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(N-Salicylidene-β-alanine)[1,1-bis-(3,5-dimethylpyrazol-1-yl)methane]-copper(II)

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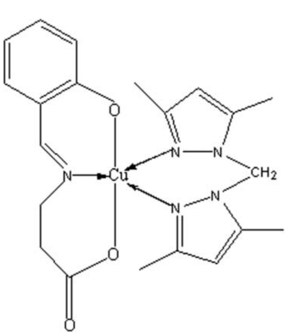
Key indicators: single-crystal X-ray study; T = 273 K; mean σ(C–C) = 0.005 Å; R factor = 0.038; wR factor = 0.099; data-to-parameter ratio = 13.3.

In the title compound, $[Cu(C_{10}H_9NO_3)(C_{11}H_{16}N_4)]$, the Cu^{II} atom is five-coordinated in a distorted square-pyramidal geometry. The basal positions are occupied by three donor atoms from the tridentate Schiff base ligand and by one N atom from a 1,1-bis(3,5-dimethylpyrazol-1-yl)methane ligand. The apical position is occupied by the other N atom of this ligand. The asymmetric unit contains two molecules. There are only van der Waals contacts in the crystal packing.

Related literature

For related literature, see: Plesch *et al.* (1997); Raso *et al.* (1996, 1999); Wang *et al.* (2005); Warda (1997, 1998*a*,*b*,*c*); Reddy *et al.* (2002).



Experimental

Crystal data

$[Cu(C_{10}H_9NO_3)(C_{11}H_{16}N_4)]$
M_r = 459.00
Triclinic, $P\overline{1}$
a = 8.1395 (9) Å
b = 14.3894 (16) Å
c = 19.271 (2) Å
α = 71.760 (1)°
β = 79.411 (1)°
γ = 79.966 (1)°
V = 2090.6 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.08 mm^{-1}
T = 273 (2) K
0.30 × 0.30 × 0.25 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.738, T_{max} = 0.774
10962 measured reflections
7278 independent reflections
5692 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.099
S = 1.03
7278 reflections
549 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.909 (2)	Cu1—N4	2.051 (2)
Cu1—O2	1.950 (2)	Cu1—N2	2.338 (2)
Cu1—N1	1.981 (2)		
O1—Cu1—O2	167.05 (10)	N1—Cu1—N4	167.45 (9)
O1—Cu1—N1	92.36 (9)	O1—Cu1—N2	95.31 (9)
O2—Cu1—N1	91.07 (9)	O2—Cu1—N2	95.79 (9)
O1—Cu1—N4	88.32 (9)	N1—Cu1—N2	105.47 (9)
O2—Cu1—N4	85.65 (9)	N4—Cu1—N2	86.93 (9)

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); 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: CF2130).

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supplementary materials

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(*N*-Salicylidene-β-alanine)[1,1-bis(3,5-dimethylpyrazol-1-yl)methane]copper(II)

G.-Q. Zhao, C.-J. Hao, X.-J. Lu, J.-M. Xie and Y.-Z. Song

Comment

Considerable efforts have been devoted to copper(II) complexes of tridentate Schiff base ligands of the *N*-alkylidene or *N*-arylidene aminoacidato type due to their structural richness and electrochemical properties as well as their use as a potential model for a number of important biological systems (Raso *et al.*, 1996, 1999). Several stuctural studies have been performed on Schiff base copper(II) complexes derived from salicylaldehyde and animo acids (Reddy *et al.*, 2002; Wang *et al.*, 2005; Warda, 1997, 1998*a*,b,c). We report here the crystal structure of the title Cu^{II} complex.

The structure consists of discrete monomeric square-pyramidal Cu^{II} complex (Fig. 1 and Table 1). The basal positions are occupied by three donor atoms from the tridentate Schiff base ligand, which furnishes an ONO donor set, with the fourth position occupied by one N atom from the 1,1-bis(3,5-dimethylprazol-l-yl)methane ligand. The apical position is occupied by the other N atom of this igand.

The two nitrogen heterocycles are planar and lie at angles of 63.87 (10)° and 59.53 (7)° to the plane of the tridentate Schiff base. The two nitrogen heterocycles form a dihedral angle of 58.71 (14)° with each other. There are only van der Waals contacts in the crystal packing.

Experimental

The title compound was synthesized as described in the literature (Plesch *et al.*, 1997). To β-alanine (1.0 mmol) and lithium hydroxide monohydrate (1.0 mmol) in 10 ml of methanol was added salicylaldehyde (1.0 mmol in 10 ml of methanol). The yellow solution was stirred for 1 h at room temperature prior to cooling in an ice bath. The resultant mixture was added dropwise to copper(II) acetate monohydrate (1.0 mmol) and 1,1-bis(3,5-dimethylprazol-l-yl)methane (1.0 mmol) in an aqueous methanol solution (20 ml, 1;1 *v*/*v*), and heated with stirring for 2 h at 333 K. The dark green solution was filtered and left for several days; the resulting dark blue crystals were filtered off, washed with water, and dried under vacuum. Analysis found: C 54.95, H 5.49, N 15.26%; calculated: C 54.82, H 5.35, N 14.71%.

