.776\ (1)\ \text{\AA}$

$c = 11.619\ (2)\ \text{\AA}$

$\beta = 103.82\ (3)^\circ$

$V = 771.9\ (3)\ \text{\AA}^3$

$Z = 2$

$F(000) = 342$

$D_x = 1.402\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 25 reflections

$\theta = 9.7\text{--}11.9^\circ$

$\mu = 1.43\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Plate, blue

$0.80 \times 0.20 \times 0.03\ \text{mm}$

## Data collection

Enraf–Nonius CAD-4

diffractometer

Radiation source: fine-focus sealed tube

$\beta$ -filter monochromator

$\omega/2\theta$  scans

Absorption correction: part of the refinement

model ( $\Delta F$ )

(Walker & Stuart, 1983)

$T_{\min} = 0.202$ ,  $T_{\max} = 0.670$

1509 measured reflections

1429 independent reflections

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

$R_{\text{int}} = 0.030$   
 $\theta_{\text{max}} = 25.5^\circ$ ,  $\theta_{\text{min}} = 2.9^\circ$   
 $h = -17 \rightarrow 16$   
 $k = -5 \rightarrow 0$

$l = 0 \rightarrow 13$   
 3 standard reflections every 60 min  
 intensity decay: none

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.026$   
 $wR(F^2) = 0.073$   
 $S = 0.88$   
 1429 reflections  
 88 parameters  
 0 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  
 $w = 1/[\sigma^2(F_o^2) + (0.049P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.32 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.68 \text{ e } \text{\AA}^{-3}$

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

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.5000	0.5000	0.5000	0.04458 (15)
O1	0.38526 (12)	0.6395 (4)	0.39762 (14)	0.0498 (4)
O2	0.55742 (13)	0.7912 (3)	0.42774 (14)	0.0498 (4)
N1	0.40843 (14)	0.8595 (4)	0.34077 (15)	0.0447 (4)
N2	0.49421 (15)	0.9440 (4)	0.35334 (17)	0.0481 (5)
C1	0.33006 (17)	1.0104 (6)	0.26151 (19)	0.0506 (5)
H11	0.3559	1.1716	0.2288	0.061*
H12	0.2855	1.0778	0.3063	0.061*
C2	0.2767 (2)	0.8251 (6)	0.1611 (2)	0.0577 (6)
H21	0.3225	0.7366	0.1232	0.069*
H22	0.2431	0.6788	0.1928	0.069*
C3	0.20524 (19)	0.9925 (7)	0.0702 (2)	0.0647 (6)
H31	0.2394	1.1373	0.0383	0.078*
H32	0.1606	1.0840	0.1091	0.078*
C4	0.1491 (3)	0.8157 (8)	-0.0308 (3)	0.0848 (10)
H41	0.1094	0.6844	0.0000	0.102*
H42	0.1937	0.7083	-0.0641	0.102*
C5	0.0852 (3)	0.9888 (11)	-0.1285 (3)	0.1163 (15)
H51	0.0516	0.8669	-0.1903	0.174*
H52	0.1242	1.1171	-0.1603	0.174*
H53	0.0396	1.0918	-0.0966	0.174*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cu1	0.0460 (2)	0.0446 (2)	0.0432 (2)	-0.0028 (2)	0.01086 (14)	0.0008 (2)
O1	0.0449 (9)	0.0472 (9)	0.0562 (9)	-0.0053 (8)	0.0097 (7)	0.0084 (8)
O2	0.0473 (10)	0.0532 (9)	0.0505 (9)	-0.0062 (8)	0.0147 (7)	0.0020 (7)
N1	0.0485 (12)	0.0428 (11)	0.0428 (9)	-0.0033 (9)	0.0112 (8)	-0.0001 (8)
N2	0.0508 (12)	0.0499 (14)	0.0448 (10)	-0.0036 (9)	0.0137 (8)	0.0016 (8)
C1	0.0521 (13)	0.0470 (11)	0.0533 (11)	0.0052 (14)	0.0138 (10)	0.0037 (14)
C2	0.0538 (15)	0.0578 (16)	0.0584 (14)	0.0037 (13)	0.0073 (12)	-0.0015 (12)
C3	0.0556 (15)	0.0693 (15)	0.0641 (14)	0.0041 (17)	0.0042 (11)	0.0016 (17)
C4	0.069 (2)	0.092 (3)	0.081 (2)	0.0044 (19)	-0.0064 (16)	-0.0107 (19)
C5	0.099 (3)	0.140 (4)	0.086 (2)	-0.002 (3)	-0.025 (2)	-0.002 (3)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Cu1—O1	1.9042 (17)	C2—H21	0.9700
Cu1—O1 <sup>i</sup>	1.9042 (17)	C2—H22	0.9700
Cu1—O2 <sup>i</sup>	1.9095 (16)	C3—C4	1.512 (4)
Cu1—O2	1.9095 (16)	C3—H31	0.9700
O1—N1	1.325 (3)	C3—H32	0.9700
O2—N2	1.314 (2)	C4—C5	1.521 (5)
N1—N2	1.268 (3)	C4—H41	0.9700
N1—C1	1.461 (3)	C4—H42	0.9700
C1—C2	1.518 (4)	C5—H51	0.9600
C1—H11	0.9700	C5—H52	0.9600
C1—H12	0.9700	C5—H53	0.9600
C2—C3	1.512 (4)		
O1—Cu1—O1 <sup>i</sup>	180.0	C3—C2—H22	109.4
O1—Cu1—O2 <sup>i</sup>	97.54 (7)	C1—C2—H22	109.4
O1 <sup>i</sup> —Cu1—O2 <sup>i</sup>	82.46 (7)	H21—C2—H22	108.0
O1—Cu1—O2	82.46 (7)	C2—C3—C4	113.1 (3)
O1 <sup>i</sup> —Cu1—O2	97.54 (7)	C2—C3—H31	109.0
O2 <sup>i</sup> —Cu1—O2	180.0	C4—C3—H31	109.0
N1—O1—Cu1	107.90 (13)	C2—C3—H32	109.0
N2—O2—Cu1	113.09 (14)	C4—C3—H32	109.0
N2—N1—O1	123.09 (19)	H31—C3—H32	107.8
N2—N1—C1	119.6 (2)	C3—C4—C5	112.9 (3)
O1—N1—C1	117.35 (19)	C3—C4—H41	109.0
N1—N2—O2	113.32 (18)	C5—C4—H41	109.0
N1—C1—C2	111.5 (2)	C3—C4—H42	109.0
N1—C1—H11	109.3	C5—C4—H42	109.0
C2—C1—H11	109.3	H41—C4—H42	107.8
N1—C1—H12	109.3	C4—C5—H51	109.5
C2—C1—H12	109.3	C4—C5—H52	109.5
H11—C1—H12	108.0	H51—C5—H52	109.5
C3—C2—C1	111.2 (2)	C4—C5—H53	109.5

C3—C2—H21	109.4	H51—C5—H53	109.5
C1—C2—H21	109.4	H52—C5—H53	109.5

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