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Di-μ-methoxido-κ^4O:O-bis[bis(3-methyl-5-phenyl-1H-pyrazole-κN^2)copper(II)] bis(perchlorate)

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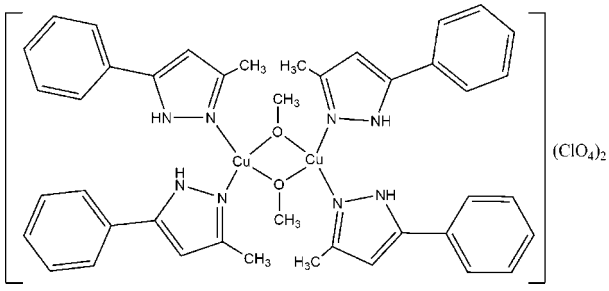
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.009 Å; R factor = 0.049; wR factor = 0.137; data-to-parameter ratio = 15.1.

In the title complex, $[Cu(CH_3O)_2(C_{40}H_{40}N_8)](ClO_4)_2$, two copper ions are bridged by two methoxide O atoms. Each Cu^{II} is further coordinated by two neutral 3-methyl-5-phenyl-1H-pyrazole ligands and adopts a distorted square-planar geometry. The two perchlorate anions lie on opposite sides of the Cu_2O_2 plane and there is evidence for interaction between two of the O atoms from each perchlorate anion with the Cu^{II} centers.

Related literature

For related literature, see: Jacobsen & Cohen (2004); Parkin (2004); Puerta & Cohen (2003); Tekeste & Vahrenkamp (2007).



Experimental

Crystal data

$[Cu(CH_3O)_2(C_{40}H_{40}N_8)](ClO_4)_2$
M_r = 1020.85
Monoclinic, $P2_1/c$
a = 13.8398 (12) Å
b = 17.4607 (16) Å
c = 20.3779 (18) Å
β = 98.316 (1)°
V = 4872.6 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.04 mm^{-1}
T = 293 (2) K
0.15 × 0.13 × 0.11 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2006)
T_{min} = 0.859, T_{max} = 0.894
48197 measured reflections
9045 independent reflections
5370 reflections with $I > 2\sigma(I)$
R_{int} = 0.074

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.137
S = 1.00
9045 reflections
599 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Sheldrick, 1997*b*) and *publCIF* (Version 1.0_c; Westrip, 2007).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2335).

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supplementary materials

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Di-μ-methoxido-κ^4O:O-bis[bis(3-methyl-5-phenyl-1H-pyrazole-κN^2)copper(II)] bis(perchlorate)

H. He and A. G. Sykes

Comment

3-methyl-5-phenyl-1*H*-pyrazole has been widely used as starting material for the preparation of the trispyrazolylborate anion, and as a very good ligand for modeling complexes of several metalloenzymes (Tekeste & Vahrenkamp 2007; Jacobsen & Cohen, 2004; Puerta & Cohen, 2003; Parkin, 2004). However, its interaction with transition metal ions is rare. Reported here is the single-crystal structure of a dicopper(II) complex of this ligand.

In the title compound (I) two methoxide anions hold two copper ions together with O as the bridging atoms. The distance between Cu1 and Cu2 is 2.9583 (7) Å. Each copper ion is further coordinated by two pyrazolyl N atoms. Copper adopts an approximate square planar geometry. Atoms N1, N2, N3, N4, Cu1, and Cu2 are almost coplanar with a torsion angle of 3.4 (3)° between the N1/N2/Cu2 and N3/N4/Cu1 planes. The two bridging methoxyl groups are located on either side of this plane. The torsion angles between the O1/Cu1/Cu2 and O2/Cu1/Cu2 planes and that containing the atoms N1/N2/N3/N4/Cu1/Cu2 are 12.30 (16)° and −12.30 (16)°, respectively. The Cu1/O1/Cu2/O2 ring is also planar with an r.m.s. deviation from the best fit meanplane of 0.0002. The O4, O9 and O3, O8 atoms from the two perchlorate anions point towards the Cu1 and Cu2 centers with distances 2.722 (3), 2.755 (3), 2.790 (3), and 2.869 (3) Å for O3—Cu2, O4—Cu1, O8—Cu2, and O9—Cu1, respectively. This indicates some level of interaction between the perchlorate anions and the Cu^{II} cations.

Experimental

3-methyl-5-phenyl-1*H*-pyrazole (0.16 g, 0.1 mmol), prepared according to the literature (Puerta & Cohen, 2003), was dissolved in dichloromethane (10 ml) at room temperature. To this solution, copper(II) perchlorate hexahydrate (0.18 g, 0.05 mmol) in methanol (2 ml) was added. The resulting blue solution was stirred for two hours. The mixture was filtered and the filtrate kept at room temperature. Blue crystals were obtained after one week by slow evaporation.

Refinement

H atoms on N5, N6, N7, and N8 are refined while the other hydrogen atoms are geometrically constrained and refined in riding mode as follows: methyl C—H = 0.96 Å, U_{iso}(H) = 1.5U_{eq}(C); aromatic C—H = 0.93 Å, U_{iso}(H) = 1.2U_{eq}(C). High and increasing temperature factors for the C atoms of the C1···C6 and C31···C36 benzene rings suggested possible disorder but this was not investigated further.

