metal-organic compounds

(Dicyanamido)[2-(2-pyridylmethyl-iminomethyl)phenolato]copper(II) monohydrate

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The title compound, $[Cu(C_{13}H_{11}N_2O)(C_2N_3)]\cdot H_2O$, is a mononuclear copper(II) complex in which the Cu^{II} ion has a slightly distorted square-planar geometry and is coordinated by two N atoms and one O atom from the Schiff base ligand and by an N atom from dicyanamide. The O atoms of water molecules contribute to O—H⋯N, O—H⋯O hydrogen bonds, leading to the formation of sheets parallel to the *ac* plane. There are also weak interactions between inversion-related molecules.

Related literature

For related literature, see: You & Zhu (2004); Li & Zhang (2004); You *et al.* (2004); Zhang *et al.* (2005).
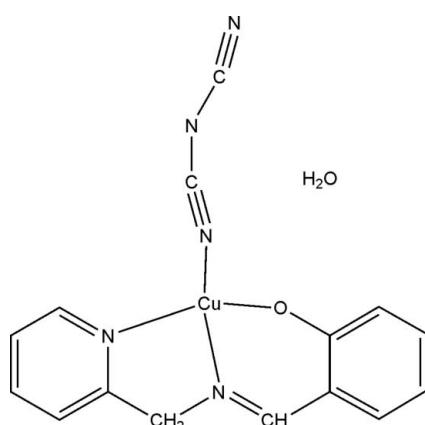
Experimental

Crystal data

$[Cu(C_{13}H_{11}N_2O)(C_2N_3)]\cdot H_2O$	$V = 1469.9$ (3) Å^3
$M_r = 358.84$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.8851$ (12) Å	$\mu = 1.50$ mm^{-1}
$b = 7.0240$ (6) Å	$T = 293$ (2) K
$c = 21.398$ (3) Å	$0.2 \times 0.2 \times 0.2$ mm
$\beta = 98.382$ (9)°	

Data collection

Rigaku Mercury2 CCD diffractometer	14839 measured reflections
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)	3487 independent reflections
$T_{min} = 0.693$, $T_{max} = 0.741$	2664 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.048$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$	208 parameters
$wR(F^2) = 0.115$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{max} = 0.61$ e Å^{-3}
3487 reflections	$\Delta\rho_{min} = -0.35$ e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1W—H1WA⋯N5^i	0.88	2.08	2.947 (4)	173
O1W—H1WB⋯O1	0.88	2.04	2.909 (3)	167
O1W—H1WB⋯N3	0.88	2.69	3.157 (3)	115

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL*.

References

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supplementary materials

(Dicyanamido)[2-(2-pyridylmethyliminomethyl)phenolato]copper(II) monohydrate

Q.-H. Zhao, L. Zhang, L. Du and R.-B. Fang

Comment

Transition metal compounds containing Schiff base ligands have been of great interest for many years. These compounds play an important role in the development of coordination chemistry due to their potential applications in catalysis and enzymatic reactions, magnetism and molecular architecture (You & Zhu, 2004; Li & Zhang, 2004). Here we report the structure of a complex that is formed by $Cu(CH_3COO)_2$, the Schiff base ligand 2-(pyridin-2-ylmethyliminomethyl)phenol and sodium dicyanamide.

As shown in Fig. 1, the asymmetric unit consists of a mononuclear $[Cu(C_{13}H_{11}N_2O)N(CN)_2]$ and a H-bonded water molecule. The central Cu^{II} ion is four-coordinate and adopts a slightly distorted square-planar geometry that is defined by two N atoms and one O atom from the Schiff base ligand and another N atom from dicyanamide. The C7=N1 and C8—N1 distances of 1.293 (4) Å and 1.466 (4) Å indicate double and single bonds respectively. The bond angles around the Cu^{II} centre show some deviations from ideal square-planar geometry (You *et al.*, 2004). Also, the closeness of the planes of inversion related molecules imply weak intramolecular interactions cross an inversion centre such that the distance between Cu1 and O1 of an inversion related phenolato is 2.814 (2) Å, which is much longer than Cu—O bond length.

