

Crystal and Molecular Structure of *trans*-Di(benzoato-*O*)bis(1,3-diamino-2-hydroxypropane-*N,N'*)copper(II) at 193 and 296 K

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The structure of the title compound was determined by single-crystal X-ray methods. *trans*-Di(benzoato-*O*)bis(1,3-diamino-2-hydroxypropane-*N,N'*)copper(II) crystallises in the monoclinic crystal system, space group $P2_1/c$, no. 14, $Z=2$. At 193 K $a=6.507(9)$, $b=7.182(7)$, $c=24.300(8)$ Å, $\beta=95.02(7)^\circ$ and $V=1131(2)$ Å³; at 296 K $a=6.519(2)$, $b=7.205(2)$, $c=24.445(5)$ Å, $\beta=95.12(2)^\circ$ and $V=1144(1)$ Å³. The copper(II) displays elongated pseudo-octahedral coordination polyhedron with the site symmetry C_1 . The 1,3-diamino-2-hydroxypropane forms a six-membered chelate ring displaying a chair conformation in the equatorial direction. The non-coordinated hydroxyl group in the chelate ring forms a hydrogen bond to a neighbouring coordinated oxygen atom of the carboxylate group. The axially situated carboxylate group is twisted about 82° with respect to the analogous compound, where the equatorial ligand is 1,3-diaminopropane without a hydroxyl group. The non-coordinated oxygen is now projected in between the two chelate rings. The only significant difference upon cooling is seen in the compression of the axial Cu–O bond length from 2.479(3) to 2.459(2) Å. Based upon EHMO calculations, the amount of d–s mixing as a rationale for the axial elongation is about 6%.

In the systematic study going on in our laboratory we are studying monomeric *trans*-Mtn₂bzO₂ complexes (where M is a metal in the first transition metal series, tn is 1,3-diaminopropane and bzO is a benzoate anion).^{1–3} The most common coordination mode around the central metal cation is 4+2. In a recent article we reported the structure of *trans*-di(4-chlorobenzoato-*O*)bis(1,3-diaminopropane-*N,N'*)cobalt(III) 4-chlorobenzoate displaying distortion isomerism, where the most significant difference between two independent complex units was the orientation of the *para*-chlorobenzoate anions.³ To continue our studies on the coordination modes in benzoato complexes, a new complex containing 1,3-diamino-2-hydroxypropane instead of 1,3-diaminopropane was synthesised.

1,3-Diamino-2-hydroxypropane displays great versatility as a ligand. In solid copper(II) complexes it can exist as a non-coordinated cation,⁴ or it coordinates either bi- or tridentately, as a neutral or anionic ligand forming various monomeric,⁵ trimeric⁶ or polymeric⁷ complexes.

Since in catena- μ -(terephthalato-*O*)bis(1,3-diamino-2-hydroxypropane-*N,N'*)copper(II) (CUTERE hereafter) the hydroxyl group is not coordinated,⁸ we decided to use the benzoate anion as a counter-ion and compare the structure with *trans*-di(benzoato-*O*)bis(1,3-diaminopropane-*N,N'*)copper(II) (CUBENZ hereafter).⁹ The reason for this is to study the possible effect of the hydroxyl group on the axial ligand. In a CFF study it was stated that there are major interactions between an axial ligand and an equatorial 1,3-diaminopropane ligand.¹⁰

Tetragonally elongated pseudo-octahedra in the copper(II) complexes are known to be temperature-dependent, if the tetragonality T is >0.85 .¹¹ Because the T value in the *trans*-Cutn₂bzO₂ complexes is near to this value, we decided to make the measurements also at a lower temperature.

Experimental

Syntheses. The title compound was synthesised according to the method described in Ref 8. A copper complex solution was prepared from CuO (4.00 g, Baker

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Analyzed, each) and 1,3-diamino-2-hydroxypropane (18.03 g, Aldrich, p.a.). The unreacted CuO was weighted and then the calculated equivalent amounts of benzoic acid (7.32 g, B. D. H. Ltd., p.a.) was added. Dark blue crystals were separated after two days. They were washed with EtOH, dried in air and recrystallised from EtOH/H₂O (10/1, v/v) solution. Copper was analyzed electrogravimetrically; Anal. calcd. for C₂₀H₃₀CuN₄O₆: Cu, 13.07; C, 49.42; N, 11.53; H, 6.22. Found: Cu, 13.03%; C, 49.4; N, 11.75; H, 6.47.