Figures

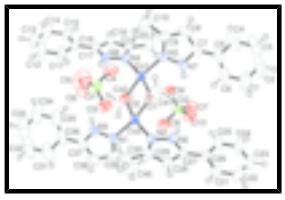


Fig. 1. The structure of (I) with displacement ellipsoids drawn at the 30% probability level. Hydrogen atoms are drawn as small circles of arbitrary radii.

Di-μ-methoxido-κ^4*O*:*O*-bis[bis(3-methyl-5-phenyl-1*H*-pyrazole- κ*N*^{2})copper(II)] bis(perchlorate)

Crystal data

$[Cu(CH_3O)_2(C_{40}H_{40}N_8)](ClO_4)_2$	F_{000} = 2104
M_r = 1020.85	D_x = 1.392 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 9998 reflections
a = 13.8398 (12) Å	θ = 1.0–25.5º
b = 17.4607 (16) Å	μ = 1.04 mm^{-1}
c = 20.3779 (18) Å	T = 293 (2) K
β = 98.3160 (10)º	Block, green
V = 4872.6 (8) Å^3	0.15 × 0.13 × 0.11 mm
Z = 4	

Data collection

Bruker APEXII CCD area-detector diffractometer	9045 independent reflections
Radiation source: fine-focus sealed tube	5370 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.074
T = 293(2) K	θ_{max} = 25.5º
φ and ω scans	θ_{min} = 1.9º
Absorption correction: multi-scan (SADABS; Bruker, 2006)	h = −16→16
T_{min} = 0.859, T_{max} = 0.894	k = −21→21
48197 measured reflections	l = −24→24

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.049	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.137	$w = 1/[\sigma^2(F_o^2) + (0.0637P)^2 + 2.32P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.00	$(\Delta/\sigma)_{max}$ = 0.003

9045 reflections	$\Delta\rho_{max}$ = 0.46 e Å^{-3}
599 parameters	$\Delta\rho_{min}$ = −0.26 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 $F^2 > \sigma(F^2)$ 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}
C1	1.3406 (6)	0.4300 (5)	0.5628 (4)	0.145 (4)
H1	1.3318	0.4611	0.5985	0.175*
C2	1.4292 (6)	0.4221 (6)	0.5433 (6)	0.150 (4)
H2	1.4813	0.4490	0.5664	0.180*
C3	1.4469 (5)	0.3770 (5)	0.4917 (6)	0.129 (4)
H3	1.5093	0.3726	0.4802	0.155*
C4	1.3675 (4)	0.3376 (4)	0.4566 (4)	0.115 (3)
H4	1.3766	0.3079	0.4201	0.138*
C5	1.2766 (4)	0.3425 (3)	0.4754 (3)	0.0762 (17)
C6	1.2628 (5)	0.3900 (5)	0.5277 (4)	0.116 (3)
H6	1.2007	0.3952	0.5395	0.139*
C7	1.1920 (3)	0.3031 (3)	0.4369 (3)	0.0603 (13)
C8	1.1693 (4)	0.2811 (3)	0.3721 (3)	0.0744 (16)
H8	1.2095	0.2858	0.3395	0.089*
C9	1.0756 (4)	0.2504 (3)	0.3632 (2)	0.0599 (13)
C10	1.0161 (5)	0.2209 (4)	0.3027 (2)	0.100 (2)
H10A	1.0288	0.1672	0.2982	0.150*
H10B	1.0327	0.2478	0.2648	0.150*
H10C	0.9482	0.2284	0.3056	0.150*
C11	0.6050 (4)	0.0721 (4)	0.3064 (3)	0.104 (2)
H11	0.6100	0.1199	0.3267	0.125*
C12	0.5160 (4)	0.0492 (4)	0.2717 (4)	0.138 (3)
H12	0.4625	0.0819	0.2680	0.165*
C13	0.5072 (5)	−0.0208 (4)	0.2432 (4)	0.109 (2)
H13	0.4472	−0.0372	0.2212	0.130*
C14	0.5860 (5)	−0.0666 (4)	0.2469 (3)	0.0900 (19)
H14	0.5808	−0.1143	0.2264	0.108*
C15	0.6742 (4)	−0.0434 (3)	0.2809 (3)	0.0735 (16)