Refinement

All H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93 Å (CH) or 0.97 Å (CH_2) and $U_{iso}(H) = 1.2U_{eq}(C)$, and with C—H = 0.96 Å (CH_3) and $U_{iso}(H) = 1.5U_{eq}(C)$.

Figures

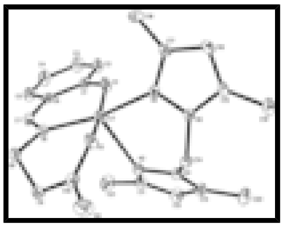

Fig. 1. The molecular structure of the title compound, showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted.

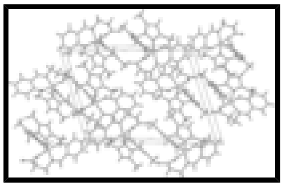

Fig. 2. A view of the crystal packing along the *a* axis.

(*N*-Salicylidene-β-alanine)[1,1-bis(3,5-dimethylpyrazol-1-yl)methane] copper(II)

Crystal data

$[Cu(C_{10}H_9NO_3)(C_{11}H_{16}N_4)]$	$Z = 4$
$M_r = 459.00$	$F_{000} = 956$
Triclinic, $P\bar{1}$	$D_x = 1.458$ Mg m^{-3}
Hall symbol: -P 1	Mo *K*α radiation λ = 0.71073 Å
a = 8.1395 (9) Å	Cell parameters from 4237 reflections
b = 14.3894 (16) Å	θ = 2.3–26.4°
c = 19.271 (2) Å	μ = 1.08 mm^{-1}
α = 71.760 (1)°	*T* = 273 (2) K
β = 79.411 (1)°	Block, dark green
γ = 79.966 (1)°	0.30 × 0.30 × 0.25 mm
V = 2090.6 (4) Å^3	

Data collection

Bruker SMART CCD diffractometer	7278 independent reflections
Radiation source: fine-focus sealed tube	5692 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.021$
T = 273(2) K	$\theta_{max} = 25.1°$
φ and ω scans	$\theta_{min} = 2.3°$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -9 \rightarrow 9$
$T_{min} = 0.738$, $T_{max} = 0.774$	$k = -16 \rightarrow 17$
10962 measured reflections	$l = -21 \rightarrow 22$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map

Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.038$	H-atom parameters constrained
$wR(F^2) = 0.099$	$w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 1.188P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.001$
7278 reflections	$\Delta\rho_{max} = 0.28$ e Å^{-3}
549 parameters	$\Delta\rho_{min} = -0.32$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > 2\text{sigma}(F^2)$ 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	0.58096 (4)	0.58610 (3)	0.174452 (19)	0.03384 (11)
O1	0.4334 (3)	0.53347 (16)	0.26219 (12)	0.0476 (6)
O2	0.6849 (3)	0.64875 (15)	0.07478 (11)	0.0416 (5)
O3	0.9243 (3)	0.6862 (2)	0.00468 (14)	0.0688 (8)
N1	0.6090 (3)	0.69887 (17)	0.20759 (13)	0.0343 (5)
N2	0.8122 (3)	0.46820 (18)	0.20680 (13)	0.0370 (6)
N3	0.8477 (3)	0.39843 (18)	0.16911 (13)	0.0351 (6)
N4	0.5103 (3)	0.49029 (17)	0.12917 (13)	0.0333 (5)
N5	0.6220 (3)	0.42616 (17)	0.09848 (13)	0.0332 (5)
C1	0.4029 (4)	0.5579 (2)	0.32336 (16)	0.0385 (7)
C2	0.3138 (4)	0.4978 (2)	0.38614 (18)	0.0502 (9)
H2	0.2784	0.4412	0.3832	0.060*
C3	0.2780 (5)	0.5211 (3)	0.45176 (19)	0.0582 (10)
H3	0.2205	0.4794	0.4926	0.070*
C4	0.3261 (5)	0.6054 (3)	0.45813 (19)	0.0610 (10)
H4	0.3006	0.6206	0.5027	0.073*
C5	0.4110 (4)	0.6656 (3)	0.39841 (18)	0.0483 (8)
H5	0.4427	0.7225	0.4026	0.058*
C6	0.4524 (3)	0.6442 (2)	0.33040 (16)	0.0355 (7)
C7	0.5474 (4)	0.7100 (2)	0.27160 (16)	0.0371 (7)
H7	0.5668	0.7669	0.2803	0.045*
C8	0.7002 (4)	0.7775 (2)	0.15535 (17)	0.0395 (7)

