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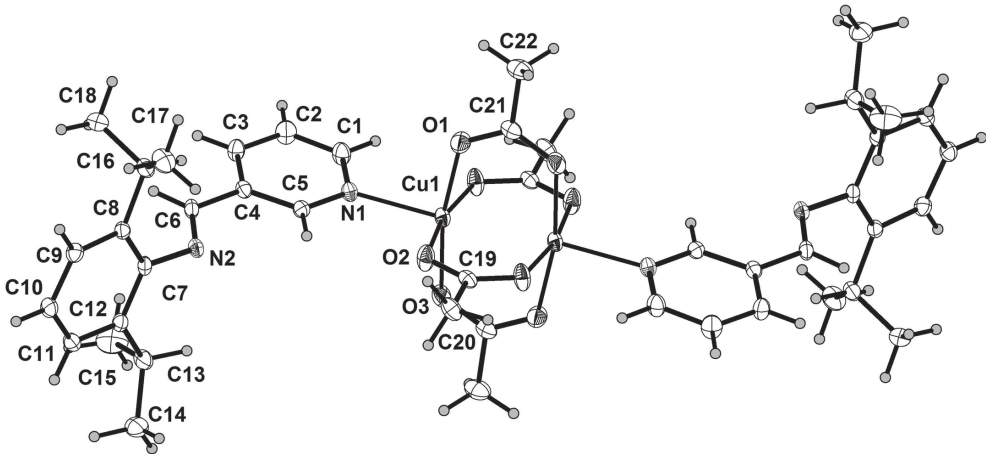
Crystal structure of tetrakis(μ_2-acetato-κ^2*O*:*O*′)-bis{[(*E*)-2,6-diisopropyl-*N*-(pyridin-3-ylmethylene)aniline]copper (II)}, $C_{44}H_{56}Cu_2N_4O_8$



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Abstract

$C_{44}H_{56}Cu_2N_4O_8$, monoclinic, $P2_1/c$ (no. 14), $a = 11.1061(10)$ Å, $b = 20.5117(17)$ Å, $c = 9.8185(9)$ Å, $\beta = 101.302(2)°$, $V = 2193.27(15)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0283$, $wR_{ref}(F^2) = 0.0753$, $T = 100$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Block, blue
Size:	0.32 × 0.25 × 0.18 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	1.02 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω-scans (0.5° scan width)
$2\theta_{max}$, completeness:	28.7°, >98%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	25678, 5527, 0.032
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4676
$N(param)_{refined}$:	264
Programs:	Bruker programs [1], SHELX [2], WinGX and ORTEP [3]

Source of material

The title compound was prepared though reaction of copper(II) acetate monohydrate (0.4045 g, 2 mmol) and (*E*)-2,6-diisopropyl-*N*-(pyridin-3-ylmethylene)aniline (0.5348 g, 2 mmol) in ethanol for 12 h. A sky blue precipitate was obtained that was disolved in dichloromethane and layered with hexane to give crystals. Yield 0.7556 g 84%.