H15	0.7278	−0.0760	0.2833	0.088*
C16	0.6847 (3)	0.0265 (3)	0.3113 (2)	0.0541 (12)
C17	0.7801 (3)	0.0507 (2)	0.3463 (2)	0.0447 (10)
C18	0.8683 (3)	0.0142 (2)	0.3584 (2)	0.0546 (12)
H18	0.8818	−0.0353	0.3455	0.065*
C19	0.9336 (3)	0.0642 (2)	0.3935 (2)	0.0455 (11)
C20	1.0388 (3)	0.0524 (3)	0.4190 (3)	0.0712 (15)
H20A	1.0774	0.0664	0.3854	0.107*
H20B	1.0499	−0.0005	0.4305	0.107*
H20C	1.0569	0.0836	0.4576	0.107*
C21	1.0570 (4)	0.5592 (3)	0.7408 (3)	0.0678 (14)
H21	1.0018	0.5893	0.7417	0.081*
C22	1.1443 (5)	0.5828 (3)	0.7750 (3)	0.0867 (18)
H22	1.1473	0.6282	0.7990	0.104*
C23	1.2264 (5)	0.5408 (4)	0.7742 (3)	0.105 (2)
H23	1.2857	0.5577	0.7968	0.126*
C24	1.2208 (4)	0.4735 (4)	0.7399 (4)	0.142 (4)
H24	1.2764	0.4437	0.7398	0.171*
C25	1.1329 (4)	0.4497 (4)	0.7052 (4)	0.108 (2)
H25	1.1302	0.4041	0.6815	0.129*
C26	1.0491 (3)	0.4922 (3)	0.7051 (2)	0.0522 (12)
C27	0.9549 (3)	0.4678 (2)	0.6698 (2)	0.0463 (11)
C28	0.8646 (3)	0.5012 (3)	0.6625 (2)	0.0571 (13)
H28	0.8491	0.5480	0.6802	0.069*
C29	0.8006 (3)	0.4529 (2)	0.6241 (2)	0.0499 (11)
C30	0.6931 (3)	0.4608 (3)	0.6028 (3)	0.0749 (16)
H30A	0.6757	0.4374	0.5601	0.112*
H30B	0.6760	0.5141	0.6001	0.112*
H30C	0.6586	0.4360	0.6345	0.112*
C31	0.3854 (5)	0.1563 (5)	0.5683 (4)	0.138 (3)
H31	0.3797	0.1802	0.6084	0.166*
C32	0.3057 (6)	0.1176 (7)	0.5348 (6)	0.156 (4)
H32	0.2468	0.1169	0.5517	0.187*
C33	0.3140 (8)	0.0807 (6)	0.4775 (7)	0.166 (5)
H33	0.2616	0.0529	0.4558	0.199*
C34	0.3981 (6)	0.0844 (6)	0.4519 (5)	0.176 (4)
H34	0.4032	0.0603	0.4118	0.211*
C35	0.4776 (5)	0.1240 (5)	0.4853 (5)	0.140 (3)
H35	0.5355	0.1259	0.4672	0.168*
C36	0.4724 (4)	0.1602 (4)	0.5438 (4)	0.0803 (18)
C37	0.5561 (4)	0.2010 (3)	0.5797 (3)	0.0625 (14)
C38	0.5858 (4)	0.2149 (3)	0.6456 (3)	0.0786 (17)
H38	0.5531	0.2006	0.6805	0.094*
C39	0.6743 (4)	0.2547 (3)	0.6508 (2)	0.0597 (13)
C40	0.7380 (5)	0.2824 (3)	0.7117 (2)	0.0892 (19)
H40A	0.8050	0.2819	0.7043	0.134*
H40B	0.7305	0.2495	0.7483	0.134*
H40C	0.7196	0.3337	0.7216	0.134*
C41	0.9313 (4)	0.3916 (2)	0.4734 (2)	0.0634 (13)