H8A	0.7313	0.8174	0.1820	0.047*
H8B	0.6266	0.8197	0.1206	0.047*
C9	0.8570 (4)	0.7367 (2)	0.11345 (17)	0.0403 (7)
H9A	0.9238	0.6888	0.1486	0.048*
H9B	0.9235	0.7900	0.0868	0.048*
C10	0.8223 (4)	0.6881 (2)	0.05944 (17)	0.0399 (7)
C11	0.8719 (4)	0.4232 (2)	0.27010 (17)	0.0410 (7)
C12	0.9458 (4)	0.3281 (2)	0.27292 (18)	0.0491 (8)
H12	0.9984	0.2833	0.3112	0.059*
C13	0.9267 (4)	0.3126 (2)	0.20848 (17)	0.0423 (7)
C14	0.8011 (3)	0.4254 (2)	0.09625 (15)	0.0356 (7)
H14A	0.8627	0.3789	0.0706	0.043*
H14B	0.8322	0.4903	0.0688	0.043*
C15	0.5418 (4)	0.3773 (2)	0.06804 (15)	0.0359 (7)
C16	0.3739 (4)	0.4101 (2)	0.07960 (17)	0.0403 (7)
H16	0.2867	0.3902	0.0647	0.048*
C17	0.3592 (3)	0.4794 (2)	0.11823 (16)	0.0345 (7)
C18	0.2039 (4)	0.5365 (3)	0.1456 (2)	0.0518 (9)
H18A	0.1735	0.5067	0.1974	0.078*
H18B	0.1137	0.5365	0.1197	0.078*
H18C	0.2242	0.6031	0.1372	0.078*
C19	0.6310 (4)	0.3002 (2)	0.03268 (18)	0.0513 (9)
H19A	0.7300	0.3234	0.0008	0.077*
H19B	0.5575	0.2866	0.0044	0.077*
H19C	0.6629	0.2410	0.0702	0.077*
C20	0.9746 (5)	0.2231 (2)	0.1821 (2)	0.0609 (10)
H20A	0.8746	0.1980	0.1797	0.091*
H20B	1.0406	0.1735	0.2157	0.091*
H20C	1.0394	0.2402	0.1340	0.091*
C21	0.8604 (5)	0.4779 (3)	0.32599 (19)	0.0625 (10)
H21A	0.8639	0.5469	0.3012	0.094*
H21B	0.9534	0.4528	0.3537	0.094*
H21C	0.7566	0.4690	0.3588	0.094*
Cu2	0.21027 (4)	0.07442 (3)	0.707187 (19)	0.03530 (11)
O4	0.1065 (3)	0.00959 (16)	0.80327 (12)	0.0508 (6)
O5	0.3530 (3)	0.14150 (15)	0.61784 (12)	0.0445 (5)
O6	0.3500 (4)	0.1832 (2)	0.49747 (15)	0.0931 (10)
N6	0.0558 (3)	0.19775 (18)	0.70325 (14)	0.0384 (6)
N7	0.3991 (3)	−0.04190 (17)	0.72357 (13)	0.0359 (6)
N8	0.4269 (3)	−0.10560 (17)	0.68146 (13)	0.0354 (6)
N9	0.0951 (3)	−0.00214 (19)	0.64183 (14)	0.0412 (6)
N10	0.2008 (3)	−0.06555 (18)	0.60895 (14)	0.0408 (6)
C22	−0.0234 (4)	0.0411 (2)	0.84367 (17)	0.0419 (7)
C23	−0.0794 (4)	−0.0222 (3)	0.91284 (19)	0.0548 (9)
H23	−0.0241	−0.0859	0.9280	0.066*
C24	−0.2142 (5)	0.0080 (3)	0.95840 (19)	0.0603 (10)
H24	−0.2479	−0.0355	1.0040	0.072*
C25	−0.3012 (4)	0.1020 (3)	0.9380 (2)	0.0607 (10)
