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(2,2′-Dicarboxy-4,4′-carbonyldibenzoato)bis(1,10-phenanthroline)-copper(II) dihydrate

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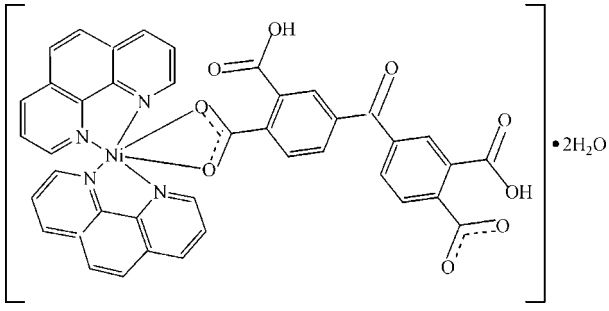
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.044; wR factor = 0.127; data-to-parameter ratio = 13.1.

In the title compound, $[Cu(C_{17}H_8O_9)(C_{12}H_8N_2)_2]\cdot 2H_2O$, the Cu^{II} cation is hexacoordinated by two carboxylate O atoms from one of the two deprotonated carboxyl groups in the 3,3,4,4-benzophenone tetracarboxylate, and four N atoms from two 1,10-phenanthrolines, showing a slightly distorted octahedral geometry. A network of hydrogen bonds links the units into a three-dimensional structure.

Related literature

For uses of carboxylic acids in materials science, see: Church & Halvorson (1959). For uses in biological systems, see: Chung *et al.* (1971); Okabe & Oya (2000); Serre *et al.* (2005); Pocker & Fong (1980); Scapin *et al.* (1997); Kim *et al.* (2001).



Experimental

Crystal data

$[Cu(C_{17}H_8O_9)(C_{12}H_8N_2)_2]\cdot 2H_2O$
M_r = 816.21
Monoclinic, $P2_1/c$
a = 14.3011 (9) Å
b = 16.9401 (10) Å
c = 14.9839 (9) Å
β = 101.371 (1)°
V = 3558.8 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.69 mm^{-1}
T = 293 (2) K
0.15 × 0.15 × 0.15 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.904, T_{max} = 0.904
17576 measured reflections
6912 independent reflections
3976 reflections with $I > 2\sigma(I)$
R_{int} = 0.061

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.127
S = 1.00
6912 reflections
528 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.86 e Å^{-3}
$\Delta\rho_{min}$ = −0.84 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O11—H4*W*···O6^{i}	0.83 (4)	2.58 (5)	2.764 (14)	94 (4)
O3—H3*A*···O8^{ii}	0.82	2.56	3.198 (4)	136
O3—H3*A*···O9^{ii}	0.82	1.77	2.555 (3)	161

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: EZ2087).

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supplementary materials

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(2,2'-Dicarboxy-4,4'-carbonyldibenzoato)bis(1,10-phenanthroline)copper(II) dihydrate

L.-J. Hao and T.-L. Yu

Comment

In recent years, carboxylic acids have been widely used as polydentate ligands that can coordinate to transition or rare earth ions, yielding complexes with interesting properties that are useful in materials science (Church & Halvorson, 1959; Chung *et al.*, 1971) and in biological systems (Okabe & Oya, 2000; Serre *et al.*, 2005; Pocker & Fong, 1980; Scapin *et al.*, 1997). For example, Kim *et al.* (2001) focused on the syntheses of transition metal complexes containing benzene carboxylate and rigid aromatic pyridine ligands in order to study their electronic conductivity and magnetic properties. The importance of transition metal dicarboxylate complexes motivated us to pursue synthetic strategies for these compounds, using 3,3,4,4-benzophenone tetracarboxylate as a polydentate ligand. Here we report the synthesis and X-ray crystal structure analysis of the title compound.

The molecular structure of the title compound is shown in Fig. 1. The Cu(II) ion is hexa-coordinated, with two carboxylate oxygen atoms from the 3,3,4,4-benzophenone tetracarboxylate and four nitrogen atoms from two 1,10-phenanthrolines, showing a slightly distorted octahedral geometry. The Cu—O bond and Cu—N distances are in the ranges 2.378 (2)–2.0837 (19) and 2.114 (3)–2.179 (3) Å, respectively.

Experimental

A mixture of copper acetate (0.5 mmol, 0.149 g), 3,3,4,4-benzophenone tetracarboxylic acid (0.5 mmol, 0.162 g), and 1,10-phenanthroline (0.5 mmol, 0.10 g) in 20 ml of a 1:1 solution of water and ethanol was sealed in a 30 ml Teflon-lined stainless steel autoclave, and kept at 150 °C for 2 days. Green, block-shaped crystals were obtained at a yield of 20% after slowly cooling to room temperature. Anal. Calc. for $C_{41}H_{28}CuN_4O_{11}$: C 60.28, H 3.43, N 6.86, Cu 7.84%; Found: C 60.33, H 3.49, N 6.81, Cu 7.80%.