H41A	0.8726	0.4210	0.4729	0.095*
H41B	0.9444	0.3845	0.4289	0.095*
H41C	0.9849	0.4183	0.4987	0.095*
C42	0.8036 (3)	0.1299 (2)	0.5335 (2)	0.0563 (12)
H42A	0.7612	0.1001	0.5018	0.084*
H42B	0.7747	0.1354	0.5733	0.084*
H42C	0.8655	0.1045	0.5436	0.084*
N1	0.6971 (3)	0.2664 (2)	0.59041 (17)	0.0473 (9)
N2	0.8477 (2)	0.3908 (2)	0.60875 (17)	0.0466 (9)
N3	1.0426 (2)	0.2502 (2)	0.42132 (17)	0.0481 (9)
N4	0.8888 (2)	0.12950 (19)	0.40318 (17)	0.0449 (9)
N5	0.6243 (3)	0.2336 (2)	0.5482 (2)	0.0530 (11)
N6	0.9418 (3)	0.4019 (2)	0.63658 (19)	0.0497 (10)
N7	1.1142 (3)	0.2828 (2)	0.4645 (2)	0.0515 (10)
N8	0.7954 (3)	0.1194 (2)	0.3738 (2)	0.0487 (11)
O1	0.91953 (19)	0.31904 (14)	0.50286 (13)	0.0421 (7)
O2	0.81754 (18)	0.20320 (14)	0.50649 (13)	0.0388 (6)
O3	0.6912 (2)	0.35140 (18)	0.44912 (16)	0.0700 (10)
O4	0.7729 (3)	0.2916 (2)	0.36896 (16)	0.0741 (10)
O5	0.6229 (3)	0.3515 (3)	0.3371 (2)	0.1208 (17)
O6	0.6324 (3)	0.2375 (2)	0.39973 (18)	0.0806 (11)
O7	1.1032 (2)	0.28455 (17)	0.61243 (16)	0.0623 (9)
O8	0.9631 (2)	0.22786 (18)	0.64244 (15)	0.0600 (8)
O9	1.0497 (2)	0.16613 (17)	0.56659 (15)	0.0612 (9)
O10	1.1167 (3)	0.17362 (19)	0.67927 (16)	0.0747 (10)
Cl1	0.67889 (10)	0.30902 (7)	0.38767 (6)	0.0641 (4)
Cl2	1.05868 (8)	0.21234 (6)	0.62539 (5)	0.0481 (3)
Cu1	0.92039 (4)	0.22382 (3)	0.45477 (2)	0.04138 (16)
Cu2	0.81615 (4)	0.29804 (3)	0.55465 (2)	0.04131 (16)
H43	1.107 (3)	0.283 (3)	0.502 (2)	0.056 (16)*
H44	0.983 (3)	0.372 (2)	0.6319 (17)	0.026 (11)*
H45	0.762 (3)	0.149 (2)	0.3770 (19)	0.028 (13)*
H46	0.628 (3)	0.231 (3)	0.512 (2)	0.053 (17)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.114 (6)	0.194 (9)	0.118 (6)	−0.086 (6)	−0.017 (5)	−0.001 (6)
C2	0.053 (5)	0.170 (10)	0.214 (12)	−0.032 (6)	−0.024 (6)	0.066 (8)
C3	0.040 (4)	0.101 (6)	0.245 (12)	0.007 (4)	0.016 (6)	0.055 (7)
C4	0.055 (4)	0.076 (4)	0.217 (9)	0.004 (3)	0.029 (5)	0.039 (5)
C5	0.044 (3)	0.076 (4)	0.109 (5)	−0.008 (3)	0.011 (3)	0.027 (4)
C6	0.079 (5)	0.163 (7)	0.105 (6)	−0.065 (5)	0.010 (4)	−0.004 (5)
C7	0.045 (3)	0.063 (3)	0.077 (4)	0.007 (2)	0.022 (3)	0.018 (3)
C8	0.088 (4)	0.067 (4)	0.081 (4)	−0.002 (3)	0.053 (3)	0.008 (3)
C9	0.086 (4)	0.053 (3)	0.044 (3)	−0.003 (3)	0.018 (3)	0.005 (2)
C10	0.163 (6)	0.101 (5)	0.036 (3)	−0.027 (4)	0.012 (4)	−0.003 (3)
C11	0.054 (4)	0.093 (5)	0.156 (6)	−0.005 (3)	−0.015 (4)	−0.068 (4)