H25	−0.3925	0.1216	0.9693	0.073*

C26	−0.2507 (4)	0.1650 (3)	0.8713 (2)	0.0504 (9)
H26	−0.3085	0.2282	0.8575	0.061*
C27	−0.1127 (4)	0.1372 (2)	0.82239 (17)	0.0397 (7)
C28	−0.0660 (4)	0.2086 (2)	0.75413 (18)	0.0422 (7)
H28	−0.1310	0.2700	0.7455	0.051*
C29	0.0811 (4)	0.2820 (2)	0.63729 (18)	0.0485 (8)
H29A	0.1741	0.3137	0.6406	0.058*
H29B	−0.0194	0.3298	0.6351	0.058*
C30	0.1183 (4)	0.2501 (2)	0.56744 (18)	0.0491 (8)
H30A	0.0299	0.2130	0.5670	0.059*
H30B	0.1150	0.3085	0.5252	0.059*
C31	0.2861 (4)	0.1879 (2)	0.5588 (2)	0.0490 (8)
C32	0.4749 (4)	−0.0889 (2)	0.78276 (16)	0.0400 (7)
C33	0.5498 (4)	−0.1817 (2)	0.77863 (17)	0.0458 (8)
H33	0.6106	−0.2285	0.8132	0.055*
C34	0.5175 (4)	−0.1916 (2)	0.71435 (17)	0.0421 (7)
C35	0.3806 (4)	−0.0713 (2)	0.60784 (16)	0.0399 (7)
H35A	0.4391	−0.1158	0.5800	0.048*
H35B	0.4158	−0.0066	0.5831	0.048*
C36	0.1155 (5)	−0.1129 (3)	0.57916 (18)	0.0500 (8)
C37	−0.0493 (5)	−0.0793 (3)	0.59379 (19)	0.0563 (10)
H37	−0.1395	−0.0979	0.5801	0.068*
C38	−0.0586 (4)	−0.0117 (2)	0.63313 (17)	0.0460 (8)
C39	0.4752 (5)	−0.0416 (3)	0.84147 (19)	0.0584 (10)
H39A	0.3668	−0.0419	0.8713	0.088*
H39B	0.4991	0.0251	0.8191	0.088*
H39C	0.5599	−0.0777	0.8719	0.088*
C40	0.5618 (5)	−0.2776 (3)	0.6837 (2)	0.0649 (11)
H40A	0.6226	−0.2572	0.6349	0.097*
H40B	0.4606	−0.3017	0.6817	0.097*
H40C	0.6307	−0.3289	0.7148	0.097*
C41	−0.2082 (4)	0.0455 (3)	0.6650 (2)	0.0626 (10)
H41A	−0.1936	0.1142	0.6489	0.094*
H41B	−0.2195	0.0221	0.7179	0.094*
H41C	−0.3078	0.0370	0.6487	0.094*
C42	0.2024 (6)	−0.1860 (3)	0.5398 (2)	0.0785 (13)
H42A	0.1201	−0.2135	0.5250	0.118*
H42B	0.2682	−0.2377	0.5721	0.118*
H42C	0.2750	−0.1538	0.4969	0.118*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0376 (2)	0.0323 (2)	0.0349 (2)	−0.00795 (15)	0.00134 (15)	−0.01615 (16)
O1	0.0608 (14)	0.0458 (13)	0.0427 (13)	−0.0227 (11)	0.0148 (10)	−0.0259 (11)
O2	0.0507 (13)	0.0455 (13)	0.0336 (11)	−0.0191 (10)	−0.0007 (10)	−0.0145 (10)
O3	0.0617 (16)	0.097 (2)	0.0567 (16)	−0.0254 (15)	0.0212 (13)	−0.0440 (15)
N1	0.0346 (13)	0.0295 (13)	0.0404 (14)	−0.0034 (10)	−0.0027 (11)	−0.0139 (11)

