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(Cyanato-κN){1-[(*E*)-phenyl(pyridin-2-yl-κN)methylidene]semicarbazidato-κ²N¹,O}copper(II)

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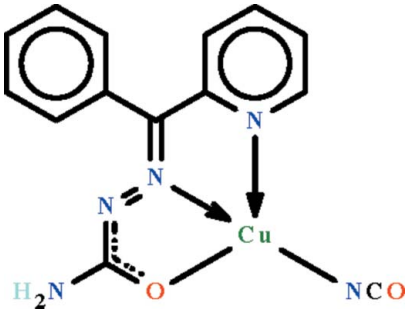
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.029; wR factor = 0.093; data-to-parameter ratio = 14.8.

The Cu^{II} atom in the title compound, [Cu($C_{13}H_{11}N_4O$)(NCO)], is *N*,*N*′,*O*-chelated by the mono-deprotonated Schiff base ligand and it is also covalently bonded to the nitrogen end of the cyanate ion. The Cu^{II} atom shows a square-planar coordination that is distorted towards square-pyramidal owing to an intermolecular Cu···$N_{cyanate}$ interaction [2.623 (2) Å], which gives a centrosymmetric dimer. In the square-planar description, the Cu^{II} atom is displaced out of the square plane [r.m.s. deviation = 0.048 Å] by 0.084 (1) Å in the direction of the apical occupant. In the crystal, adjacent complex dimers are linked by an amine N—H···N hydrogen-bond pair, also giving a centrosymmetric cyclic association [graph set $R_2^2(8)$], generating a linear chain parallel to [110].

Related literature

For the synthesis of the Schiff base, see: de Lima *et al.* (2008). For a related copper(II) derivative, see: Peŕez-Rebolledo *et al.* (2006). For graph-set notation, see: Etter *et al.* (1990).



Experimental

Crystal data

[Cu($C_{13}H_{11}N_4O$)(NCO)]
M_r = 344.82
Monoclinic, $P2_1/n$
a = 8.7601 (1) Å
b = 7.6732 (1) Å
c = 20.0819 (3) Å
β = 96.7467 (7)°
V = 1340.52 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.64 mm^{-1}
T = 293 K
0.30 × 0.25 × 0.20 mm

Data collection

Bruker Kappa APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.638, T_{max} = 0.735
11886 measured reflections
3069 independent reflections
2728 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.093
S = 1.03
3069 reflections
208 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H41···N3^{i}	0.88 (1)	2.27 (1)	3.139 (2)	173 (3)

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

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2010); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZS2226).

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supporting information

Acta Cryst. (2012). E**68**, m1180 [doi:10.1107/S1600536812035386]

(Cyanato-κN){1-[(*E*)-phenyl(pyridin-2-yl-κN)methylidene]semicarbazidato-$\kappa^2 N^1,O$}copper(II)

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S1. Comment

2-Benzoylpyridine semicarbazone (de Lima *et al.*, 2008) is a Schiff base that is capable of *N*,*N*′,*O*-chelation to transition metal ions. This feature has been documented in a copper(II) dichloride adduct in which the Schiff base exists as a neutral molecule (Peŕez-Rebolledo *et al.*, 2006). However, the Cu^{II} atom in the title compound [$Cu(NCO)(C_{13}H_{11}N_4O)$] (Scheme I) is *N*,*N*′,*O*-chelated by the mono-deprotonated Schiff base ligand and it is also covalently bonded to the nitrogen end of the cyanate ion. The metal center shows square-planar coordination that is distorted towards square-pyramidal coordination owing to an intermolecular $Cu\cdots N_{cyanate}$ interaction [2.623 (2) Å], which generates a centrosymmetric dimer (Fig. 1). The geometry is better interpreted as square planar as the $Cu\cdots N_{cyanate}\cdots Cu$ angle is too acute [93.0 (1)°].

Adjacent dimers are linked by an amine N—H···N hydrogen-bond pair (Table 1), also giving a centrosymmetric cyclic association [graph set $R^2_2(8)$ (Etter *et al.*, 1990], generating a linear chain parallel to [1 1 0].

S2. Experimental

A methanol solution (20 ml) of 2-benzoylpyridine semicarbazone (0.240 g, 1 mmol) (de Lima *et al.*, 2008), copper sulfate pentahydrate (0.249 g, 1 mmol) and sodium cyanate (0.065 g, 1 mmol) was heated for 5 h. The dark green solid was collected and recrystallized from methanol.