The water molecule is involved in intermolecular (O1W—H1WA···N5) and intramolecular hydrogen bonds (O1W—H1WB···O1, O1W—H1WB···N3), which leads to sheets parallel to the *ac* plane (Fig. 2).

Experimental

All chemicals used (reagent grade) were commercially available. Salicylaldehyde (0.122 g, 1 mmol) was dissolved in ethanol (5 mL) and ethanol solution (5 mL) containing 2-aminomethylpyridine (0.108 g, 1 mmol) was added slowly with stirring. The resulting yellow solution was continuously stirred for about 30 min at room temperature, and then $Cu(CH_3COO)_2·H_2O$ (0.200 g, 1 mmol) in aqueous solution (5 mL) was added with stirring homogeneously. Dark blue crystals suitable for X-ray ananlysis were obtained by slow evaporation at room temperature over several days (Zhang *et al.*, 2005).

Refinement

Water H atoms were located in a difference map and refined with distance restraints of O1W—H = 0.87 (2). Other H atoms were placed in calculated positions and allowed to ride on their attached C atoms with $U_{iso}(H) = 1.2Ueq(C)$.

supplementary materials

Figures
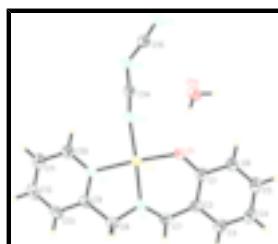
Fig. 1. The molecular structure of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.
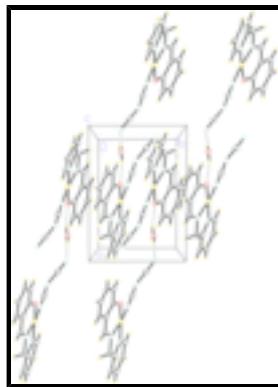
Fig. 2. A crystal packing diagram of the title compound, viewed along the *c* axis. Hydrogen bonds are shown as dashed lines.

(Dicyanamido)[2-(2-pyridylmethyliminomethyl)phenolato]copper(II) monohydrate

Crystal data

$[Cu(C_{13}H_{11}N_2O)(C_2N_3)]\cdot H_2O$	$F_{000} = 732$
$M_r = 358.84$	$D_x = 1.622$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 3146 reflections
$a = 9.8851$ (12) Å	$\theta = 3.0–27.5º$
$b = 7.0240$ (6) Å	$\mu = 1.50$ mm^{-1}
$c = 21.398$ (3) Å	$T = 293$ (2) K
$\beta = 98.382$ (9)º	Prism, colourless
$V = 1469.9$ (3) Å^3	$0.2 \times 0.2 \times 0.2$ mm
$Z = 4$	

Data collection

Rigaku Mercury2 CCD diffractometer	3487 independent reflections
Radiation source: fine-focus sealed tube	2664 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.048$
Detector resolution: 13.6612 pixels mm^{-1}	$\theta_{max} = 27.9º$
$T = 293(2)$ K	$\theta_{min} = 2.6º$
ω scans	$h = -13 \rightarrow 13$
Absorption correction: multi-scan	$k = -9 \rightarrow 9$

(CrystalClear; Rigaku, 2005)