N2	0.0356 (13)	0.0414 (15)	0.0385 (14)	−0.0040 (11)	−0.0030 (11)	−0.0194 (12)
N3	0.0348 (13)	0.0370 (14)	0.0362 (14)	−0.0029 (11)	−0.0027 (11)	−0.0165 (11)
N4	0.0323 (13)	0.0340 (14)	0.0376 (14)	−0.0051 (10)	−0.0006 (10)	−0.0177 (11)
N5	0.0357 (13)	0.0326 (14)	0.0345 (13)	−0.0035 (11)	−0.0020 (10)	−0.0163 (11)
C1	0.0379 (16)	0.0374 (18)	0.0406 (18)	−0.0018 (13)	0.0015 (14)	−0.0174 (14)
C2	0.063 (2)	0.0390 (19)	0.048 (2)	−0.0130 (16)	0.0105 (17)	−0.0192 (16)
C3	0.077 (3)	0.050 (2)	0.041 (2)	−0.0127 (19)	0.0141 (18)	−0.0141 (17)
C4	0.086 (3)	0.061 (2)	0.038 (2)	−0.011 (2)	0.0102 (19)	−0.0263 (18)
C5	0.059 (2)	0.047 (2)	0.045 (2)	−0.0056 (16)	−0.0029 (16)	−0.0253 (16)
C6	0.0333 (15)	0.0375 (17)	0.0376 (17)	0.0010 (13)	−0.0021 (13)	−0.0183 (14)
C7	0.0384 (16)	0.0320 (17)	0.0451 (18)	−0.0022 (13)	−0.0041 (14)	−0.0192 (14)
C8	0.0465 (18)	0.0308 (17)	0.0442 (18)	−0.0072 (14)	−0.0024 (14)	−0.0161 (14)
C9	0.0390 (17)	0.0402 (18)	0.0432 (18)	−0.0116 (14)	−0.0002 (14)	−0.0136 (14)
C10	0.0428 (18)	0.0358 (18)	0.0390 (18)	−0.0015 (14)	−0.0019 (14)	−0.0118 (14)
C11	0.0400 (17)	0.048 (2)	0.0357 (17)	−0.0046 (14)	−0.0038 (14)	−0.0143 (15)
C12	0.053 (2)	0.046 (2)	0.0403 (19)	−0.0016 (16)	−0.0098 (16)	−0.0029 (15)
C13	0.0433 (18)	0.0354 (18)	0.0437 (19)	−0.0035 (14)	−0.0004 (14)	−0.0091 (14)
C14	0.0330 (15)	0.0406 (18)	0.0350 (16)	−0.0060 (13)	0.0026 (12)	−0.0170 (14)
C15	0.0515 (19)	0.0305 (16)	0.0286 (15)	−0.0108 (14)	−0.0057 (13)	−0.0096 (13)
C16	0.0460 (18)	0.0378 (18)	0.0428 (18)	−0.0151 (14)	−0.0135 (14)	−0.0102 (14)
C17	0.0350 (16)	0.0322 (16)	0.0351 (16)	−0.0086 (12)	−0.0045 (13)	−0.0060 (13)
C18	0.0338 (17)	0.056 (2)	0.065 (2)	−0.0071 (15)	0.0011 (16)	−0.0211 (18)
C19	0.068 (2)	0.045 (2)	0.049 (2)	−0.0092 (17)	−0.0047 (17)	−0.0255 (17)
C20	0.077 (3)	0.037 (2)	0.065 (2)	0.0064 (18)	−0.012 (2)	−0.0153 (18)
C21	0.075 (3)	0.070 (3)	0.048 (2)	0.003 (2)	−0.0165 (19)	−0.0269 (19)
Cu2	0.0369 (2)	0.0303 (2)	0.0386 (2)	−0.00238 (15)	−0.00030 (16)	−0.01353 (16)
O4	0.0543 (14)	0.0409 (13)	0.0459 (13)	0.0047 (10)	0.0116 (11)	−0.0128 (11)
O5	0.0414 (12)	0.0387 (13)	0.0503 (14)	−0.0092 (10)	0.0020 (10)	−0.0107 (11)
O6	0.110 (2)	0.100 (2)	0.0443 (17)	0.0131 (19)	0.0170 (16)	−0.0155 (16)
N6	0.0402 (14)	0.0340 (14)	0.0420 (15)	−0.0008 (11)	−0.0076 (12)	−0.0136 (12)
N7	0.0374 (13)	0.0344 (14)	0.0367 (14)	−0.0028 (11)	0.0001 (11)	−0.0152 (11)
N8	0.0386 (13)	0.0309 (14)	0.0357 (14)	−0.0014 (11)	0.0007 (11)	−0.0134 (11)
N9	0.0398 (14)	0.0406 (15)	0.0460 (16)	−0.0069 (12)	−0.0022 (12)	−0.0174 (13)
N10	0.0486 (15)	0.0388 (15)	0.0401 (15)	−0.0072 (12)	−0.0071 (12)	−0.0172 (12)
C22	0.0420 (18)	0.0465 (19)	0.0405 (18)	−0.0009 (15)	−0.0019 (14)	−0.0221 (15)
C23	0.059 (2)	0.054 (2)	0.045 (2)	0.0020 (17)	0.0024 (17)	−0.0157 (17)
C24	0.063 (2)	0.073 (3)	0.041 (2)	−0.005 (2)	0.0063 (17)	−0.0198 (19)
C25	0.047 (2)	0.086 (3)	0.054 (2)	−0.001 (2)	0.0048 (17)	−0.037 (2)
C26	0.0385 (18)	0.060 (2)	0.060 (2)	0.0059 (16)	−0.0076 (16)	−0.0344 (19)
C27	0.0355 (16)	0.0443 (19)	0.0461 (19)	−0.0036 (14)	−0.0057 (14)	−0.0236 (15)
C28	0.0411 (17)	0.0375 (18)	0.052 (2)	0.0031 (14)	−0.0102 (15)	−0.0210 (15)
C29	0.054 (2)	0.0316 (18)	0.055 (2)	−0.0013 (15)	−0.0068 (16)	−0.0094 (15)
C30	0.058 (2)	0.044 (2)	0.0414 (19)	−0.0116 (16)	−0.0104 (16)	−0.0027 (15)
C31	0.058 (2)	0.0383 (19)	0.049 (2)	−0.0148 (16)	0.0031 (17)	−0.0115 (16)
C32	0.0394 (17)	0.0414 (18)	0.0370 (17)	−0.0038 (14)	−0.0010 (14)	−0.0113 (14)
C33	0.0531 (19)	0.0360 (18)	0.0392 (18)	0.0032 (15)	−0.0052 (15)	−0.0036 (14)
C34	0.0483 (18)	0.0292 (17)	0.0415 (18)	−0.0023 (14)	0.0059 (15)	−0.0081 (14)
C35	0.0447 (18)	0.0381 (18)	0.0370 (17)	−0.0035 (14)	0.0024 (14)	−0.0164 (14)
C36	0.069 (2)	0.046 (2)	0.0407 (19)	−0.0137 (18)	−0.0169 (17)	−0.0115 (16)