C12	0.057 (4)	0.121 (6)	0.222 (9)	−0.003 (4)	−0.025 (5)	−0.076 (6)
C13	0.070 (4)	0.119 (6)	0.129 (6)	−0.034 (4)	−0.010 (4)	−0.042 (5)
C14	0.095 (5)	0.077 (4)	0.094 (5)	−0.038 (4)	0.000 (4)	−0.035 (4)
C15	0.070 (4)	0.069 (4)	0.078 (4)	−0.017 (3)	−0.002 (3)	−0.025 (3)
C16	0.053 (3)	0.049 (3)	0.059 (3)	−0.015 (2)	0.001 (2)	−0.014 (2)
C17	0.053 (3)	0.037 (2)	0.044 (3)	−0.007 (2)	0.004 (2)	−0.007 (2)
C18	0.060 (3)	0.036 (3)	0.065 (3)	0.004 (2)	0.002 (2)	−0.012 (2)
C19	0.044 (3)	0.042 (3)	0.048 (3)	0.005 (2)	0.000 (2)	−0.006 (2)
C20	0.057 (3)	0.064 (3)	0.087 (4)	0.017 (3)	−0.008 (3)	−0.008 (3)
C21	0.067 (3)	0.060 (3)	0.075 (4)	−0.006 (3)	0.006 (3)	−0.022 (3)
C22	0.088 (5)	0.078 (4)	0.090 (4)	−0.023 (4)	−0.002 (4)	−0.038 (3)
C23	0.064 (4)	0.128 (6)	0.118 (5)	−0.035 (4)	−0.003 (4)	−0.054 (5)
C24	0.049 (4)	0.143 (7)	0.227 (9)	−0.002 (4)	−0.007 (5)	−0.114 (7)
C25	0.052 (4)	0.099 (5)	0.166 (7)	−0.002 (3)	−0.003 (4)	−0.080 (5)
C26	0.050 (3)	0.049 (3)	0.058 (3)	−0.008 (2)	0.008 (2)	−0.017 (2)
C27	0.048 (3)	0.042 (3)	0.048 (3)	−0.002 (2)	0.006 (2)	−0.009 (2)
C28	0.056 (3)	0.040 (3)	0.074 (3)	0.009 (2)	0.004 (3)	−0.019 (2)
C29	0.049 (3)	0.045 (3)	0.055 (3)	0.007 (2)	0.002 (2)	−0.005 (2)
C30	0.059 (3)	0.067 (3)	0.093 (4)	0.016 (3)	−0.008 (3)	−0.013 (3)
C31	0.079 (5)	0.192 (9)	0.146 (7)	−0.037 (5)	0.028 (5)	0.055 (6)
C32	0.060 (5)	0.189 (11)	0.216 (12)	−0.048 (6)	0.007 (7)	0.067 (9)
C33	0.089 (7)	0.148 (9)	0.246 (14)	−0.055 (6)	−0.021 (9)	0.034 (9)
C34	0.103 (6)	0.212 (11)	0.205 (10)	−0.082 (7)	−0.005 (7)	−0.065 (8)
C35	0.075 (5)	0.170 (8)	0.174 (8)	−0.055 (5)	0.012 (5)	−0.048 (7)
C36	0.042 (3)	0.082 (4)	0.116 (5)	−0.010 (3)	0.008 (3)	0.030 (4)
C37	0.049 (3)	0.068 (3)	0.073 (4)	−0.001 (3)	0.016 (3)	0.020 (3)
C38	0.074 (4)	0.095 (4)	0.074 (4)	0.002 (3)	0.032 (3)	0.024 (3)
C39	0.070 (3)	0.065 (3)	0.045 (3)	0.008 (3)	0.012 (3)	0.009 (2)
C40	0.125 (5)	0.103 (5)	0.040 (3)	−0.001 (4)	0.011 (3)	0.006 (3)
C41	0.071 (3)	0.041 (3)	0.079 (4)	−0.011 (2)	0.014 (3)	0.004 (2)
C42	0.061 (3)	0.041 (3)	0.066 (3)	−0.006 (2)	0.004 (2)	0.006 (2)
N1	0.048 (2)	0.057 (2)	0.038 (2)	−0.0045 (18)	0.0074 (17)	−0.0015 (18)
N2	0.040 (2)	0.048 (2)	0.050 (2)	0.0016 (17)	−0.0012 (17)	−0.0106 (17)
N3	0.046 (2)	0.058 (2)	0.041 (2)	−0.0086 (18)	0.0082 (18)	−0.0062 (18)
N4	0.035 (2)	0.046 (2)	0.051 (2)	0.0014 (16)	−0.0033 (17)	−0.0119 (17)
N5	0.047 (2)	0.062 (3)	0.050 (3)	−0.0082 (19)	0.008 (2)	0.003 (2)
N6	0.039 (2)	0.041 (2)	0.067 (3)	0.0070 (19)	0.003 (2)	−0.0185 (19)
N7	0.043 (2)	0.070 (3)	0.043 (3)	−0.0155 (19)	0.012 (2)	−0.002 (2)
N8	0.039 (2)	0.040 (2)	0.063 (3)	0.0051 (19)	−0.0055 (19)	−0.017 (2)
O1	0.0455 (17)	0.0345 (16)	0.0464 (17)	−0.0067 (13)	0.0071 (13)	−0.0025 (13)
O2	0.0406 (16)	0.0321 (15)	0.0427 (16)	−0.0039 (12)	0.0022 (13)	−0.0004 (12)
O3	0.082 (2)	0.060 (2)	0.069 (2)	0.0104 (18)	0.0119 (19)	−0.0156 (18)
O4	0.086 (3)	0.087 (3)	0.051 (2)	0.027 (2)	0.0145 (19)	−0.0009 (18)
O5	0.140 (4)	0.122 (4)	0.089 (3)	0.055 (3)	−0.020 (3)	0.038 (3)
O6	0.090 (3)	0.067 (2)	0.078 (3)	−0.009 (2)	−0.012 (2)	−0.009 (2)
O7	0.068 (2)	0.0473 (19)	0.070 (2)	−0.0116 (16)	0.0054 (18)	−0.0071 (16)
O8	0.062 (2)	0.070 (2)	0.0490 (19)	0.0081 (17)	0.0131 (16)	−0.0004 (16)
O9	0.075 (2)	0.056 (2)	0.0518 (19)	0.0008 (17)	0.0075 (16)	−0.0175 (16)
O10	0.092 (3)	0.066 (2)	0.059 (2)	0.027 (2)	−0.0120 (19)	−0.0032 (18)

Cl1	0.0831 (9)	0.0561 (8)	0.0482 (7)	0.0204 (7)	−0.0069 (6)	0.0045 (6)
Cl2	0.0587 (7)	0.0424 (6)	0.0413 (6)	0.0062 (5)	0.0008 (5)	−0.0058 (5)
Cu1	0.0388 (3)	0.0408 (3)	0.0432 (3)	−0.0056 (2)	0.0013 (2)	−0.0087 (2)
Cu2	0.0413 (3)	0.0400 (3)	0.0414 (3)	−0.0044 (2)	0.0020 (2)	−0.0067 (2)

Geometric parameters (Å, °)