$T_{min} = 0.693$, $T_{max} = 0.741$

14839 measured reflections

$l = -28 \rightarrow 28$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.042$	H-atom parameters constrained
$wR(F^2) = 0.115$	$w = 1/[\sigma^2(F_o^2) + (0.0583P)^2 + 0.2406P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$
3487 reflections	$\Delta\rho_{max} = 0.61$ e Å^{-3}
208 parameters	$\Delta\rho_{min} = -0.35$ 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 $F^2 > 2\sigma(F^2)$ 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	0.56134 (3)	0.30788 (5)	0.548195 (15)	0.04185 (13)
O1	0.42489 (19)	0.2985 (3)	0.47469 (10)	0.0489 (5)
N2	0.7131 (2)	0.3036 (3)	0.62161 (11)	0.0411 (5)
N1	0.6994 (2)	0.1915 (3)	0.50553 (12)	0.0463 (6)
C1	0.4349 (3)	0.2127 (4)	0.41987 (14)	0.0439 (6)
N3	0.4226 (2)	0.3912 (4)	0.59818 (11)	0.0477 (5)
O1W	0.1486 (2)	0.3114 (5)	0.50627 (14)	0.0968 (11)
H1WA	0.0984	0.3091	0.4690	0.116*
H1WB	0.2322	0.3266	0.4974	0.116*
C10	0.7040 (3)	0.3557 (4)	0.68161 (15)	0.0508 (7)
H10A	0.6219	0.4051	0.6908	0.061*
C7	0.6801 (3)	0.1162 (4)	0.44982 (13)	0.0454 (6)
H7A	0.7536	0.0521	0.4370	0.055*
C6	0.3203 (3)	0.2118 (4)	0.37236 (14)	0.0501 (7)
H6A	0.2384	0.2647	0.3805	0.060*

N4	0.2314 (2)	0.4829 (5)	0.65140 (12)	0.0617 (7)
C14	0.3289 (3)	0.4396 (4)	0.62031 (12)	0.0436 (6)
C3	0.5580 (3)	0.0428 (4)	0.34622 (14)	0.0525 (7)
H3A	0.6374	−0.0163	0.3377	0.063*
C8	0.8366 (3)	0.1772 (5)	0.54199 (15)	0.0582 (8)
H8A	0.8986	0.2615	0.5242	0.070*
H8B	0.8704	0.0480	0.5400	0.070*
C13	0.9430 (3)	0.2075 (5)	0.65564 (17)	0.0584 (8)
H13A	1.0241	0.1562	0.6460	0.070*
C2	0.5558 (3)	0.1225 (4)	0.40608 (13)	0.0441 (6)
C11	0.8115 (4)	0.3384 (5)	0.72932 (16)	0.0616 (8)
H11A	0.8030	0.3780	0.7700	0.074*
C4	0.4466 (3)	0.0493 (5)	0.29979 (15)	0.0594 (8)
H4B	0.4506	−0.0014	0.2600	0.071*
C9	0.8314 (3)	0.2302 (4)	0.60885 (14)	0.0456 (6)
C12	0.9325 (3)	0.2615 (5)	0.71624 (18)	0.0652 (9)
H12A	1.0062	0.2464	0.7482	0.078*
C5	0.3281 (3)	0.1335 (4)	0.31392 (15)	0.0549 (8)
H5A	0.2514	0.1373	0.2831	0.066*
C15	0.1320 (3)	0.5962 (5)	0.62805 (14)	0.0545 (7)
N5	0.0420 (3)	0.6967 (5)	0.61320 (16)	0.0770 (9)