C37	0.070 (3)	0.053 (2)	0.055 (2)	−0.0258 (19)	−0.0263 (19)	−0.0087 (18)
C38	0.0466 (19)	0.044 (2)	0.0429 (19)	−0.0168 (15)	−0.0091 (15)	0.0009 (15)
C39	0.075 (3)	0.056 (2)	0.049 (2)	−0.0026 (19)	−0.0186 (19)	−0.0198 (18)
C40	0.090 (3)	0.038 (2)	0.061 (2)	0.0075 (19)	−0.002 (2)	−0.0203 (18)
C41	0.043 (2)	0.072 (3)	0.070 (3)	−0.0163 (18)	−0.0062 (18)	−0.013 (2)
C42	0.111 (4)	0.074 (3)	0.072 (3)	−0.012 (3)	−0.021 (3)	−0.046 (2)

Geometric parameters (Å, °)

Cu1—O1	1.909 (2)	Cu2—O4	1.905 (2)
Cu1—O2	1.950 (2)	Cu2—O5	1.965 (2)
Cu1—N1	1.981 (2)	Cu2—N6	1.977 (2)
Cu1—N4	2.051 (2)	Cu2—N7	2.053 (2)
Cu1—N2	2.338 (2)	Cu2—N9	2.311 (2)
O1—C1	1.302 (3)	O4—C22	1.296 (3)
O2—C10	1.286 (4)	O5—C31	1.289 (4)
O3—C10	1.221 (3)	O6—C31	1.218 (4)
N1—C7	1.291 (4)	N6—C28	1.286 (4)
N1—C8	1.466 (4)	N6—C29	1.468 (4)
N2—C11	1.325 (4)	N7—C32	1.330 (4)
N2—N3	1.377 (3)	N7—N8	1.370 (3)
N3—C13	1.353 (4)	N8—C34	1.357 (4)
N3—C14	1.439 (4)	N8—C35	1.446 (4)
N4—C17	1.329 (3)	N9—C38	1.328 (4)
N4—N5	1.371 (3)	N9—N10	1.365 (3)
N5—C15	1.350 (3)	N10—C36	1.353 (4)
N5—C14	1.449 (3)	N10—C35	1.448 (4)
C1—C2	1.407 (4)	C22—C23	1.406 (5)
C1—C6	1.422 (4)	C22—C27	1.418 (4)
C2—C3	1.375 (4)	C23—C24	1.372 (4)
C2—H2	0.930	C23—H23	0.930
C3—C4	1.384 (5)	C24—C25	1.386 (5)
C3—H3	0.930	C24—H24	0.930
C4—C5	1.359 (5)	C25—C26	1.358 (5)
C4—H4	0.930	C25—H25	0.930
C5—C6	1.408 (4)	C26—C27	1.415 (4)
C5—H5	0.930	C26—H26	0.930
C6—C7	1.429 (4)	C27—C28	1.427 (4)
C7—H7	0.930	C28—H28	0.930
C8—C9	1.511 (4)	C29—C30	1.518 (4)
C8—H8A	0.970	C29—H29A	0.970
C8—H8B	0.970	C29—H29B	0.970
C9—C10	1.511 (4)	C30—C31	1.509 (5)
C9—H9A	0.970	C30—H30A	0.970
C9—H9B	0.970	C30—H30B	0.970
C11—C12	1.385 (4)	C32—C33	1.388 (4)
C11—C21	1.502 (4)	C32—C39	1.492 (4)
C12—C13	1.368 (4)	C33—C34	1.367 (4)
C12—H12	0.930	C33—H33	0.930

C13—C20	1.494 (4)	C34—C40	1.494 (4)
C14—H14A	0.970	C35—H35A	0.970
C14—H14B	0.970	C35—H35B	0.970
C15—C16	1.367 (4)	C36—C37	1.353 (5)
C15—C19	1.495 (4)	C36—C42	1.492 (5)
C16—C17	1.397 (4)	C37—C38	1.394 (5)
C16—H16	0.930	C37—H37	0.930
C17—C18	1.489 (4)	C38—C41	1.493 (5)
C18—H18A	0.960	C39—H39A	0.960
C18—H18B	0.960	C39—H39B	0.960
C18—H18C	0.960	C39—H39C	0.960
C19—H19A	0.960	C40—H40A	0.960
C19—H19B	0.960	C40—H40B	0.960
C19—H19C	0.960	C40—H40C	0.960
C20—H20A	0.960	C41—H41A	0.960
C20—H20B	0.960	C41—H41B	0.960
C20—H20C	0.960	C41—H41C	0.960
C21—H21A	0.960	C42—H42A	0.960
C21—H21B	0.960	C42—H42B	0.960
C21—H21C	0.960	C42—H42C	0.960

O1—Cu1—O2	167.05 (10)	O4—Cu2—O5	169.07 (10)
O1—Cu1—N1	92.36 (9)	O4—Cu2—N6	92.37 (10)
O2—Cu1—N1	91.07 (9)	O5—Cu2—N6	90.98 (10)
O1—Cu1—N4	88.32 (9)	O4—Cu2—N7	86.25 (9)
O2—Cu1—N4	85.65 (9)	O5—Cu2—N7	88.24 (9)
N1—Cu1—N4	167.45 (9)	N6—Cu2—N7	167.58 (10)
O1—Cu1—N2	95.31 (9)	O4—Cu2—N9	97.73 (10)
O2—Cu1—N2	95.79 (9)	O5—Cu2—N9	91.56 (9)
N1—Cu1—N2	105.47 (9)	N6—Cu2—N9	103.91 (9)
N4—Cu1—N2	86.93 (9)	N7—Cu2—N9	88.50 (9)
C1—O1—Cu1	128.68 (19)	C22—O4—Cu2	129.5 (2)
C10—O2—Cu1	124.47 (19)	C31—O5—Cu2	119.3 (2)
C7—N1—C8	117.1 (2)	C28—N6—C29	118.0 (3)
C7—N1—Cu1	124.5 (2)	C28—N6—Cu2	124.4 (2)
C8—N1—Cu1	118.30 (18)	C29—N6—Cu2	117.6 (2)
C11—N2—N3	104.3 (2)	C32—N7—N8	105.7 (2)
C11—N2—Cu1	133.2 (2)	C32—N7—Cu2	130.5 (2)
N3—N2—Cu1	114.78 (16)	N8—N7—Cu2	120.62 (18)
C13—N3—N2	111.9 (2)	C34—N8—N7	111.1 (2)
C13—N3—C14	129.8 (2)	C34—N8—C35	128.9 (2)
N2—N3—C14	118.2 (2)	N7—N8—C35	119.4 (2)
C17—N4—N5	105.5 (2)	C38—N9—N10	105.1 (2)
C17—N4—Cu1	130.58 (19)	C38—N9—Cu2	136.6 (2)
N5—N4—Cu1	123.80 (17)	N10—N9—Cu2	117.74 (18)
C15—N5—N4	111.2 (2)	C36—N10—N9	111.8 (3)
C15—N5—C14	129.2 (2)	C36—N10—C35	129.4 (3)
N4—N5—C14	119.4 (2)	N9—N10—C35	118.8 (2)
O1—C1—C2	119.3 (3)	O4—C22—C23	118.9 (3)
O1—C1—C6	123.5 (3)	O4—C22—C27	123.6 (3)