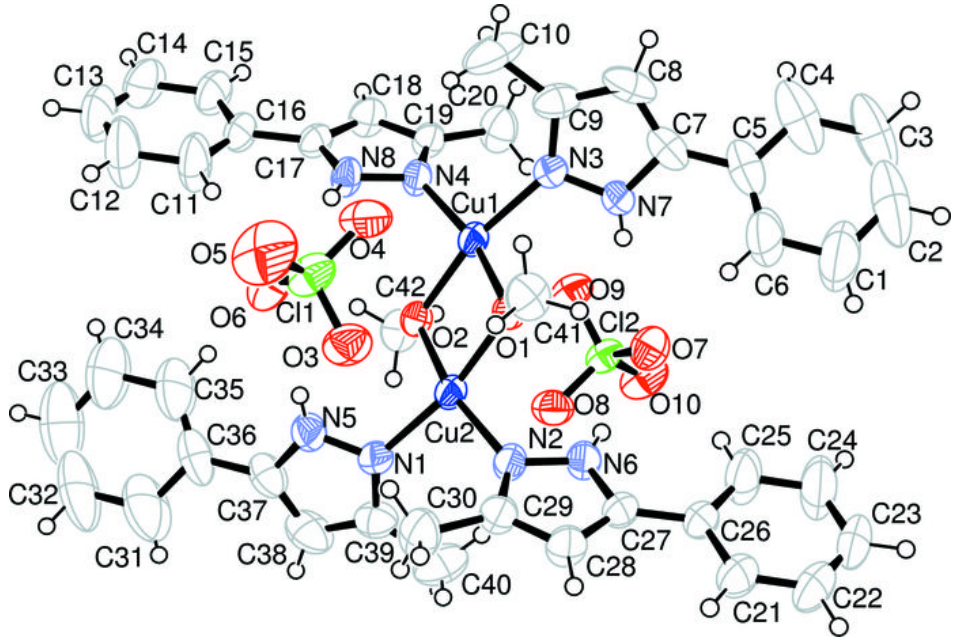
C1—C2	1.351 (11)	C30—H30B	0.9600
C1—C6	1.391 (8)	C30—H30C	0.9600
C1—H1	0.9300	C31—C36	1.372 (8)
C2—C3	1.363 (12)	C31—C32	1.386 (11)
C2—H2	0.9300	C31—H31	0.9300
C3—C4	1.402 (10)	C32—C33	1.353 (13)
C3—H3	0.9300	C32—H32	0.9300
C4—C5	1.369 (7)	C33—C34	1.344 (12)
C4—H4	0.9300	C33—H33	0.9300
C5—C6	1.386 (9)	C34—C35	1.391 (9)
C5—C7	1.481 (7)	C34—H34	0.9300
C6—H6	0.9300	C35—C36	1.360 (9)
C7—N7	1.334 (6)	C35—H35	0.9300
C7—C8	1.368 (7)	C36—C37	1.462 (8)
C8—C9	1.391 (7)	C37—N5	1.343 (6)
C8—H8	0.9300	C37—C38	1.367 (7)
C9—N3	1.329 (5)	C38—C39	1.399 (7)
C9—C10	1.473 (7)	C38—H38	0.9300
C10—H10A	0.9600	C39—N1	1.330 (5)
C10—H10B	0.9600	C39—C40	1.495 (7)
C10—H10C	0.9600	C40—H40A	0.9600
C11—C16	1.352 (7)	C40—H40B	0.9600
C11—C12	1.388 (7)	C40—H40C	0.9600
C11—H11	0.9300	C41—O1	1.421 (5)
C12—C13	1.350 (9)	C41—H41A	0.9600
C12—H12	0.9300	C41—H41B	0.9600
C13—C14	1.346 (8)	C41—H41C	0.9600
C13—H13	0.9300	C42—O2	1.418 (5)
C14—C15	1.375 (7)	C42—H42A	0.9600
C14—H14	0.9300	C42—H42B	0.9600
C15—C16	1.367 (6)	C42—H42C	0.9600
C15—H15	0.9300	N1—N5	1.354 (5)
C16—C17	1.470 (6)	N1—Cu2	1.975 (3)
C17—N8	1.329 (5)	N2—N6	1.357 (5)
C17—C18	1.367 (6)	N2—Cu2	1.973 (3)
C18—C19	1.380 (6)	N3—N7	1.353 (5)
C18—H18	0.9300	N3—Cu1	1.968 (3)
C19—N4	1.325 (5)	N4—N8	1.356 (5)
C19—C20	1.488 (6)	N4—Cu1	1.969 (3)
C20—H20A	0.9600	N5—H46	0.75 (4)
C20—H20B	0.9600	N6—H44	0.80 (3)
C20—H20C	0.9600	N7—H43	0.78 (4)