Crystal data. [Cu(tnOH)₂(bzO)₂], C₂₀H₃₀CuN₄O₆, $M_r = 486.03$, monoclinic, space group $P2_1/c$ no. 14, at 193 K: $a = 6.507(9)$, $b = 7.182(7)$, $c = 24.300(8)$ Å, $\beta = 95.02(7)^\circ$, $V = 1131(2)$ Å³; at 296 K: $a = 6.519(2)$, $b = 7.205(2)$, $c = 24.445(5)$ Å, $\beta = 95.12(2)^\circ$, $V = 1143(1)$; $\lambda = 0.71073$ Å, $F(000) = 510$, $Z = 2$, at 193 K $D_c = 1.427$ g cm⁻³, at 296 K $D_c = 1.404$ g cm⁻³, $D_m = 1.405$ g cm⁻³. Dark blue plates. Crystal dimensions 0.45 × 0.25 × 0.25 mm for the measurement at 193 K; at 296 K 0.40 × 0.30 × 0.15 mm, $\mu = 10.10$ and 9.96 cm⁻¹ at 193 and 296 K, respectively.

Data collection and processing. Rigaku AFC7S diffractometer, $\omega/2\theta$ scan mode, at 193 K: scan speed 2–8° min⁻¹, graphite monochromated Mo K_α radiation, 2761 unique reflections measured ($3 \leq 2\theta \leq 53^\circ$), giving 1985 observed reflections with $I > 2\sigma(I_0)$. No decay, but experimental ψ -scan absorption, as well as Lorentz and polarization corrections were made. At 296 K: scan speed 4–16° min⁻¹, graphite monochromated Mo K_α radiation, 2815 unique reflections measured ($3 \leq 2\theta \leq 54^\circ$), giving 1755 observed reflections with $I > 2\sigma(I_0)$. Experimental ψ -scan absorption, as well as Lorentz and polarization corrections, were made, but decay measurements were not.

Structure analysis and refinement. Direct methods were followed by difference Fourier techniques.¹² Full-matrix least-squares refinement was made with all non-hydrogen atoms anisotropic and the hydrogens with overall isotropic temperature parameters. The weighting scheme $w = 1/[\sigma^2(F_o)]$ with F_o from counting statistics gave satisfactory agreement analyses. At 193 K the final R and R' values are 0.044 and 0.047, respectively; at 296 K $R = 0.049$ and $R' = 0.045$. The neutral atom scattering factors and correction factors for anomalous scattering were those included in the program package. The calculations were carried out with XTAL software.¹³

Magnetic measurements. Magnetic susceptibility measurements were carried out in the temperature range 70–300 K in a He atmosphere by a Faraday magnetometer (Oxford Instruments). Hg[Co(NCS)₄] was used as a standard for calibration.¹⁴ Susceptibility measurements were carried out at 0.8 T. All data were corrected for diamagnetism by making use of Pascal's constants¹⁵ and for TIP. The magnetic susceptibility obeyed the

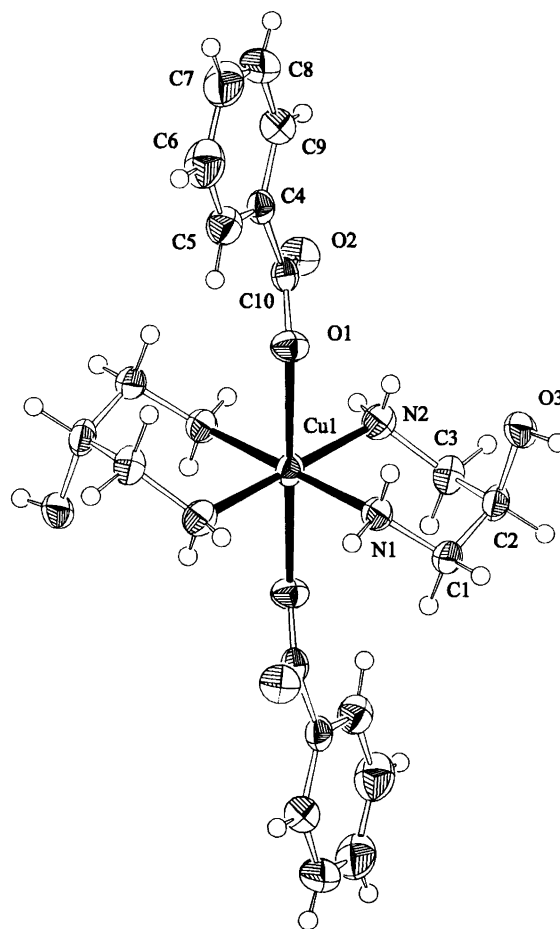


Fig. 1. ORTEP drawing of the complex unit of the title compound measured at 193 K showing the numbering scheme for the non-hydrogen atoms. The thermal ellipsoids are depicted at 50% probability level.