Refinement

The H atoms of the water molecule were located from difference density maps and were refined with distance restraints of d(H–H) = 1.38 (2) Å, d(O—H) = 0.88 (2) Å, and with a fixed U_{iso} of 0.80 Å^2. All other H atoms were placed in calculated positions with a C—H bond distance of 0.93 Å and U_{iso}(H) = 1.2U_{eq} of the carrier atom.

Figures

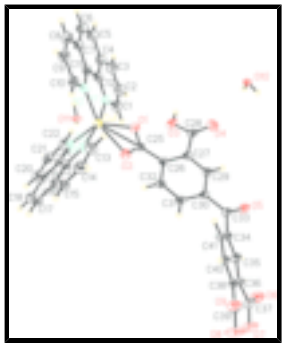


Fig. 1. A view of the the title compound, showing the atomic numbering scheme and 30% probability displacement ellipsoids.

(2,2'-Dicarboxy-4,4'-carbonyldibenzoato)bis(1,10-phenanthroline)copper(II) dihydrate

Crystal data

$[Cu(C_{17}H_8O_9)(C_{12}H_8N_2)_2]\cdot 2H_2O$	F_{000} = 1676
M_r = 816.21	D_x = 1.523 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 6912 reflections
a = 14.3011 (9) Å	θ = 1.5–26.0º
b = 16.9401 (10) Å	μ = 0.69 mm^{-1}
c = 14.9839 (9) Å	T = 293 (2) K
β = 101.371 (1)º	Block, green
V = 3558.8 (4) Å^3	0.15 × 0.15 × 0.15 mm
Z = 4	

Data collection

Bruker APEXII CCD area-detector diffractometer	6912 independent reflections
Radiation source: fine-focus sealed tube	3976 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.061
T = 293(2) K	θ_{max} = 26.0º
φ and ω scans	θ_{min} = 1.5º
Absorption correction: multi-scan (SADABS; Bruker, 2001)	h = −16→17
T_{min} = 0.904, T_{max} = 0.904	k = −20→20
17576 measured reflections	l = −9→17

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.044	H atoms treated by a mixture of

	independent and constrained refinement
$wR(F^2) = 0.127$	$w = 1/[\sigma^2(F_o^2) + (0.0662P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} < 0.001$
6912 reflections	$\Delta\rho_{max} = 0.86$ e Å^{-3}
528 parameters	$\Delta\rho_{min} = -0.84$ e Å^{-3}
6 restraints	Extinction correction: SHELXL97 (Sheldrick, 1997)
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.00

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}
C1	0.8370 (3)	0.4926 (3)	0.2632 (3)	0.0593 (11)
H1	0.7917	0.4526	0.2510	0.071*
C2	0.9332 (3)	0.4719 (3)	0.2790 (3)	0.0715 (13)
H2	0.9509	0.4193	0.2771	0.086*
C3	1.0000 (3)	0.5284 (3)	0.2971 (3)	0.0723 (13)
H3	1.0642	0.5148	0.3062	0.087*
C4	0.9735 (3)	0.6076 (3)	0.3024 (3)	0.0625 (12)
C5	1.0388 (3)	0.6732 (3)	0.3252 (3)	0.0756 (14)
H5	1.1040	0.6635	0.3379	0.091*
C6	1.0082 (3)	0.7460 (3)	0.3285 (3)	0.0752 (14)
H6	1.0525	0.7865	0.3426	0.090*
C7	0.9086 (3)	0.7648 (3)	0.3108 (3)	0.0588 (11)
C8	0.8728 (3)	0.8412 (3)	0.3158 (3)	0.0691 (12)
H8	0.9144	0.8836	0.3295	0.083*
C9	0.7774 (3)	0.8531 (3)	0.3006 (3)	0.0644 (12)
H9	0.7529	0.9035	0.3049	0.077*
C10	0.7162 (3)	0.7889 (2)	0.2785 (3)	0.0573 (11)
H10	0.6508	0.7980	0.2677	0.069*
C11	0.8423 (2)	0.7034 (2)	0.2890 (3)	0.0486 (10)
C12	0.8751 (2)	0.6237 (2)	0.2842 (3)	0.0497 (10)
C13	0.4743 (3)	0.7042 (3)	0.2495 (3)	0.0657 (12)
H13	0.5002	0.7128	0.3107	0.079*
C14	0.3821 (3)	0.7304 (3)	0.2149 (4)	0.0725 (13)