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.03160 (19)	0.0507 (2)	0.0433 (2)	0.00257 (13)	0.00549 (13)	0.00151 (14)
O1	0.0344 (10)	0.0648 (13)	0.0469 (11)	0.0028 (8)	0.0043 (8)	−0.0062 (9)
N2	0.0357 (11)	0.0430 (12)	0.0442 (13)	0.0004 (9)	0.0047 (9)	0.0042 (9)
N1	0.0312 (11)	0.0562 (14)	0.0521 (14)	−0.0002 (9)	0.0083 (10)	0.0005 (11)
C1	0.0412 (14)	0.0423 (15)	0.0486 (17)	−0.0065 (11)	0.0073 (11)	0.0018 (12)
N3	0.0408 (12)	0.0539 (14)	0.0489 (14)	0.0061 (11)	0.0080 (10)	0.0039 (11)
O1W	0.0436 (13)	0.174 (3)	0.0718 (18)	−0.0051 (16)	0.0055 (12)	−0.0185 (18)
C10	0.0467 (16)	0.0547 (16)	0.0497 (17)	0.0006 (13)	0.0028 (13)	0.0026 (13)
C7	0.0406 (14)	0.0480 (15)	0.0501 (17)	0.0011 (12)	0.0145 (12)	0.0022 (13)
C6	0.0427 (15)	0.0533 (17)	0.0525 (18)	−0.0056 (12)	0.0004 (12)	−0.0015 (13)
N4	0.0453 (14)	0.096 (2)	0.0449 (14)	0.0191 (14)	0.0118 (11)	0.0100 (14)
C14	0.0391 (14)	0.0506 (15)	0.0396 (14)	0.0007 (11)	0.0008 (11)	0.0042 (12)
C3	0.0577 (17)	0.0534 (17)	0.0491 (17)	−0.0048 (13)	0.0165 (14)	0.0012 (13)
C8	0.0320 (14)	0.082 (2)	0.061 (2)	0.0052 (14)	0.0089 (13)	−0.0044 (16)
C13	0.0336 (15)	0.069 (2)	0.070 (2)	0.0030 (13)	−0.0012 (13)	−0.0001 (17)
C2	0.0431 (14)	0.0453 (14)	0.0448 (16)	−0.0048 (11)	0.0099 (11)	0.0029 (12)
C11	0.065 (2)	0.068 (2)	0.0484 (18)	−0.0034 (16)	−0.0009 (15)	−0.0006 (15)
C4	0.073 (2)	0.0593 (19)	0.0467 (18)	−0.0120 (16)	0.0101 (15)	−0.0048 (14)
C9	0.0321 (13)	0.0475 (15)	0.0569 (17)	−0.0037 (11)	0.0056 (11)	0.0026 (13)
C12	0.0453 (18)	0.073 (2)	0.071 (2)	−0.0014 (16)	−0.0122 (15)	0.0050 (18)
C5	0.0582 (18)	0.0539 (16)	0.0496 (18)	−0.0096 (14)	−0.0025 (14)	0.0038 (14)
C15	0.0403 (15)	0.079 (2)	0.0451 (16)	0.0023 (15)	0.0084 (12)	−0.0045 (15)
N5	0.0517 (17)	0.104 (3)	0.074 (2)	0.0257 (16)	0.0057 (14)	−0.0008 (17)

Geometric parameters (Å, °)

Cu1—O1	1.9181 (19)	C6—H6A	0.9300
Cu1—N1	1.931 (2)	N4—C14	1.284 (4)
Cu1—N3	1.948 (2)	N4—C15	1.306 (4)
Cu1—N2	2.008 (2)	C3—C4	1.372 (4)
O1—C1	1.335 (4)	C3—C2	1.401 (4)
N2—C9	1.342 (4)	C3—H3A	0.9300
N2—C10	1.351 (4)	C8—C9	1.487 (4)
N1—C7	1.293 (4)	C8—H8A	0.9700
N1—C8	1.466 (4)	C8—H8B	0.9700
C1—C6	1.407 (4)	C13—C12	1.369 (5)
C1—C2	1.421 (4)	C13—C9	1.386 (4)
N3—C14	1.152 (3)	C13—H13A	0.9300
O1W—H1WA	0.8754	C11—C12	1.377 (5)
O1W—H1WB	0.8814	C11—H11A	0.9300
C10—C11	1.367 (4)	C4—C5	1.384 (4)
C10—H10A	0.9300	C4—H4B	0.9300
C7—C2	1.432 (4)	C12—H12A	0.9300
C7—H7A	0.9300	C5—H5A	0.9300
C6—C5	1.379 (4)	C15—N5	1.144 (4)
O1—Cu1—N1	93.37 (9)	C4—C3—H3A	119.0
O1—Cu1—N3	89.62 (9)	C2—C3—H3A	119.0
N1—Cu1—N3	171.71 (10)	N1—C8—C9	109.6 (2)
O1—Cu1—N2	175.47 (9)	N1—C8—H8A	109.7
N1—Cu1—N2	82.22 (10)	C9—C8—H8A	109.7
N3—Cu1—N2	94.61 (10)	N1—C8—H8B	109.7
C1—O1—Cu1	127.05 (18)	C9—C8—H8B	109.7
C9—N2—C10	118.6 (2)	H8A—C8—H8B	108.2
C9—N2—Cu1	114.9 (2)	C12—C13—C9	119.3 (3)
C10—N2—Cu1	126.45 (19)	C12—C13—H13A	120.3
C7—N1—C8	117.6 (2)	C9—C13—H13A	120.3
C7—N1—Cu1	126.15 (19)	C3—C2—C1	119.5 (3)
C8—N1—Cu1	116.1 (2)	C3—C2—C7	117.3 (3)
O1—C1—C6	118.8 (3)	C1—C2—C7	123.0 (3)
O1—C1—C2	123.8 (3)	C10—C11—C12	119.1 (3)
C6—C1—C2	117.4 (3)	C10—C11—H11A	120.5
C14—N3—Cu1	170.9 (2)	C12—C11—H11A	120.5
H1WA—O1W—H1WB	103.3	C3—C4—C5	118.1 (3)
N2—C10—C11	122.3 (3)	C3—C4—H4B	120.9
N2—C10—H10A	118.9	C5—C4—H4B	120.9
C11—C10—H10A	118.9	N2—C9—C13	121.5 (3)
N1—C7—C2	125.9 (3)	N2—C9—C8	116.4 (2)
N1—C7—H7A	117.0	C13—C9—C8	122.1 (3)
C2—C7—H7A	117.0	C13—C12—C11	119.3 (3)
C5—C6—C1	120.8 (3)	C13—C12—H12A	120.4
C5—C6—H6A	119.6	C11—C12—H12A	120.4
C1—C6—H6A	119.6	C6—C5—C4	122.0 (3)