C2—C1—C6	117.2 (3)	C23—C22—C27	117.4 (3)
C3—C2—C1	121.3 (3)	C24—C23—C22	121.3 (3)
C3—C2—H2	119.4	C24—C23—H23	119.3
C1—C2—H2	119.4	C22—C23—H23	119.3
C2—C3—C4	121.2 (3)	C23—C24—C25	121.4 (4)
C2—C3—H3	119.4	C23—C24—H24	119.3
C4—C3—H3	119.4	C25—C24—H24	119.3
C5—C4—C3	119.1 (3)	C26—C25—C24	118.8 (3)
C5—C4—H4	120.4	C26—C25—H25	120.6
C3—C4—H4	120.4	C24—C25—H25	120.6
C4—C5—C6	121.7 (3)	C25—C26—C27	121.9 (3)
C4—C5—H5	119.1	C25—C26—H26	119.0
C6—C5—H5	119.1	C27—C26—H26	119.0
C5—C6—C1	119.5 (3)	C26—C27—C22	119.1 (3)
C5—C6—C7	117.6 (3)	C26—C27—C28	118.2 (3)
C1—C6—C7	122.9 (3)	C22—C27—C28	122.6 (3)
N1—C7—C6	126.8 (3)	N6—C28—C27	127.4 (3)
N1—C7—H7	116.6	N6—C28—H28	116.3
C6—C7—H7	116.6	C27—C28—H28	116.3
N1—C8—C9	111.8 (2)	N6—C29—C30	111.4 (3)
N1—C8—H8A	109.2	N6—C29—H29A	109.3
C9—C8—H8A	109.2	C30—C29—H29A	109.3
N1—C8—H8B	109.2	N6—C29—H29B	109.3
C9—C8—H8B	109.2	C30—C29—H29B	109.3
H8A—C8—H8B	107.9	H29A—C29—H29B	108.0
C8—C9—C10	114.0 (3)	C31—C30—C29	114.4 (3)
C8—C9—H9A	108.7	C31—C30—H30A	108.7
C10—C9—H9A	108.7	C29—C30—H30A	108.7
C8—C9—H9B	108.7	C31—C30—H30B	108.7
C10—C9—H9B	108.7	C29—C30—H30B	108.7
H9A—C9—H9B	107.6	H30A—C30—H30B	107.6
O3—C10—O2	123.0 (3)	O6—C31—O5	123.6 (3)
O3—C10—C9	119.9 (3)	O6—C31—C30	119.1 (3)
O2—C10—C9	117.1 (3)	O5—C31—C30	117.3 (3)
N2—C11—C12	111.3 (3)	N7—C32—C33	110.0 (3)
N2—C11—C21	120.0 (3)	N7—C32—C39	121.5 (3)
C12—C11—C21	128.7 (3)	C33—C32—C39	128.5 (3)
C13—C12—C11	106.8 (3)	C34—C33—C32	107.2 (3)
C13—C12—H12	126.6	C34—C33—H33	126.4
C11—C12—H12	126.6	C32—C33—H33	126.4
N3—C13—C12	105.7 (3)	N8—C34—C33	106.0 (3)
N3—C13—C20	123.4 (3)	N8—C34—C40	123.9 (3)
C12—C13—C20	130.9 (3)	C33—C34—C40	130.0 (3)
N3—C14—N5	111.7 (2)	N8—C35—N10	111.8 (2)
N3—C14—H14A	109.3	N8—C35—H35A	109.3
N5—C14—H14A	109.3	N10—C35—H35A	109.3
N3—C14—H14B	109.3	N8—C35—H35B	109.3
N5—C14—H14B	109.3	N10—C35—H35B	109.3
H14A—C14—H14B	107.9	H35A—C35—H35B	107.9