H14	0.3469	0.7549	0.2531	0.087*
C15	0.3435 (3)	0.7201 (2)	0.1253 (3)	0.0622 (12)
H15	0.2826	0.7388	0.1014	0.075*
C16	0.3957 (2)	0.6813 (2)	0.0699 (3)	0.0490 (10)
C17	0.3613 (3)	0.6667 (2)	−0.0247 (3)	0.0604 (12)
H17	0.3008	0.6841	−0.0520	0.072*
C18	0.4146 (3)	0.6282 (2)	−0.0746 (3)	0.0573 (11)
H18	0.3899	0.6187	−0.1359	0.069*
C19	0.5088 (3)	0.6014 (2)	−0.0358 (3)	0.0479 (9)
C20	0.5678 (3)	0.5606 (2)	−0.0853 (3)	0.0567 (11)
H20	0.5466	0.5503	−0.1469	0.068*
C21	0.6558 (3)	0.5365 (2)	−0.0428 (3)	0.0584 (11)
H21	0.6948	0.5087	−0.0746	0.070*
C22	0.6866 (3)	0.5537 (2)	0.0485 (3)	0.0523 (10)
H22	0.7475	0.5374	0.0766	0.063*
C23	0.5450 (2)	0.6154 (2)	0.0557 (3)	0.0390 (8)
C24	0.4882 (2)	0.6564 (2)	0.1100 (3)	0.0418 (9)
C25	0.5931 (2)	0.5078 (2)	0.3286 (3)	0.0412 (9)
C26	0.5346 (2)	0.45871 (19)	0.3815 (2)	0.0358 (8)
C27	0.5710 (2)	0.40717 (19)	0.4523 (2)	0.0367 (8)
C28	0.6751 (2)	0.3964 (2)	0.4895 (3)	0.0428 (9)
C29	0.5087 (2)	0.3617 (2)	0.4913 (2)	0.0377 (8)
H29	0.5335	0.3274	0.5386	0.045*
C30	0.4100 (2)	0.36606 (19)	0.4614 (2)	0.0339 (8)
C31	0.3744 (2)	0.4195 (2)	0.3933 (2)	0.0392 (9)
H31	0.3088	0.4247	0.3740	0.047*
C32	0.4356 (2)	0.4653 (2)	0.3536 (2)	0.0427 (9)
H32	0.4104	0.5008	0.3079	0.051*
C33	0.3490 (2)	0.3106 (2)	0.5019 (2)	0.0361 (8)
C34	0.2422 (2)	0.31950 (19)	0.4831 (2)	0.0360 (8)
C35	0.1875 (2)	0.2517 (2)	0.4652 (2)	0.0410 (9)
H35	0.2185	0.2039	0.4617	0.049*
C36	0.0881 (2)	0.2516 (2)	0.4520 (3)	0.0433 (9)
C37	0.0438 (3)	0.1704 (2)	0.4357 (3)	0.0600 (12)
C38	0.0422 (2)	0.3247 (2)	0.4594 (3)	0.0392 (8)
C39	−0.0641 (2)	0.3395 (2)	0.4486 (3)	0.0541 (11)
C40	0.0981 (2)	0.3921 (2)	0.4798 (3)	0.0411 (9)
H40	0.0681	0.4398	0.4866	0.049*
C41	0.1964 (2)	0.39093 (19)	0.4903 (3)	0.0385 (8)
H41	0.2313	0.4374	0.5019	0.046*
Cu1	0.66501 (3)	0.61130 (3)	0.23968 (3)	0.04183 (16)
N1	0.8075 (2)	0.5662 (2)	0.2648 (2)	0.0497 (8)
N2	0.7463 (2)	0.71606 (18)	0.2723 (2)	0.0472 (8)
N3	0.5263 (2)	0.66769 (19)	0.1986 (2)	0.0494 (8)
N4	0.63421 (19)	0.59196 (16)	0.0981 (2)	0.0451 (8)
O1	0.62329 (16)	0.57379 (14)	0.35849 (17)	0.0443 (6)
O2	0.60284 (18)	0.48301 (17)	0.25289 (18)	0.0618 (8)
O3	0.72864 (16)	0.42358 (16)	0.4347 (2)	0.0560 (7)
H3A	0.7832	0.4069	0.4508	0.084*