Curie–Weiss law in the temperature range; $C = 0.397(3)$ cm³ K mol⁻¹ and $\Theta = 3.2(6)$ K.

Spectra. The ESR spectrum of the powdered sample was run at 293(1) K as reported in Ref. 8. 2,2,6,6-Tetramethylpiperidin-1-oxyl was used as a calibration standard and 2.0055 as the splitting factor¹⁶ for the compound. The title compound displays an axial ESR spectrum with g values typical for *trans*-CuL₂L'₂ complexes; $g_{\parallel} = 2.206$ and $g_{\perp} = 2.041$.

Extended Hückel calculations. The calculations were carried out by using CACAO¹⁷ installed on a local PC. The atomic coordinates obtained from the single-crystal X-ray analyses were used as input.

Results and discussion

Description of the molecular structure

The coordinates and equivalent isotropic thermal displacement parameters for the non-hydrogen atoms are given Table 1 and the bonding parameters in Table 2.

Table 1. Atomic positional and isotropic displacement parameters for the non-hydrogen atoms in the title compound.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} ^a
<i>T</i> = 193 K				
Cu1	0.50000	0.50000	0.50000	0.0280 (2)
O1	0.6005 (3)	0.6956 (3)	0.42374 (9)	0.0346 (7)
O2	0.9410 (3)	0.6593 (3)	0.44127 (9)	0.0399 (8)
O3	0.4012 (4)	0.0225 (3)	0.4277 (1)	0.0370 (8)
N1	0.6849 (4)	0.2825 (4)	0.4815 (1)	0.0317 (9)
N2	0.2720 (4)	0.3849 (4)	0.4491 (1)	0.0334 (9)
C1	0.6921 (5)	0.2306 (5)	0.4232 (1)	0.034 (1)
C2	0.4829 (5)	0.1709 (4)	0.3969 (1)	0.033 (1)
C3	0.3209 (6)	0.3236 (5)	0.3939 (1)	0.035 (1)
C4	0.8145 (5)	0.7833 (4)	0.3540 (1)	0.031 (1)
C5	0.6503 (6)	0.7914 (5)	0.3138 (1)	0.040 (1)
C6	0.6764 (7)	0.8688 (6)	0.2625 (2)	0.054 (2)
C7	0.8657 (9)	0.9405 (6)	0.2523 (2)	0.062 (2)
C8	1.0279 (7)	0.9322 (7)	0.2919 (2)	0.058 (2)
C9	1.0050 (6)	0.8523 (5)	0.3427 (2)	0.043 (1)
C10	0.7845 (5)	0.7059 (4)	0.4106 (1)	0.029 (1)
<i>T</i> = 296 K				
Cu1	0.5000	0.5000	0.5000	0.0417 (2)
O1	0.6041 (4)	0.6988 (4)	0.4245 (1)	0.050 (1)
O2	0.9409 (4)	0.6591 (4)	0.4413 (1)	0.059 (1)
O3	0.4018 (5)	0.0245 (4)	0.4276 (1)	0.054 (1)
N1	0.6846 (6)	0.2843 (5)	0.4816 (2)	0.048 (1)
N2	0.2731 (5)	0.3855 (5)	0.4493 (2)	0.045 (1)
C1	0.6917 (7)	0.2317 (6)	0.4233 (2)	0.049 (2)
C2	0.4813 (7)	0.1720 (6)	0.3978 (2)	0.049 (1)
C3	0.3216 (8)	0.3250 (7)	0.3942 (2)	0.053 (2)
C4	0.8165 (6)	0.7822 (6)	0.3550 (2)	0.045 (1)
C5	0.6528 (8)	0.7926 (7)	0.3148 (2)	0.060 (2)
C6	0.679 (1)	0.8674 (9)	0.2640 (2)	0.081 (2)
C7	0.867 (1)	0.9365 (9)	0.2539 (2)	0.093 (3)
C8	1.028 (1)	0.9287 (9)	0.2927 (2)	0.086 (3)
C9	1.0046 (8)	0.8506 (8)	0.3430 (2)	0.064 (2)
C10	0.7847 (7)	0.7070 (6)	0.4116 (2)	0.043 (1)

^a $U_{eq} = 1/3(\text{trace of the orthogonalized } U_{ij} \text{ matrix})$.