C21—C22	1.367 (7)	N8—H45	0.70 (4)
C21—C26	1.374 (6)	O1—Cu1	1.931 (3)
C21—H21	0.9300	O1—Cu2	1.932 (3)
C22—C23	1.354 (8)	O2—Cu1	1.924 (3)
C22—H22	0.9300	O2—Cu2	1.926 (2)
C23—C24	1.364 (8)	O3—Cl1	1.443 (3)
C23—H23	0.9300	O3—Cu2	2.722 (3)
C24—C25	1.380 (7)	O4—Cl1	1.441 (4)
C24—H24	0.9300	O4—Cu1	2.755 (3)
C25—C26	1.376 (6)	O5—Cl1	1.407 (4)
C25—H25	0.9300	O6—Cl1	1.441 (4)
C26—C27	1.458 (6)	O7—Cl2	1.444 (3)
C27—N6	1.334 (5)	O8—Cl2	1.441 (3)
C27—C28	1.367 (6)	O8—Cu2	2.790 (3)
C28—C29	1.382 (6)	O9—Cl2	1.435 (3)
C28—H28	0.9300	O9—Cu1	2.869 (3)
C29—N2	1.325 (5)	O10—Cl2	1.433 (3)
C29—C30	1.495 (6)	Cu1—Cu2	2.9583 (7)
C30—H30A	0.9600		
C2—C1—C6	117.7 (9)	C31—C36—C37	121.0 (7)
C2—C1—H1	121.1	N5—C37—C38	105.2 (5)
C6—C1—H1	121.1	N5—C37—C36	121.8 (5)
C1—C2—C3	123.9 (9)	C38—C37—C36	133.0 (5)
C1—C2—H2	118.0	C37—C38—C39	107.4 (5)
C3—C2—H2	118.0	C37—C38—H38	126.3
C2—C3—C4	117.5 (8)	C39—C38—H38	126.3
C2—C3—H3	121.2	N1—C39—C38	109.1 (5)
C4—C3—H3	121.2	N1—C39—C40	121.8 (5)
C5—C4—C3	120.7 (8)	C38—C39—C40	129.0 (5)
C5—C4—H4	119.6	C39—C40—H40A	109.5
C3—C4—H4	119.6	C39—C40—H40B	109.5
C4—C5—C6	119.1 (6)	H40A—C40—H40B	109.5
C4—C5—C7	120.7 (7)	C39—C40—H40C	109.5
C6—C5—C7	120.0 (5)	H40A—C40—H40C	109.5
C5—C6—C1	120.9 (7)	H40B—C40—H40C	109.5
C5—C6—H6	119.5	O1—C41—H41A	109.5
C1—C6—H6	119.5	O1—C41—H41B	109.5
N7—C7—C8	104.2 (5)	H41A—C41—H41B	109.5
N7—C7—C5	121.6 (5)	O1—C41—H41C	109.5
C8—C7—C5	134.1 (5)	H41A—C41—H41C	109.5
C7—C8—C9	108.3 (4)	H41B—C41—H41C	109.5
C7—C8—H8	125.9	O2—C42—H42A	109.5
C9—C8—H8	125.9	O2—C42—H42B	109.5
N3—C9—C8	108.6 (4)	H42A—C42—H42B	109.5
N3—C9—C10	121.6 (5)	O2—C42—H42C	109.5
C8—C9—C10	129.8 (5)	H42A—C42—H42C	109.5
C9—C10—H10A	109.5	H42B—C42—H42C	109.5
C9—C10—H10B	109.5	C39—N1—N5	105.6 (4)
H10A—C10—H10B	109.5	C39—N1—Cu2	135.0 (3)

C9—C10—H10C	109.5	N5—N1—Cu2	117.9 (3)
H10A—C10—H10C	109.5	C29—N2—N6	105.1 (3)
H10B—C10—H10C	109.5	C29—N2—Cu2	136.6 (3)
C16—C11—C12	121.5 (5)	N6—N2—Cu2	118.2 (3)
C16—C11—H11	119.3	C9—N3—N7	105.4 (4)
C12—C11—H11	119.3	C9—N3—Cu1	137.1 (3)
C13—C12—C11	119.8 (6)	N7—N3—Cu1	117.3 (3)
C13—C12—H12	120.1	C19—N4—N8	105.1 (3)
C11—C12—H12	120.1	C19—N4—Cu1	136.6 (3)
C14—C13—C12	119.5 (6)	N8—N4—Cu1	117.9 (3)
C14—C13—H13	120.2	C37—N5—N1	112.6 (4)
C12—C13—H13	120.2	C37—N5—H46	127 (4)
C13—C14—C15	120.4 (6)	N1—N5—H46	120 (4)
C13—C14—H14	119.8	C27—N6—N2	112.7 (4)
C15—C14—H14	119.8	C27—N6—H44	126 (3)
C16—C15—C14	121.3 (6)	N2—N6—H44	121 (3)
C16—C15—H15	119.3	C7—N7—N3	113.4 (4)
C14—C15—H15	119.3	C7—N7—H43	130 (4)
C11—C16—C15	117.4 (5)	N3—N7—H43	116 (3)
C11—C16—C17	122.2 (4)	C17—N8—N4	112.7 (4)
C15—C16—C17	120.4 (5)	C17—N8—H45	129 (3)
N8—C17—C18	105.2 (4)	N4—N8—H45	118 (3)
N8—C17—C16	122.8 (4)	C41—O1—Cu1	123.0 (3)
C18—C17—C16	132.0 (4)	C41—O1—Cu2	122.6 (3)
C17—C18—C19	107.4 (4)	Cu1—O1—Cu2	99.97 (11)
C17—C18—H18	126.3	C42—O2—Cu1	122.3 (2)
C19—C18—H18	126.3	C42—O2—Cu2	124.5 (3)
N4—C19—C18	109.6 (4)	Cu1—O2—Cu2	100.42 (11)
N4—C19—C20	121.5 (4)	Cl1—O3—Cu2	119.47 (17)
C18—C19—C20	128.9 (4)	Cl1—O4—Cu1	122.49 (18)
C19—C20—H20A	109.5	Cl2—O8—Cu2	122.50 (16)
C19—C20—H20B	109.5	Cl2—O9—Cu1	115.77 (17)
H20A—C20—H20B	109.5	O5—Cl1—O4	109.9 (2)
C19—C20—H20C	109.5	O5—Cl1—O6	111.7 (3)
H20A—C20—H20C	109.5	O4—Cl1—O6	107.7 (2)
H20B—C20—H20C	109.5	O5—Cl1—O3	110.4 (3)
C22—C21—C26	121.6 (5)	O4—Cl1—O3	109.9 (2)
C22—C21—H21	119.2	O6—Cl1—O3	107.2 (2)
C26—C21—H21	119.2	O10—Cl2—O9	110.2 (2)
C23—C22—C21	120.8 (5)	O10—Cl2—O8	109.6 (2)
C23—C22—H22	119.6	O9—Cl2—O8	109.57 (19)
C21—C22—H22	119.6	O10—Cl2—O7	110.2 (2)
C22—C23—C24	119.1 (5)	O9—Cl2—O7	109.0 (2)
C22—C23—H23	120.4	O8—Cl2—O7	108.08 (19)
C24—C23—H23	120.4	O2—Cu1—O1	79.85 (11)
C23—C24—C25	120.2 (6)	O2—Cu1—N3	167.14 (13)
C23—C24—H24	119.9	O1—Cu1—N3	92.45 (13)
C25—C24—H24	119.9	O2—Cu1—N4	90.65 (13)
C26—C25—C24	121.3 (5)	O1—Cu1—N4	166.97 (13)