Experimental details

All hydrogen atoms were placed in idealized positions and refined in riding models with U_{iso} assigned the values of 1.2 times those of their parent atoms and the distances of C—H were constrained to 0.93 Å for all the aromatic H atoms, 0.96 Å for methyl hydrogens and 0.98 Å for methine hydrogen.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
C1	0.42735(14)	0.84025(8)	0.25417(17)	0.0194(3)
H1	0.3612	0.8704	0.2441	0.023*
C2	0.42480(15)	0.78620(8)	0.33738(18)	0.0221(3)
H2	0.3578	0.7793	0.3828	0.027*
C3	0.52134(14)	0.74203(8)	0.35381(16)	0.0181(3)
H3	0.5216	0.7046	0.4109	0.022*
C4	0.61768(13)	0.75361(7)	0.28516(15)	0.0135(3)
C5	0.61223(13)	0.80931(7)	0.20224(15)	0.0135(3)
H5	0.6775	0.8172	0.1547	0.016*
C6	0.72206(13)	0.70754(7)	0.30142(15)	0.0148(3)
H6	0.7263	0.6727	0.3659	0.018*
C7	0.90572(13)	0.66830(7)	0.24978(15)	0.0136(3)
C8	1.00373(13)	0.67256(7)	0.36445(15)	0.0140(3)
C9	1.10227(14)	0.62954(8)	0.36973(15)	0.0159(3)
H9	1.1700	0.6322	0.4454	0.019*
C10	1.10367(14)	0.58314(8)	0.26750(16)	0.0171(3)
H10	1.1707	0.5537	0.2744	0.021*
C11	1.00621(14)	0.57998(8)	0.15483(16)	0.0170(3)
H11	1.0073	0.5482	0.0847	0.020*
C12	0.90718(13)	0.62247(7)	0.14292(15)	0.0145(3)
C13	0.79870(14)	0.61684(8)	0.02196(16)	0.0201(3)
H13	0.7617	0.6612	0.0037	0.024*
C14	0.83619(17)	0.59318(10)	−0.11184(17)	0.0272(4)
H14A	0.7633	0.5904	−0.1862	0.041*
H14B	0.8949	0.6240	−0.1387	0.041*
H14C	0.8744	0.5501	−0.0962	0.041*
C15	0.70070(17)	0.57193(11)	0.0607(2)	0.0331(4)
H15A	0.6313	0.5687	−0.0179	0.050*
H15B	0.7358	0.5285	0.0834	0.050*
H15C	0.6722	0.5898	0.1414	0.050*
C16	1.00516(14)	0.71915(8)	0.48554(16)	0.0167(3)
H16	0.9325	0.7487	0.4615	0.020*
C17	1.12142(15)	0.76140(9)	0.51546(18)	0.0246(4)
H17A	1.1181	0.7904	0.5939	0.037*
H17B	1.1939	0.7332	0.5384	0.037*
H17C	1.1266	0.7875	0.4332	0.037*
C18	0.99229(17)	0.67992(9)	0.61509(17)	0.0243(3)
H18A	0.9932	0.7097	0.6933	0.036*
H18B	0.9146	0.6558	0.5967	0.036*
H18C	1.0608	0.6492	0.6380	0.036*
C19	0.71767(13)	0.98619(7)	−0.03791(15)	0.0146(3)
C20	0.84622(14)	0.98026(8)	−0.06287(18)	0.0203(3)
H20A	0.8688	1.0205	−0.1057	0.030*
H20B	0.8510	0.9434	−0.1250	0.030*
H20C	0.9029	0.9731	0.0258	0.030*
C21	0.57472(13)	1.06026(8)	0.22624(16)	0.0169(3)
C22	0.61568(16)	1.09716(9)	0.36129(17)	0.0257(4)
H22A	0.6237	1.0668	0.4395	0.039*
H22B	0.5547	1.1306	0.3702	0.039*
H22C	0.6951	1.1180	0.3613	0.039*
N1	0.51943(11)	0.85205(6)	0.18668(13)	0.0145(2)
N2	0.80586(11)	0.71351(6)	0.23143(13)	0.0148(3)
O1	0.56977(11)	0.99928(6)	0.23156(11)	0.0228(3)
O2	0.67803(10)	0.94048(6)	0.02725(13)	0.0231(3)
O3	0.45062(12)	0.90597(6)	−0.11736(12)	0.0265(3)
O4	0.34195(10)	0.96346(6)	0.08361(13)	0.0216(2)
Cu1	0.51172(2)	0.94417(2)	0.06731(2)	0.01267(6)

Discussion

The title compound is a discrete complex bearing the centrosymmetric dinuclear copper(II) paddle wheel unit where four acetate ligands bridge the copper(II) ions. The axial positions are occupied by a N atom of (*E*)-2,6-diisopropyl-*N*-(pyridin-3-ylmethylene)aniline ligand, as shown in the figure. This paddle wheel has been previously reported in copper(II) acetate complexes [4, 5]. The distance between the bridged copper(II) ions is 2.6317(4) Å, typically for dimeric copper(II) carboxylates [6]. The copper(II) ions are slightly displaced from the basal plane of the four acetate O atoms by a distance of 0.198 Å towards the pyridine nitrogen, a trend that has also been reported [7]. The copper(II) ions are thus in a distorted square bipyramidal geometrical environment courtesy of the aforementioned coordination [8]. The asymmetric unit of the title compound bears half of the complex, i.e. one copper(II) ion, one (*E*)-2,6-diisopropyl-*N*-(pyridin-3-ylmethylene)aniline ligand and two acetate groups, the other half of the molecule is generated by $-x+1$, $-y+2$, $-z$ symmetry. The phenyl and pyridyl rings are not coplanar and the angle between the mean planes of the phenyl ring including the imine N atom to that of the pyridyl ring including the imine C atom is 82.00(4)°. This angle is clearly larger than that reported for the free ligand, i.e. 60.00° [9]. The azomethine (C=N) bond length in the complex is 1.267(2) Å, similar to the one in the ligand 1.270(1) Å [9]. The two C—N bonds in the pyridyl moiety of the complex are 1.35 and 1.34 Å, slightly longer than their equivalent bonds in the pyridyl moiety of the free ligand [9]. The N(1)—Cu(1), O(1)—Cu(1) and O(2)—Cu(1) bond distances are 2.2162(13), 1.9716(11) and 1.9639(11) Å, respectively, which are similar to those of previously reported copper(II) complexes [10, 11].

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