O4	0.70660 (18)	0.3663 (2)	0.5624 (2)	0.0740 (8)
O5	0.38447 (16)	0.25576 (14)	0.54750 (18)	0.0476 (5)
O6	0.0945 (2)	0.11279 (17)	0.4451 (3)	0.0797 (9)
O7	−0.04731 (19)	0.16318 (18)	0.4096 (3)	0.0849 (9)
H7	−0.0719	0.2071	0.4039	0.153*
O8	−0.12265 (18)	0.28825 (19)	0.4100 (3)	0.1021 (12)
O9	−0.09096 (16)	0.40276 (15)	0.4745 (2)	0.0529 (6)
O10	0.7694 (4)	0.4462 (5)	0.7582 (5)	0.072 (3)
O11	0.1075 (10)	0.9558 (9)	0.4964 (13)	0.071 (3)
H1W	0.7161 (12)	0.443 (3)	0.771 (3)	0.080*
H2W	0.8127 (19)	0.447 (4)	0.8053 (19)	0.080*
H3W	0.096 (3)	0.933 (4)	0.4435 (16)	0.080*
H4W	0.158 (2)	0.980 (3)	0.516 (2)	0.080*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.055 (2)	0.065 (3)	0.062 (3)	0.012 (2)	0.022 (2)	0.010 (2)
C2	0.064 (3)	0.074 (3)	0.083 (4)	0.024 (2)	0.030 (3)	0.017 (3)
C3	0.045 (2)	0.102 (4)	0.074 (3)	0.022 (2)	0.021 (2)	0.019 (3)
C4	0.040 (2)	0.090 (3)	0.059 (3)	0.009 (2)	0.015 (2)	0.017 (3)
C5	0.034 (2)	0.119 (4)	0.075 (4)	−0.007 (3)	0.012 (2)	0.014 (3)
C6	0.052 (3)	0.092 (4)	0.085 (4)	−0.015 (3)	0.020 (3)	0.006 (3)
C7	0.050 (2)	0.076 (3)	0.051 (3)	−0.010 (2)	0.011 (2)	0.011 (2)
C8	0.076 (3)	0.070 (3)	0.062 (3)	−0.017 (3)	0.014 (3)	0.005 (2)
C9	0.075 (3)	0.058 (3)	0.060 (3)	−0.002 (2)	0.014 (2)	0.006 (2)
C10	0.058 (2)	0.064 (3)	0.052 (3)	0.007 (2)	0.013 (2)	0.014 (2)
C11	0.040 (2)	0.067 (3)	0.040 (2)	−0.0021 (18)	0.0122 (18)	0.011 (2)
C12	0.0363 (19)	0.068 (3)	0.048 (3)	0.0039 (18)	0.0166 (18)	0.013 (2)
C13	0.050 (2)	0.093 (3)	0.057 (3)	0.015 (2)	0.017 (2)	−0.007 (3)
C14	0.052 (3)	0.091 (3)	0.075 (4)	0.017 (2)	0.015 (3)	−0.014 (3)
C15	0.043 (2)	0.065 (3)	0.073 (3)	0.011 (2)	0.001 (2)	0.002 (3)
C16	0.041 (2)	0.046 (2)	0.057 (3)	0.0018 (17)	0.002 (2)	0.007 (2)
C17	0.046 (2)	0.059 (3)	0.066 (3)	−0.002 (2)	−0.014 (2)	0.006 (2)
C18	0.061 (3)	0.056 (3)	0.048 (3)	−0.009 (2)	−0.005 (2)	0.003 (2)
C19	0.057 (2)	0.041 (2)	0.046 (3)	−0.0150 (18)	0.011 (2)	0.0048 (19)
C20	0.075 (3)	0.051 (2)	0.048 (3)	−0.018 (2)	0.020 (2)	−0.006 (2)
C21	0.067 (3)	0.058 (3)	0.058 (3)	−0.010 (2)	0.031 (2)	−0.008 (2)
C22	0.045 (2)	0.055 (2)	0.062 (3)	−0.0040 (18)	0.022 (2)	0.002 (2)
C23	0.0411 (19)	0.0355 (18)	0.040 (2)	−0.0067 (15)	0.0076 (17)	0.0052 (17)
C24	0.0393 (19)	0.039 (2)	0.046 (3)	−0.0018 (16)	0.0061 (18)	0.0069 (18)
C25	0.0253 (17)	0.055 (2)	0.043 (2)	0.0009 (16)	0.0065 (16)	0.000 (2)
C26	0.0303 (17)	0.044 (2)	0.035 (2)	−0.0038 (15)	0.0109 (15)	−0.0096 (17)
C27	0.0267 (16)	0.043 (2)	0.042 (2)	0.0000 (14)	0.0091 (16)	−0.0068 (17)
C28	0.0290 (17)	0.047 (2)	0.053 (3)	0.0011 (16)	0.0092 (18)	0.003 (2)
C29	0.0290 (17)	0.0428 (19)	0.041 (2)	0.0045 (14)	0.0071 (16)	0.0004 (17)
C30	0.0245 (15)	0.0402 (19)	0.038 (2)	0.0002 (14)	0.0091 (15)	−0.0085 (17)
C31	0.0231 (16)	0.050 (2)	0.043 (2)	0.0017 (15)	0.0019 (15)	−0.0027 (19)