S3. Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H = 0.93 Å) and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2U_{eq}(C). The amino H-atoms were located in a difference Fourier map, and were refined with a distance restraint of N—H = 0.88±0.01 Å and their displacement parameters refined. Only one H-atom is involved in the formation of a hydrogen bond.

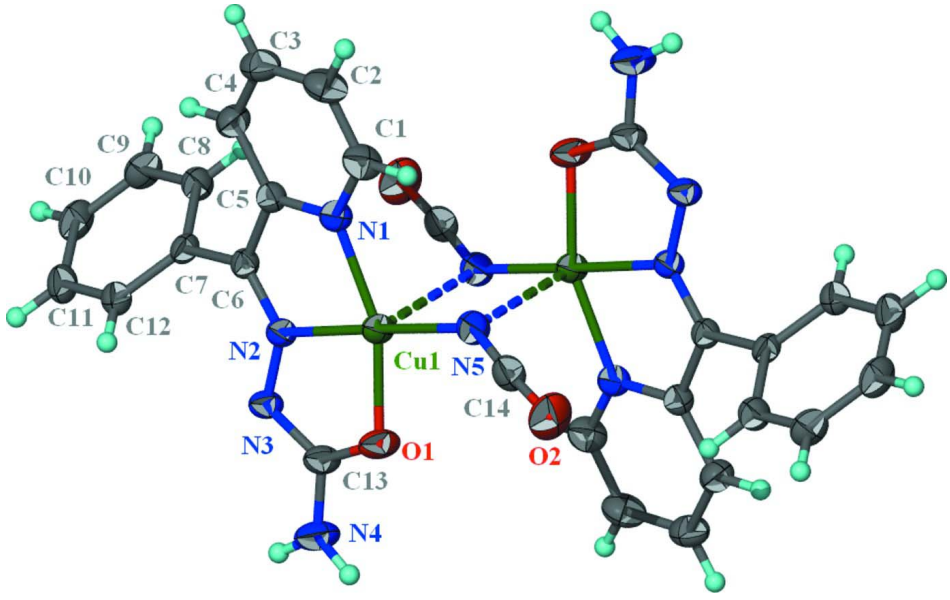

Figure 1

Thermal ellipsoid plot (Barbour, 2001) of two molecules of [Cu(NCO)($C_{13}H_{11}N_4O$)] that are linked by Cu···$N_{cyanate}$ interactions (dashed bonds), at the 50% probability level. Hydrogen atoms are drawn as spheres of arbitrary radius.

(Cyanato-*κN*){1-[(*E*)-phenyl(pyridin-2-yl- *κN*)methylidene]semicarbazidato-*κ*^{2}*N*^{1},*O*}copper(II)

Crystal data

[Cu($C_{13}H_{11}N_4O$)(NCO)]
M_r = 344.82
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 8.7601 (1) Å
b = 7.6732 (1) Å
c = 20.0819 (3) Å
β = 96.7467 (7)°
V = 1340.52 (3) Å^3
Z = 4

$F(000)$ = 700
D_x = 1.709 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 838 reflections
θ = 2.4–28.3°
μ = 1.64 mm^{-1}
T = 293 K
Prism, dark green
0.30 × 0.25 × 0.20 mm

Data collection

Bruker Kappa APEXII diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.638, T_{max} = 0.735

11886 measured reflections
3069 independent reflections
2728 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 27.5°, θ_{min} = 2.7°
h = −10→11
k = −9→9
l = −26→26