The complex unit is depicted in Fig. 1 with the numbering scheme.

The coordination polyhedron around the central copper(II) atom is a tetragonally elongated pseudo-octahedron. The tetragonality *T* of the title compound is 0.827 at 193 and 0.821 at 296 K. The change of the tetragonality is mainly due to axial compression, as seen in the Cu–O bond lengths (Table 2). Also the volume of the unit cell is compressed upon cooling. As expected, the isotropic thermal displacement parameters get smaller at the same time.

The molecular structure will now be compared primarily with that of CUBENZ, although the structures were determined at different temperatures. Since the coordination polyhedra represent practically static and not fluxional geometry, this kind of comparison is adequate.¹¹

The structure of the complex unit shows at first glance remarkable similarity with CUBENZ. The central copper(II) ion sits at a centre of symmetry, and the six-membered chelate ring displays a chair conformation. The benzoate anions occupy the axial coordination sites.

The bond lengths and angles do not seem to differ markedly from the values reported for CUBENZ. However, upon closer inspection there are a number of other, significant differences.

The main differences are seen in the axial direction. Some characteristic values are shown in Table 3. As torsion in Table 3 we describe the rotation of the carboxylate group with respect to an aromatic ring. There is always rotation involved in every compound. No doubt, the wide angle in CUORME is due to the sterical influence of a methyl group at the *ortho* position. The difference in the title compound and CUBENZ is also significant; obviously the bond connecting the carboxylate group to aromatic ring allows easy rotation.

Let us define the torsional angle N1–Cu1–O1–O2 as the twist of the carboxylate group with respect to the chelate ring. As can be seen from Table 3, there are three distinctive categories for the twist. Let the non-coordinated oxygen O2 be projected to the CuN₄ plane. Then the projection point can either sit between the two

Table 2. The bond lengths (in Å) and angles (in °) for the non-hydrogen atoms with their standard deviations in the title compound.

Atoms	193 K	296 K
Bond lengths		
Cu1–O1	2.459 (2)	2.479 (3)
Cu1–N1	2.046 (3)	2.044 (4)
Cu1–N2	2.023 (3)	2.025 (3)
O1–C10	1.268 (4)	1.253 (5)
O2–C10	1.254 (4)	1.249 (5)
O3–C2	1.430 (4)	1.414 (5)
N1–C1	1.470 (5)	1.480 (6)
N2–C3	1.474 (5)	1.477 (6)
C1–C2	1.514 (5)	1.523 (6)
C2–C3	1.518 (5)	1.517 (7)
C4–C5	1.384 (5)	1.390 (6)
C4–C9	1.385 (5)	1.384 (7)
C4–C10	1.512 (5)	1.517 (6)
C5–C6	1.390 (5)	1.379 (7)
C6–C7	1.377 (7)	1.372 (11)
C7–C8	1.366 (7)	1.353 (9)
C8–C9	1.380 (6)	1.373 (8)
Bond angles		
N1–Cu1–N2	88.2 (1)	88.4 (1)
Cu1–O1–C10	122.8 (2)	122.9 (2)
Cu1–N1–C1	118.3 (2)	118.5 (3)
Cu1–N2–C3	118.3 (2)	118.2 (3)
N1–C1–C2	112.0 (3)	111.2 (4)
O3–C2–C1	110.6 (3)	111.3 (3)
O3–C2–C3	106.0 (3)	106.9 (4)
C1–C2–C3	114.2 (3)	114.4 (4)
N2–C3–C2	112.0 (3)	111.4 (3)
C5–C4–C9	119.6 (3)	118.4 (4)
C5–C4–C10	120.3 (3)	120.4 (5)
C9–C4–C10	120.1 (3)	121.3 (4)
C4–C5–C6	120.2 (4)	120.4 (5)
C5–C6–C7	119.5 (4)	119.5 (5)
C6–C7–C8	120.4 (4)	120.8 (6)
C7–C8–C9	120.7 (4)	120.2 (6)
C4–C9–C8	119.7 (3)	120.6 (5)
O1–C10–O2	124.8 (3)	125.7 (4)
O1–C10–C4	116.8 (3)	117.2 (3)
O2–C10–C4	118.4 (3)	117.1 (4)