C32	0.0320 (18)	0.054 (2)	0.042 (2)	0.0042 (16)	0.0065 (17)	0.0023 (18)
C33	0.0315 (17)	0.0329 (19)	0.044 (2)	0.0052 (15)	0.0080 (16)	−0.0049 (17)
C34	0.0258 (16)	0.043 (2)	0.042 (2)	−0.0015 (14)	0.0128 (15)	0.0025 (17)
C35	0.0352 (19)	0.039 (2)	0.053 (2)	0.0023 (15)	0.0181 (18)	−0.0023 (18)
C36	0.0333 (18)	0.043 (2)	0.055 (3)	−0.0053 (15)	0.0130 (18)	−0.0004 (19)
C37	0.044 (2)	0.051 (3)	0.090 (4)	−0.012 (2)	0.025 (2)	−0.007 (2)
C38	0.0257 (16)	0.043 (2)	0.049 (2)	−0.0027 (15)	0.0073 (16)	0.0004 (18)
C39	0.0286 (19)	0.055 (3)	0.079 (3)	−0.0022 (18)	0.013 (2)	0.004 (2)
C40	0.0273 (16)	0.042 (2)	0.054 (2)	0.0053 (15)	0.0098 (16)	0.0020 (18)
C41	0.0265 (16)	0.0373 (19)	0.052 (2)	−0.0009 (14)	0.0095 (16)	−0.0010 (18)
Cu1	0.0311 (2)	0.0549 (3)	0.0406 (3)	0.0029 (2)	0.00990 (19)	0.0077 (2)
N1	0.0458 (18)	0.058 (2)	0.048 (2)	0.0079 (16)	0.0166 (16)	0.0102 (17)
N2	0.0412 (17)	0.057 (2)	0.044 (2)	0.0050 (15)	0.0109 (15)	0.0135 (16)
N3	0.0429 (17)	0.064 (2)	0.041 (2)	0.0053 (15)	0.0077 (16)	−0.0010 (17)
N4	0.0384 (16)	0.0452 (18)	0.055 (2)	−0.0019 (13)	0.0172 (15)	0.0076 (15)
O1	0.0424 (13)	0.0413 (14)	0.0509 (17)	−0.0039 (11)	0.0135 (12)	−0.0007 (13)
O2	0.0624 (17)	0.087 (2)	0.0431 (17)	−0.0233 (15)	0.0275 (14)	−0.0160 (16)
O3	0.0252 (12)	0.0642 (17)	0.081 (2)	0.0072 (12)	0.0155 (14)	0.0142 (15)
O4	0.0324 (13)	0.119 (2)	0.0676 (17)	0.0069 (14)	0.0020 (12)	0.0308 (16)
O5	0.0314 (12)	0.0411 (13)	0.0703 (14)	0.0044 (9)	0.0100 (10)	0.0081 (11)
O6	0.0604 (18)	0.0370 (14)	0.140 (3)	−0.0056 (13)	0.0168 (18)	−0.0061 (15)
O7	0.0422 (16)	0.0554 (17)	0.158 (3)	−0.0182 (13)	0.0219 (17)	−0.0232 (18)
O8	0.0266 (14)	0.0729 (19)	0.198 (4)	−0.0097 (13)	0.0017 (17)	−0.043 (2)
O9	0.0250 (12)	0.0535 (14)	0.0808 (17)	0.0039 (10)	0.0122 (11)	−0.0022 (12)
O10	0.065 (6)	0.083 (7)	0.061 (7)	0.008 (6)	0.017 (5)	0.018 (6)
O11	0.072 (6)	0.067 (6)	0.080 (8)	0.001 (5)	0.032 (5)	0.004 (6)

Geometric parameters (Å, °)