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.093
S = 1.03

3069 reflections
208 parameters
2 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0579P)^2 + 0.5121P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.47$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0221 (17)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.31070 (2)	0.50325 (3)	0.506177 (10)	0.03203 (12)
O1	0.28257 (17)	0.3049 (2)	0.56285 (6)	0.0473 (4)
O2	0.5831 (2)	0.6387 (3)	0.67349 (8)	0.0696 (6)
N1	0.26412 (17)	0.6848 (2)	0.43675 (7)	0.0323 (3)
N2	0.13987 (16)	0.38948 (19)	0.45304 (7)	0.0287 (3)
N3	0.09476 (17)	0.2331 (2)	0.47511 (7)	0.0332 (3)
N4	0.1503 (3)	0.0571 (3)	0.56674 (9)	0.0526 (5)
H41	0.078 (2)	−0.018 (3)	0.5525 (15)	0.057 (8)*
H42	0.196 (3)	0.034 (4)	0.6065 (8)	0.059 (8)*
N5	0.47729 (18)	0.6213 (2)	0.56268 (8)	0.0391 (4)
C1	0.3226 (2)	0.8437 (3)	0.43590 (10)	0.0425 (4)
H1	0.3972	0.8773	0.4703	0.051*
C2	0.2763 (3)	0.9611 (3)	0.38550 (13)	0.0480 (5)
H2	0.3178	1.0727	0.3862	0.058*
C3	0.1682 (2)	0.9104 (3)	0.33440 (11)	0.0448 (5)
H3	0.1354	0.9875	0.2999	0.054*
C4	0.1084 (2)	0.7441 (3)	0.33435 (9)	0.0383 (4)
H4	0.0364	0.7071	0.2995	0.046*
C5	0.15699 (19)	0.6327 (2)	0.38691 (8)	0.0299 (3)
C6	0.09472 (19)	0.4563 (3)	0.39498 (8)	0.0289 (3)
C7	−0.00451 (19)	0.3697 (2)	0.34034 (8)	0.0295 (3)
C8	0.0435 (2)	0.3596 (3)	0.27703 (9)	0.0373 (4)
H8	0.1360	0.4106	0.2691	0.045*
C9	−0.0453 (2)	0.2744 (3)	0.22558 (9)	0.0438 (5)
H9	−0.0119	0.2674	0.1834	0.053*
C10	−0.1826 (2)	0.2003 (3)	0.23667 (10)	0.0453 (5)
H10	−0.2419	0.1424	0.2021	0.054*
C11	−0.2324 (2)	0.2114 (3)	0.29881 (11)	0.0438 (5)
H11	−0.3263	0.1626	0.3060	0.053*
C12	−0.1440 (2)	0.2947 (3)	0.35081 (9)	0.0351 (4)
H12	−0.1779	0.3006	0.3929	0.042*
C13	0.1784 (2)	0.2042 (3)	0.53522 (8)	0.0369 (4)
C14	0.5253 (2)	0.6252 (3)	0.61718 (10)	0.0396 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.03601 (17)	0.03610 (18)	0.02273 (15)	−0.00921 (8)	−0.00184 (10)	−0.00184 (7)
O1	0.0603 (9)	0.0532 (9)	0.0253 (6)	−0.0211 (7)	−0.0086 (6)	0.0083 (6)
O2	0.0639 (10)	0.1105 (17)	0.0313 (7)	−0.0030 (10)	−0.0079 (7)	−0.0060 (9)
N1	0.0361 (7)	0.0323 (8)	0.0282 (7)	−0.0055 (6)	0.0017 (6)	−0.0025 (6)
N2	0.0310 (7)	0.0321 (7)	0.0227 (6)	−0.0053 (6)	0.0020 (5)	−0.0012 (5)
N3	0.0399 (7)	0.0341 (8)	0.0250 (6)	−0.0089 (6)	0.0013 (6)	0.0017 (6)
N4	0.0713 (13)	0.0508 (11)	0.0329 (9)	−0.0212 (10)	−0.0060 (8)	0.0121 (8)
N5	0.0370 (8)	0.0480 (10)	0.0316 (8)	−0.0072 (7)	0.0011 (6)	−0.0007 (7)
C1	0.0503 (11)	0.0374 (10)	0.0396 (10)	−0.0124 (8)	0.0041 (8)	−0.0064 (8)
C2	0.0609 (13)	0.0314 (9)	0.0536 (13)	−0.0093 (10)	0.0149 (10)	0.0014 (9)
C3	0.0528 (11)	0.0375 (11)	0.0452 (11)	0.0039 (9)	0.0104 (9)	0.0092 (9)
C4	0.0400 (9)	0.0381 (10)	0.0358 (9)	0.0018 (8)	−0.0002 (7)	0.0037 (8)
C5	0.0295 (7)	0.0314 (9)	0.0288 (7)	−0.0007 (6)	0.0034 (6)	−0.0017 (6)
C6	0.0270 (7)	0.0332 (8)	0.0261 (8)	−0.0013 (7)	0.0014 (6)	−0.0013 (7)
C7	0.0296 (7)	0.0297 (8)	0.0273 (7)	−0.0003 (6)	−0.0041 (6)	0.0010 (6)
C8	0.0344 (9)	0.0473 (11)	0.0295 (8)	−0.0053 (8)	0.0008 (7)	−0.0012 (8)
C9	0.0500 (11)	0.0512 (12)	0.0285 (8)	0.0002 (9)	−0.0031 (8)	−0.0051 (8)
C10	0.0465 (11)	0.0454 (12)	0.0396 (10)	−0.0040 (9)	−0.0142 (8)	−0.0070 (8)
C11	0.0317 (9)	0.0455 (11)	0.0515 (11)	−0.0083 (8)	−0.0062 (8)	0.0002 (9)
C12	0.0309 (8)	0.0368 (10)	0.0368 (9)	−0.0022 (7)	0.0013 (7)	0.0002 (7)
C13	0.0456 (10)	0.0403 (10)	0.0247 (8)	−0.0078 (8)	0.0039 (7)	0.0023 (7)
C14	0.0350 (9)	0.0442 (11)	0.0398 (10)	−0.0061 (8)	0.0060 (7)	−0.0032 (8)