chelate rings (CUTERE and the title compound), within a ring or near to an amino group (CUPABR and CUPAIO). It is noteworthy that in CUBENZ the projection point lies within the ring. Thus there are three primary possibilities for the carboxylate group to orientate itself. This can lead to conformational isomers as found in *trans*-di(4-chlorobenzoato-*O*)bis(1,3-diaminopropane-*N,N'*)cobalt(III) 4-chlorobenzoate.³

d-s Mixing. There is significant axial elongation in the title compound. The concept of *d-s* mixing has been used quite often to explain the axial elongation in Cu(II) complexes.^{29–32} In their concluding remarks

Vanquickenborne *et al.* pointed out that, owing to the *d-s* mixing, the most stabilising distortion would be produced by an asymmetrical axial elongation.³² This would then lead either to five-coordination or 4+1+1 coordination mode. Obviously this is the case neither in the title compound nor in the *trans*-Cutn₂bzO₂ series. However, five-coordination is seen in di(1,3-diaminopropane-*N,N'*)(3,5-dinitrobenzoato-*O*)copper(II) 3,5-dinitrobenzoate.³³

From the electronic point of view, the energy level of the MO including a *d_{z²}* orbital would be lowered, even below the energy levels of the other MOs containing the other 3d orbitals.³² To study this, we performed extended Hückel calculations for the title compound and CUBENZ. The results are shown in Table 4.

The axial bond length differences in the title compound at 193 and 296 K do not result in marked differences in the O contributions to the respective axial MO. In our previous study of two distortion isomers of bis(1,3-diaminobutane)copper(II) perchlorate, the two highly significantly different axial bond lengths resulted in changes in the oxygen AO contributions calculated by extended Hückel methods.³⁴ In every complex unit the HOMO (containing the unpaired electron) is essentially a *d_{x²-y²}* orbital with a noticeable contribution from the nitrogen atoms. The occupation of a 4s orbital is significant in the MO, which is mainly composed of the Cu *d_{z²}* atomic orbital. However, it lies above the orbitals composed by the Cu *d_{xy}*, *d_{xz}* and *d_{yz}* atomic orbitals. This is clearly contrary to the suggestions made by Vanquickenborne *et al.* Instead, it is the MO containing the *d_{xy}* AO, for which the energy level seems to be sensitive for changes.

Hydrogen bonding. The hydrogen bonding differs clearly from the one reported for CUBENZ, where there are one intra- and two intermolecular hydrogen bonds between the non-coordinated oxygen atom O2 and the amine groups of tn. There is no such intramolecular hydrogen bond in the title compound (Table 5). Instead, there are two intermolecular hydrogen bonds. Moreover, there is a relatively strong hydrogen bond to the coordinated oxygen O1 from the neighbouring hydroxyl group. The parameters in Table 5 suggest that this hydrogen bond gets weaker upon cooling, which is unexpected. No hydrogen bond to a coordinated oxygen atom has yet been reported in the Mtn₂bzO₂ series.

Supplementary material

Listings of the coordinates, anisotropic thermal displacement parameters, bond lengths and angles, structure factor tables and least-squares planes are available from the authors upon request.

Table 3. Descriptive parameters (in °) for the coordinational diversity of the benzoate anions.