C1—N1	1.318 (5)	C24—N3	1.345 (5)
C1—C2	1.393 (5)	C25—O2	1.244 (4)
C1—H1	0.9300	C25—O1	1.249 (4)
C2—C3	1.341 (6)	C25—C26	1.511 (5)
C2—H2	0.9300	C25—Cu1	2.539 (4)
C3—C4	1.401 (6)	C26—C27	1.392 (5)
C3—H3	0.9300	C26—C32	1.400 (4)
C4—C12	1.407 (5)	C27—C29	1.391 (5)
C4—C5	1.448 (6)	C27—C28	1.495 (5)
C5—C6	1.311 (6)	C28—O4	1.209 (4)
C5—H5	0.9300	C28—O3	1.311 (4)
C6—C7	1.433 (6)	C29—C30	1.396 (4)
C6—H6	0.9300	C29—H29	0.9300
C7—C8	1.400 (6)	C30—C31	1.383 (5)
C7—C11	1.401 (5)	C30—C33	1.491 (4)
C8—C9	1.354 (6)	C31—C32	1.388 (5)
C8—H8	0.9300	C31—H31	0.9300
C9—C10	1.393 (6)	C32—H32	0.9300
C9—H9	0.9300	C33—O5	1.205 (4)
C10—N2	1.316 (5)	C33—C34	1.504 (4)

C10—H10	0.9300	C34—C35	1.386 (4)
C11—N2	1.364 (4)	C34—C41	1.390 (4)
C11—C12	1.436 (5)	C35—C36	1.396 (4)
C12—N1	1.363 (5)	C35—H35	0.9300
C13—N3	1.321 (5)	C36—C38	1.417 (5)
C13—C14	1.391 (5)	C36—C37	1.514 (5)
C13—H13	0.9300	C37—O6	1.207 (4)
C14—C15	1.358 (6)	C37—O7	1.290 (4)
C14—H14	0.9300	C38—C40	1.393 (4)
C15—C16	1.386 (5)	C38—C39	1.518 (4)
C15—H15	0.9300	C39—O9	1.226 (4)
C16—C24	1.406 (5)	C39—O8	1.264 (4)
C16—C17	1.427 (6)	C40—C41	1.384 (4)
C17—C18	1.337 (6)	C40—H40	0.9300
C17—H17	0.9300	C41—H41	0.9300
C18—C19	1.432 (5)	Cu1—O1	2.085 (2)
C18—H18	0.9300	Cu1—N4	2.106 (3)
C19—C23	1.387 (5)	Cu1—N2	2.125 (3)
C19—C20	1.410 (5)	Cu1—N1	2.139 (3)
C20—C21	1.356 (6)	Cu1—N3	2.178 (3)
C20—H20	0.9300	Cu1—O2	2.371 (3)
C21—C22	1.383 (6)	O3—H3A	0.8200
C21—H21	0.9300	O7—H7	0.8200
C22—N4	1.325 (4)	O10—H1W	0.821 (11)
C22—H22	0.9300	O10—H2W	0.84 (3)
C23—N4	1.366 (4)	O11—H3W	0.87 (3)
C23—C24	1.438 (5)	O11—H4W	0.83 (4)
N1—C1—C2	122.9 (4)	C26—C27—C28	123.8 (3)
N1—C1—H1	118.6	O4—C28—O3	123.7 (3)
C2—C1—H1	118.5	O4—C28—C27	123.7 (3)
C3—C2—C1	119.7 (4)	O3—C28—C27	112.7 (3)
C3—C2—H2	120.2	C27—C29—C30	121.8 (3)
C1—C2—H2	120.1	C27—C29—H29	119.1
C2—C3—C4	120.3 (4)	C30—C29—H29	119.1
C2—C3—H3	119.8	C31—C30—C29	118.3 (3)
C4—C3—H3	119.9	C31—C30—C33	123.5 (3)
C3—C4—C12	116.5 (4)	C29—C30—C33	118.2 (3)
C3—C4—C5	125.5 (4)	C30—C31—C32	120.7 (3)
C12—C4—C5	118.1 (4)	C30—C31—H31	119.6
C6—C5—C4	121.8 (4)	C32—C31—H31	119.7
C6—C5—H5	119.1	C31—C32—C26	120.9 (3)
C4—C5—H5	119.1	C31—C32—H32	119.5
C5—C6—C7	121.9 (4)	C26—C32—H32	119.6
C5—C6—H6	119.1	O5—C33—C30	120.1 (3)
C7—C6—H6	119.0	O5—C33—C34	118.8 (3)
C8—C7—C11	117.4 (4)	C30—C33—C34	121.0 (3)
C8—C7—C6	123.8 (4)	C35—C34—C41	118.6 (3)
C11—C7—C6	118.7 (4)	C35—C34—C33	117.8 (3)
C9—C8—C7	119.7 (4)	C41—C34—C33	123.3 (3)