Geometric parameters (Å, º)

Cu1—O1	1.9335 (14)	C2—H2	0.9300
Cu1—N2	1.9404 (14)	C3—C4	1.379 (3)
Cu1—N5	1.9618 (16)	C3—H3	0.9300
Cu1—N1	1.9790 (15)	C4—C5	1.385 (2)
Cu1—N5^{i}	2.6225 (17)	C4—H4	0.9300
O1—C13	1.272 (2)	C5—C6	1.475 (2)
O2—C14	1.188 (2)	C6—C7	1.475 (2)
N1—C1	1.324 (2)	C7—C8	1.388 (2)
N1—C5	1.349 (2)	C7—C12	1.388 (2)
N2—C6	1.293 (2)	C8—C9	1.382 (3)
N2—N3	1.354 (2)	C8—H8	0.9300
N3—C13	1.355 (2)	C9—C10	1.372 (3)
N4—C13	1.331 (3)	C9—H9	0.9300
N4—H41	0.876 (10)	C10—C11	1.372 (3)
N4—H42	0.869 (10)	C10—H10	0.9300
N5—C14	1.126 (2)	C11—C12	1.382 (3)
C1—C2	1.380 (3)	C11—H11	0.9300
C1—H1	0.9300	C12—H12	0.9300
C2—C3	1.368 (3)		

O1—Cu1—N2	79.99 (6)	C3—C4—C5	119.16 (18)
O1—Cu1—N5	99.25 (6)	C3—C4—H4	120.4
N2—Cu1—N5	177.52 (6)	C5—C4—H4	120.4
O1—Cu1—N1	159.83 (6)	N1—C5—C4	120.48 (17)
N2—Cu1—N1	81.22 (6)	N1—C5—C6	115.08 (15)
N5—Cu1—N1	99.23 (7)	C4—C5—C6	124.40 (16)
O1—Cu1—N5^{i}	99.82 (6)	N2—C6—C7	125.67 (17)
N2—Cu1—N5^{i}	95.41 (6)	N2—C6—C5	112.66 (15)
N5—Cu1—N5^{i}	87.05 (6)	C7—C6—C5	121.65 (15)
N1—Cu1—N5^{i}	89.15 (6)	C8—C7—C12	118.85 (16)
C13—O1—Cu1	110.84 (11)	C8—C7—C6	119.40 (16)
C1—N1—C5	119.97 (16)	C12—C7—C6	121.74 (16)
C1—N1—Cu1	127.54 (13)	C9—C8—C7	120.43 (18)
C5—N1—Cu1	112.47 (12)	C9—C8—H8	119.8
C6—N2—N3	125.23 (14)	C7—C8—H8	119.8
C6—N2—Cu1	116.88 (12)	C10—C9—C8	120.13 (19)
N3—N2—Cu1	117.03 (10)	C10—C9—H9	119.9
N2—N3—C13	106.76 (14)	C8—C9—H9	119.9
C13—N4—H41	124 (2)	C9—C10—C11	120.02 (17)
C13—N4—H42	121 (2)	C9—C10—H10	120.0
H41—N4—H42	114 (3)	C11—C10—H10	120.0
C14—N5—Cu1	137.89 (16)	C10—C11—C12	120.38 (18)
N1—C1—C2	121.99 (19)	C10—C11—H11	119.8
N1—C1—H1	119.0	C12—C11—H11	119.8
C2—C1—H1	119.0	C11—C12—C7	120.18 (18)
C3—C2—C1	118.8 (2)	C11—C12—H12	119.9
C3—C2—H2	120.6	C7—C12—H12	119.9
C1—C2—H2	120.6	O1—C13—N4	118.09 (17)
C2—C3—C4	119.53 (19)	O1—C13—N3	125.08 (17)
C2—C3—H3	120.2	N4—C13—N3	116.82 (17)
C4—C3—H3	120.2	N5—C14—O2	175.1 (2)