C14—N4—C15	121.7 (3)	C6—C5—H5A	119.0
N3—C14—N4	172.7 (3)	C4—C5—H5A	119.0
C4—C3—C2	122.1 (3)	N5—C15—N4	173.6 (3)
N1—Cu1—O1—C1	7.4 (2)	C4—C3—C2—C7	−176.8 (3)
N3—Cu1—O1—C1	−164.8 (2)	O1—C1—C2—C3	−177.5 (2)
N1—Cu1—N2—C9	0.57 (19)	C6—C1—C2—C3	2.0 (4)
N3—Cu1—N2—C9	172.9 (2)	O1—C1—C2—C7	−0.6 (4)
N1—Cu1—N2—C10	−175.2 (2)	C6—C1—C2—C7	178.9 (3)
N3—Cu1—N2—C10	−2.9 (2)	N1—C7—C2—C3	175.9 (3)
O1—Cu1—N1—C7	−8.8 (3)	N1—C7—C2—C1	−1.1 (5)
N2—Cu1—N1—C7	170.1 (3)	N2—C10—C11—C12	−1.4 (5)
O1—Cu1—N1—C8	175.4 (2)	C2—C3—C4—C5	−1.7 (5)
N2—Cu1—N1—C8	−5.6 (2)	C10—N2—C9—C13	−0.1 (4)
Cu1—O1—C1—C6	176.29 (19)	Cu1—N2—C9—C13	−176.2 (2)
Cu1—O1—C1—C2	−4.3 (4)	C10—N2—C9—C8	−179.3 (3)
C9—N2—C10—C11	0.8 (4)	Cu1—N2—C9—C8	4.5 (3)
Cu1—N2—C10—C11	176.5 (2)	C12—C13—C9—N2	−0.1 (5)
C8—N1—C7—C2	−177.1 (3)	C12—C13—C9—C8	179.1 (3)
Cu1—N1—C7—C2	7.2 (4)	N1—C8—C9—N2	−8.7 (4)
O1—C1—C6—C5	176.7 (3)	N1—C8—C9—C13	172.0 (3)
C2—C1—C6—C5	−2.8 (4)	C9—C13—C12—C11	−0.4 (5)
C7—N1—C8—C9	−167.0 (3)	C10—C11—C12—C13	1.2 (5)
Cu1—N1—C8—C9	9.1 (3)	C1—C6—C5—C4	1.4 (5)
C4—C3—C2—C1	0.2 (4)	C3—C4—C5—C6	0.9 (5)

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1WA···N5ⁱ	0.88	2.08	2.947 (4)	173
O1W—H1WB···O1	0.88	2.04	2.909 (3)	167
O1W—H1WB···N3	0.88	2.69	3.157 (3)	115

Symmetry codes: (i) −x, −y+1, −z+1.

Fig. 1

Fig. 2