C26—C25—H25	119.4	N3—Cu1—N4	98.42 (14)
C24—C25—H25	119.4	O2—Cu1—O4	83.65 (11)
C21—C26—C25	117.1 (4)	O1—Cu1—O4	83.90 (11)
C21—C26—C27	120.5 (4)	N3—Cu1—O4	105.91 (13)
C25—C26—C27	122.5 (4)	N4—Cu1—O4	86.20 (12)
N6—C27—C28	104.9 (4)	O2—Cu1—O9	85.70 (10)
N6—C27—C26	123.2 (4)	O1—Cu1—O9	87.03 (10)
C28—C27—C26	131.8 (4)	N3—Cu1—O9	83.62 (12)
C27—C28—C29	107.6 (4)	N4—Cu1—O9	101.25 (12)
C27—C28—H28	126.2	O4—Cu1—O9	167.07 (9)
C29—C28—H28	126.2	O2—Cu1—Cu2	39.82 (7)
N2—C29—C28	109.6 (4)	O1—Cu1—Cu2	40.03 (8)
N2—C29—C30	120.6 (4)	N3—Cu1—Cu2	131.67 (10)
C28—C29—C30	129.7 (4)	N4—Cu1—Cu2	129.88 (10)
C29—C30—H30A	109.5	O4—Cu1—Cu2	81.86 (7)
C29—C30—H30B	109.5	O9—Cu1—Cu2	85.27 (6)
H30A—C30—H30B	109.5	O2—Cu2—O1	79.76 (11)
C29—C30—H30C	109.5	O2—Cu2—N2	166.64 (13)
H30A—C30—H30C	109.5	O1—Cu2—N2	91.59 (13)
H30B—C30—H30C	109.5	O2—Cu2—N1	91.03 (13)
C36—C31—C32	121.5 (9)	O1—Cu2—N1	168.03 (13)
C36—C31—H31	119.3	N2—Cu2—N1	98.78 (14)
C32—C31—H31	119.3	O2—Cu2—O3	86.78 (10)
C33—C32—C31	119.8 (10)	O1—Cu2—O3	86.53 (11)
C33—C32—H32	120.1	N2—Cu2—O3	102.96 (12)
C31—C32—H32	120.1	N1—Cu2—O3	85.33 (13)
C34—C33—C32	119.9 (11)	O2—Cu2—O8	83.63 (10)
C34—C33—H33	120.1	O1—Cu2—O8	84.54 (10)
C32—C33—H33	120.1	N2—Cu2—O8	85.44 (12)
C33—C34—C35	120.2 (10)	N1—Cu2—O8	102.14 (12)
C33—C34—H34	119.9	O3—Cu2—O8	167.91 (9)
C35—C34—H34	119.9	O2—Cu2—Cu1	39.76 (8)
C36—C35—C34	121.4 (8)	O1—Cu2—Cu1	40.00 (8)
C36—C35—H35	119.3	N2—Cu2—Cu1	130.82 (10)
C34—C35—H35	119.3	N1—Cu2—Cu1	130.35 (10)
C35—C36—C31	117.2 (7)	O3—Cu2—Cu1	85.62 (7)
C35—C36—C37	121.8 (6)	O8—Cu2—Cu1	82.30 (6)

Fig. 1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