N2—Cu1—O1—C13	3.55 (14)	Cu1—N1—C5—C4	179.09 (14)
N5—Cu1—O1—C13	−178.85 (14)	C1—N1—C5—C6	−177.08 (16)
N1—Cu1—O1—C13	25.1 (3)	Cu1—N1—C5—C6	1.45 (19)
N5^{i}—Cu1—O1—C13	−90.27 (14)	C3—C4—C5—N1	−1.5 (3)
O1—Cu1—N1—C1	150.16 (19)	C3—C4—C5—C6	175.87 (18)
N2—Cu1—N1—C1	171.58 (18)	N3—N2—C6—C7	−4.9 (3)
N5—Cu1—N1—C1	−5.94 (18)	Cu1—N2—C6—C7	164.10 (13)
N5^{i}—Cu1—N1—C1	−92.81 (17)	N3—N2—C6—C5	176.72 (15)
O1—Cu1—N1—C5	−28.2 (3)	Cu1—N2—C6—C5	−14.28 (19)
N2—Cu1—N1—C5	−6.80 (12)	N1—C5—C6—N2	8.2 (2)
N5—Cu1—N1—C5	175.67 (12)	C4—C5—C6—N2	−169.37 (17)
N5^{i}—Cu1—N1—C5	88.80 (12)	N1—C5—C6—C7	−170.28 (15)
O1—Cu1—N2—C6	−175.17 (14)	C4—C5—C6—C7	12.2 (3)
N1—Cu1—N2—C6	12.18 (13)	N2—C6—C7—C8	−126.9 (2)
N5^{i}—Cu1—N2—C6	−76.12 (14)	C5—C6—C7—C8	51.4 (2)
O1—Cu1—N2—N3	−5.25 (12)	N2—C6—C7—C12	51.9 (3)

N1—Cu1—N2—N3	−177.90 (13)	C5—C6—C7—C12	−129.86 (18)
N5^{i}—Cu1—N2—N3	93.80 (12)	C12—C7—C8—C9	−0.8 (3)
C6—N2—N3—C13	174.42 (17)	C6—C7—C8—C9	178.00 (19)
Cu1—N2—N3—C13	5.43 (18)	C7—C8—C9—C10	0.5 (3)
O1—Cu1—N5—C14	−22.4 (3)	C8—C9—C10—C11	0.4 (3)
N1—Cu1—N5—C14	149.4 (2)	C9—C10—C11—C12	−1.0 (3)
N5^{i}—Cu1—N5—C14	−121.9 (3)	C10—C11—C12—C7	0.8 (3)
C5—N1—C1—C2	0.7 (3)	C8—C7—C12—C11	0.2 (3)
Cu1—N1—C1—C2	−177.57 (16)	C6—C7—C12—C11	−178.62 (18)
N1—C1—C2—C3	−1.0 (3)	Cu1—O1—C13—N4	176.97 (17)
C1—C2—C3—C4	0.0 (3)	Cu1—O1—C13—N3	−1.7 (3)
C2—C3—C4—C5	1.3 (3)	N2—N3—C13—O1	−2.4 (3)
C1—N1—C5—C4	0.6 (3)	N2—N3—C13—N4	178.93 (19)

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H41···N3^{ii}	0.88 (1)	2.27 (1)	3.139 (2)	173 (3)

Symmetry code: (ii) −*x*, −*y*, −*z*+1.