C9—C8—H8	120.2	C34—C35—C36	123.3 (3)
C7—C8—H8	120.1	C34—C35—H35	118.4
C8—C9—C10	119.3 (4)	C36—C35—H35	118.3
C8—C9—H9	120.5	C35—C36—C38	117.5 (3)
C10—C9—H9	120.3	C35—C36—C37	114.0 (3)
N2—C10—C9	123.3 (4)	C38—C36—C37	128.4 (3)
N2—C10—H10	118.2	O6—C37—O7	120.5 (4)
C9—C10—H10	118.4	O6—C37—C36	119.5 (3)
N2—C11—C7	122.5 (4)	O7—C37—C36	120.0 (4)
N2—C11—C12	117.7 (3)	C40—C38—C36	118.6 (3)
C7—C11—C12	119.8 (3)	C40—C38—C39	114.0 (3)
N1—C12—C4	122.9 (4)	C36—C38—C39	127.3 (3)
N1—C12—C11	117.3 (3)	O9—C39—O8	121.6 (3)
C4—C12—C11	119.7 (4)	O9—C39—C38	118.7 (3)
N3—C13—C14	122.3 (4)	O8—C39—C38	119.6 (4)
N3—C13—H13	118.8	C41—C40—C38	122.7 (3)
C14—C13—H13	118.9	C41—C40—H40	118.7
C15—C14—C13	119.8 (4)	C38—C40—H40	118.7
C15—C14—H14	120.0	C40—C41—C34	119.2 (3)
C13—C14—H14	120.1	C40—C41—H41	120.4
C14—C15—C16	119.5 (4)	C34—C41—H41	120.4
C14—C15—H15	120.3	O1—Cu1—N4	140.77 (10)
C16—C15—H15	120.2	O1—Cu1—N2	107.09 (11)
C15—C16—C24	117.3 (4)	N4—Cu1—N2	110.97 (11)
C15—C16—C17	123.9 (4)	O1—Cu1—N1	99.44 (11)
C24—C16—C17	118.9 (4)	N4—Cu1—N1	97.14 (11)
C18—C17—C16	121.2 (4)	N2—Cu1—N1	78.41 (12)
C18—C17—H17	119.4	O1—Cu1—N3	88.70 (11)
C16—C17—H17	119.4	N4—Cu1—N3	77.60 (12)
C17—C18—C19	121.4 (4)	N2—Cu1—N3	97.19 (12)
C17—C18—H18	119.3	N1—Cu1—N3	171.58 (12)
C19—C18—H18	119.3	O1—Cu1—O2	58.28 (9)
C23—C19—C20	117.2 (4)	N4—Cu1—O2	86.22 (10)
C23—C19—C18	119.1 (4)	N2—Cu1—O2	160.63 (11)
C20—C19—C18	123.7 (4)	N1—Cu1—O2	91.00 (11)
C21—C20—C19	119.8 (4)	N3—Cu1—O2	95.17 (11)
C21—C20—H20	120.1	O1—Cu1—C25	29.28 (10)
C19—C20—H20	120.1	N4—Cu1—C25	113.30 (12)
C20—C21—C22	119.1 (4)	N2—Cu1—C25	135.70 (12)
C20—C21—H21	120.4	N1—Cu1—C25	97.53 (11)
C22—C21—H21	120.5	N3—Cu1—C25	90.63 (11)
N4—C22—C21	123.5 (4)	O2—Cu1—C25	29.08 (10)
N4—C22—H22	118.2	C1—N1—C12	117.6 (3)
C21—C22—H22	118.3	C1—N1—Cu1	129.3 (3)
N4—C23—C19	122.9 (3)	C12—N1—Cu1	113.1 (2)
N4—C23—C24	117.2 (3)	C10—N2—C11	117.7 (3)
C19—C23—C24	119.9 (3)	C10—N2—Cu1	128.9 (3)
N3—C24—C16	122.9 (4)	C11—N2—Cu1	113.4 (3)
N3—C24—C23	117.5 (3)	C13—N3—C24	118.1 (3)