N5—C15—C16	106.6 (2)	N10—C36—C37	105.8 (3)
N5—C15—C19	123.1 (3)	N10—C36—C42	122.2 (3)
C16—C15—C19	130.3 (3)	C37—C36—C42	131.9 (3)
C15—C16—C17	106.4 (3)	C36—C37—C38	107.3 (3)
C15—C16—H16	126.8	C36—C37—H37	126.3
C17—C16—H16	126.8	C38—C37—H37	126.3
N4—C17—C16	110.2 (3)	N9—C38—C37	109.9 (3)
N4—C17—C18	121.1 (3)	N9—C38—C41	119.8 (3)
C16—C17—C18	128.6 (3)	C37—C38—C41	130.3 (3)
C17—C18—H18A	109.5	C32—C39—H39A	109.5
C17—C18—H18B	109.5	C32—C39—H39B	109.5
H18A—C18—H18B	109.5	H39A—C39—H39B	109.5
C17—C18—H18C	109.5	C32—C39—H39C	109.5
H18A—C18—H18C	109.5	H39A—C39—H39C	109.5
H18B—C18—H18C	109.5	H39B—C39—H39C	109.5
C15—C19—H19A	109.5	C34—C40—H40A	109.5
C15—C19—H19B	109.5	C34—C40—H40B	109.5
H19A—C19—H19B	109.5	H40A—C40—H40B	109.5
C15—C19—H19C	109.5	C34—C40—H40C	109.5
H19A—C19—H19C	109.5	H40A—C40—H40C	109.5
H19B—C19—H19C	109.5	H40B—C40—H40C	109.5
C13—C20—H20A	109.5	C38—C41—H41A	109.5
C13—C20—H20B	109.5	C38—C41—H41B	109.5
H20A—C20—H20B	109.5	H41A—C41—H41B	109.5
C13—C20—H20C	109.5	C38—C41—H41C	109.5
H20A—C20—H20C	109.5	H41A—C41—H41C	109.5
H20B—C20—H20C	109.5	H41B—C41—H41C	109.5
C11—C21—H21A	109.5	C36—C42—H42A	109.5
C11—C21—H21B	109.5	C36—C42—H42B	109.5
H21A—C21—H21B	109.5	H42A—C42—H42B	109.5
C11—C21—H21C	109.5	C36—C42—H42C	109.5
H21A—C21—H21C	109.5	H42A—C42—H42C	109.5
H21B—C21—H21C	109.5	H42B—C42—H42C	109.5

Fig. 1

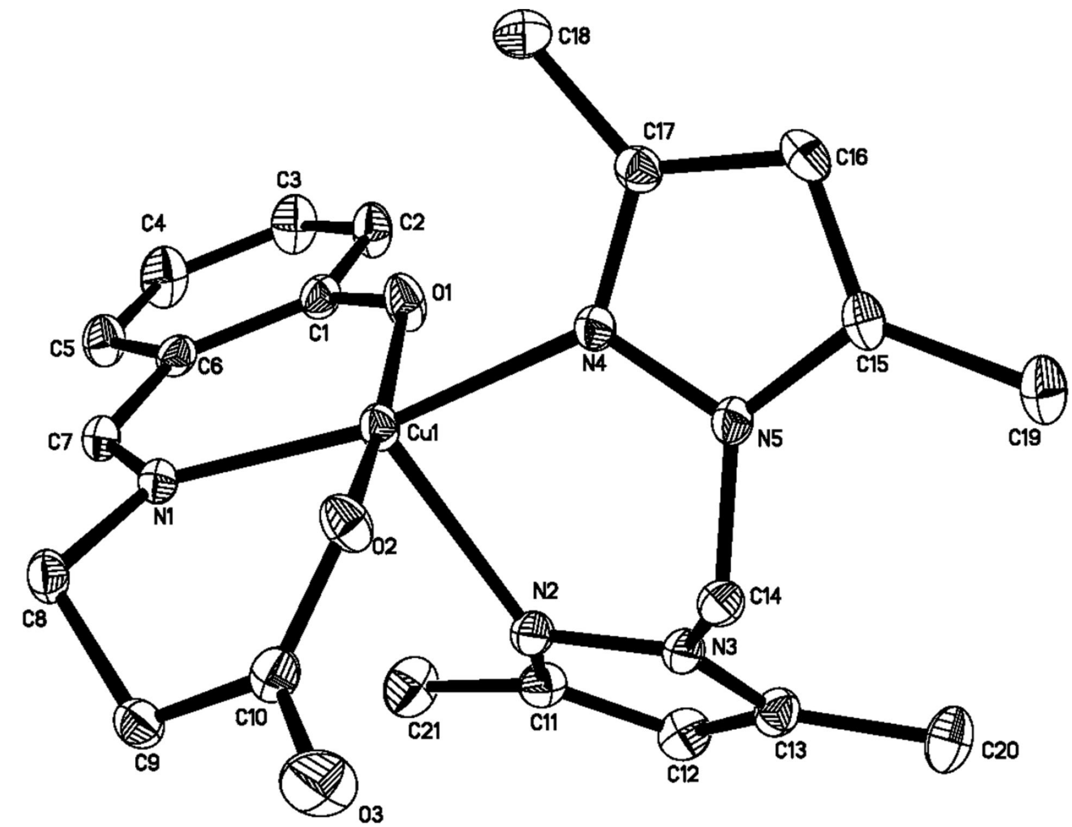
C18
C17
C16
C3
C2
C4
O1
C1
C5
C6
N4
C15
C19
C7
Cu1
N5
N1
O2
N2
C14
C8
N3
C21
C11
C10
C13
C20
C9
C12
O3

Fig. 2