Compound	Abbreviation	Twist ^a	Torsion ^b	Ref.
Title compound at 193 K		139.3	18.9	This work
Title compound at 296 K		132.0	19.1	This work
<i>trans</i> -Di(3-chlorobenzoato- <i>O</i>)bis(1,3-diaminopropane- <i>N,N'</i>)copper(II)	CUMECL	57.8	168.9	18
<i>trans</i> -Di(3-iodobenzoato- <i>O</i>)bis(1,3-diaminopropane- <i>N,N'</i>)copper(II)	CUMEIO	59.2	12.5	1
<i>trans</i> -Di(4-chlorobenzoato- <i>O</i>)bis(1,3-diaminopropane- <i>N,N'</i>)copper(II)	CUPACL	51.9	3.5	19
<i>trans</i> -Di(3-bromobenzoato- <i>O</i>)bis(1,3-diaminopropane- <i>N,N'</i>)copper(II)	CUMEBR	59.4	12.2	20
<i>trans</i> -Di(4-iodobenzoato- <i>O</i>)bis(1,3-diaminopropane- <i>N,N'</i>)copper(II)	CUPAIO	10.3	8.4	21
<i>trans</i> -Di(3-nitrobenzoato- <i>O</i>)bis(1,3-diaminopropane- <i>N,N'</i>)copper(II)	CUMENI	-44.1	3.5	22
<i>trans</i> -Di(4-methylbenzoato- <i>O</i>)bis(1,3-diaminopropane- <i>N,N'</i>)copper(II)	CUPAME	34.5	173.4	23
<i>trans</i> -Di(4-bromobenzoato- <i>O</i>)bis(1,3-diaminopropane- <i>N,N'</i>)copper(II)	CUPABR	6.7	7.4	24
<i>trans</i> -Di(4-fluorobenzoato- <i>O</i>)bis(1,3-diaminopropane- <i>N,N'</i>)copper(II)	CUPAFL	54.0	177.8	25
<i>trans</i> -Di(4-nitrobenzoato- <i>O</i>)bis(1,3-diaminopropane- <i>N,N'</i>)copper(II)	CUPANI	25.3	6.3	26
<i>trans</i> -Di(benzoato- <i>O</i>)bis(1,3-diaminopropane- <i>N,N'</i>)copper(II)	CUBENZ	54.4	7.2	9
<i>trans</i> -Di(3-methylbenzoato- <i>O</i>)bis(1,3-diaminopropane- <i>N,N'</i>)copper(II)	CUMEME	56.2	168.7	27
<i>trans</i> -Di(2-methylbenzoato- <i>O</i>)bis(1,3-diaminopropane- <i>N,N'</i>)copper(II)	CUORME	49.2	61.0	28
<i>catena-μ</i> -(Terephthalato- <i>O</i>)bis(1,3-diamino-2-hydroxypropane- <i>N,N'</i>)copper(II)	CUTERE	138.7	15.9	8

^a Twist is defined as a torsion angle N1–Cu1–O1–O2. ^b Torsion is defined as an angle between a carboxylate group and an aromatic ring.

Table 4. Description of the two highest molecular orbitals with the metal AO contributions coming from $d_{x^2-y^2}$ (HOMO) and d_{z^2} . The percentual shares refer to the contributions from copper, oxygen, nitrogen and copper 4s AO, respectively, to the corresponding MO.

Moiety ^a	Cu (%)	O1 (%)	N (%)	4s (%)	Energy/eV
t.c. 296 K $d_{x^2-y^2}$	37	<1	54	<1	-10.953
t.c. 296 K d_{z^2}	62	10	6	6	-13.358
t.c. 296 K d_{yz}	92	<1	2	<1	-13.850
t.c. 296 K d_{xz}	93	<1	2	<1	-13.872
t.c. 296 K d_{xy}	61	<1	<1	<1	-13.940
t.c. 193 K $d_{x^2-y^2}$	37	<1	56	<1	-10.986
t.c. 193 K d_{z^2}	60	8	6	6	-13.353
t.c. 193 K d_{yz}	92	<1	2	<1	-13.847
t.c. 193 K d_{xz}	93	<1	2	<1	-13.878
t.c. 193 K d_{xy}	67	<1	<1	<1	-13.947
CUBENZ $d_{x^2-y^2}$	38	<1	64	<1	-10.977
CUBENZ d_{z^2}	58	6	4	6	-13.398
CUBENZ d_{xy}	54	<1	<1	<1	-13.692
CUBENZ d_{xz}	77	<1	<1	<1	-13.836
CUBENZ d_{yz}	91	<1	<1	<1	-13.879

^a t.c., title compound.

Table 5. The possible hydrogen bonds for the title compound.

Moiety	A...H/Å	A...D/Å	A...H–D/°	Symmetry operator
193 K				
O3–H10...O1 ⁱ	1.92 (4)	2.687 (4)	164(4)	(i) $x, y-1, z$
N1–H2...O2 ⁱⁱ	2.05 (3)	2.970 (4)	165 (3)	(ii) $-x+2, -y+1, -z+1$
N2–H4...O2 ⁱⁱⁱ	2.08 (4)	2.913 (4)	176 (3)	(iii) $x-1, y, z$
296 K				
O3–H10...O1 ⁱ	1.74 (4)	2.699 (4)	161 (4)	(i)
N1–H2...O2 ⁱⁱ	2.19(4)	2.986(5)	160 (3)	(ii)
N2–H4...O2 ⁱⁱⁱ	2.07 (4)	2.930 (5)	171 (4)	(iii)

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