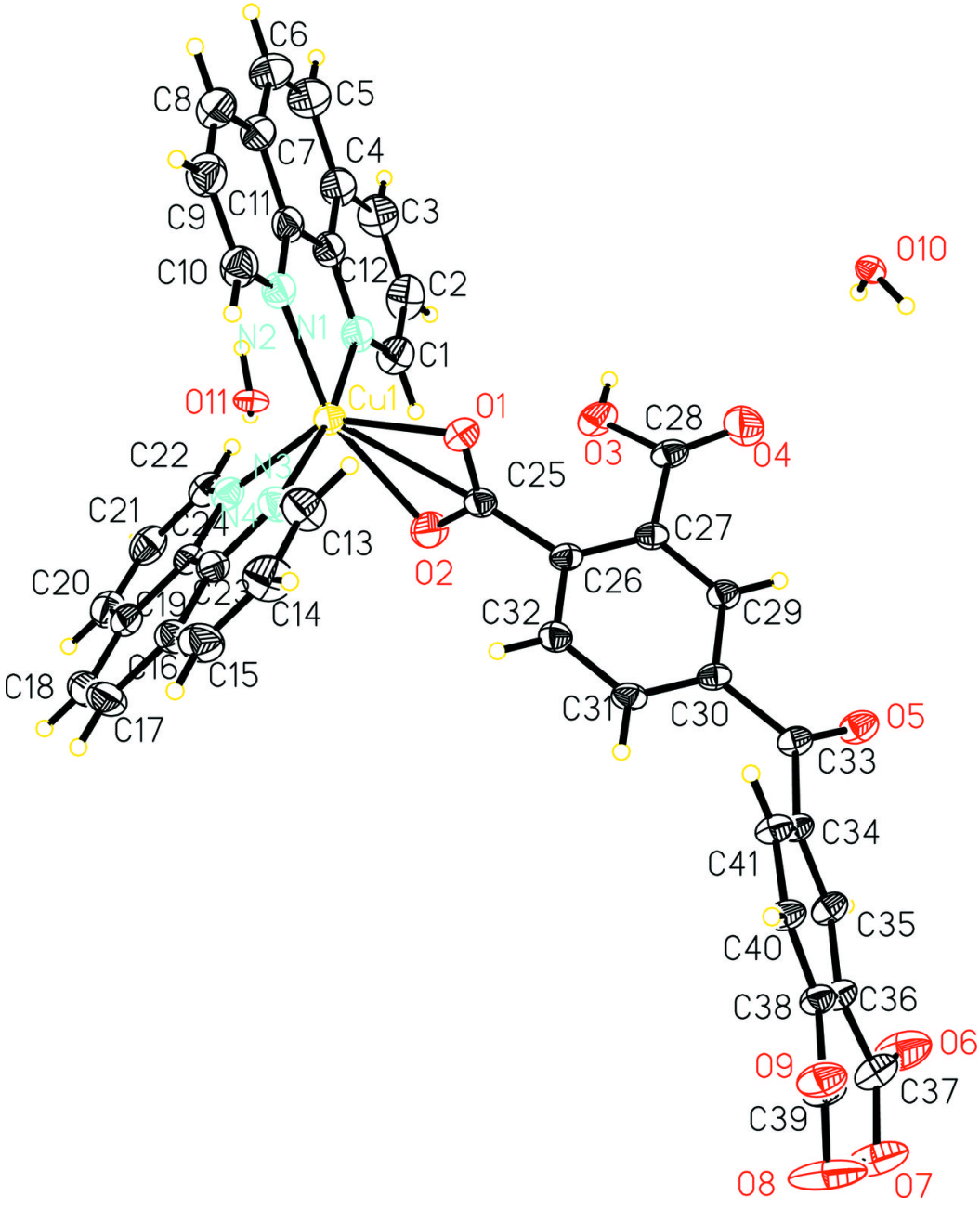
C16—C24—C23	119.5 (4)	C13—N3—Cu1	128.9 (3)
O2—C25—O1	122.5 (3)	C24—N3—Cu1	112.7 (2)
O2—C25—C26	117.8 (3)	C22—N4—C23	117.5 (3)
O1—C25—C26	119.5 (3)	C22—N4—Cu1	127.7 (3)
O2—C25—Cu1	67.9 (2)	C23—N4—Cu1	114.4 (2)
O1—C25—Cu1	54.76 (18)	C25—O1—Cu1	96.0 (2)
C26—C25—Cu1	168.3 (2)	C25—O2—Cu1	83.0 (2)
C27—C26—C32	118.8 (3)	C28—O3—H3A	109.6
C27—C26—C25	125.6 (3)	C37—O7—H7	109.4
C32—C26—C25	115.6 (3)	H1W—O10—H2W	112 (3)
C29—C27—C26	119.5 (3)	H3W—O11—H4W	122 (4)
C29—C27—C28	116.7 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O11—H4W···O6^{i}	0.83 (4)	2.58 (5)	2.764 (14)	94 (4)
O3—H3A···O8^{ii}	0.82	2.56	3.198 (4)	136
O3—H3A···O9^{ii}	0.82	1.77	2.555 (3)	161

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

Fig. 1


C6
C8
C5
C7
C4
C9
C11
C3
C10
C12
C2
N2
N1
C1
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Cu1
O1
C22
N3
C25
C21
C24
N4
C13
C27
O2
C20
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C32
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C31
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C41
C35
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C38
C36
O6
O9
C37
C39
O8
O7
O10
O3
C28
O4