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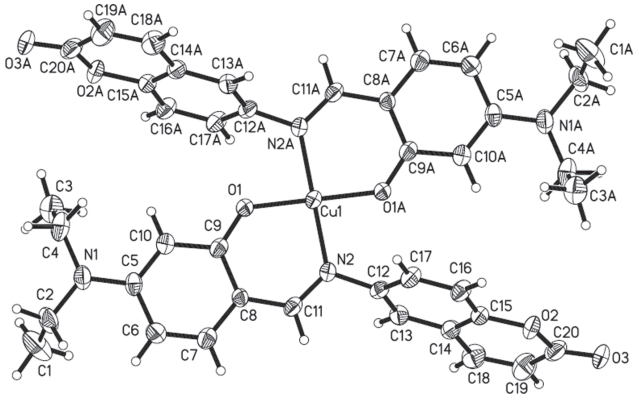
Crystal structure of bis{5-(diethylamino)-2-(((2-oxo-2H-chromen-6-yl)imino)methyl) phenolato-κ²*O*,*N*}copper(II), $C_{40}H_{38}CuN_4O_6$



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Abstract

$C_{40}H_{38}CuN_4O_6$, monoclinic, $P2_1/c$ (no. 14), $a = 10.590(4)$ Å, $b = 7.273(3)$ Å, $c = 23.345(9)$ Å, $\beta = 102.347(7)°$, $Z = 2$, $V = 1756.5(12)$ Å^3, $R_{gt}(F) = 0.0682$, $wR_{ref}(F^2) = 0.2373$, $T = 296$ 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:	Dark brown, block
Size:	0.28 × 0.26 × 0.22 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.676 mm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ and ω-scans
$2\theta_{max}$, completeness:	25°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	9830, 3074, 0.080
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1808
$N(param)_{refined}$:	234
Programs:	Bruker programs [1], SHELX [2]

Synthesis of the ligand

The ligand was synthesized according to an analogous method reported previously in the literature [3–6]. To an ethanol solution 5 mL) of 4-(diethylamino)-2-hydroxybenzaldehyde (193.3 mg, 1 mmol) was added an ethanol solution (5 mL) of 6-amino-2*H*-chromen-2-one (161.2 mg, 1 mmol). The solution was stirred under reflux at 328 K for 8 h, after cooling to room temperature. The precipitate was filtered and washed with ethanol and hexane. The product was dried under vacuum to get a yellow solid (yield 72.5%, m.p. 428–429 K). Elemental analysis-Anal. Calcd. for $C_{20}H_{20}N_2O_3$ (%): C, 71.41; H, 5.99; N, 8.33. Found (%): C, 73.47; H, 5.23; N, 8.85.

Synthesis of the title Cu(II) complex

An ethanol solution (4 mL) of copper acetate monohydrate (12.3 mg, 0.05 mmol) was added dropwise to a solution of ligand (6.0 mg, 20 mmol) in ethanol (5 mL) at room temperature. Immediately, the color of the solution turned brown, and the solution was stirred for 0.5 h. The mixture was filtered and the filtrate was allowed to stand at room temperature for about 4 weeks, several clear light red block-like single crystals. Elemental analysis-Anal. calcd. for $C_{40}H_{38}CuN_4O_6$ (%): C, 65.43; H, 5.22; N, 7.63. Found: C, 66.12; H, 5.58; N, 7.57.

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

Discussion

Schiff base and its derivatives (contain–C = N–group) have been studied extensively as a class of ligands [7–11] and are known to coordinate with metal ions through the azomethine nitrogen atom [12–15]. The presence of –C = N– along with other functional groups form more stable complexes compared to compounds with only –C = N– coordinating moiety [16–19]. Furthermore, chelating ability of coumarin derivatives has been studied to suggest their use as chelating agents

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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	0.8167(9)	−0.2655(13)	0.7506(4)	0.104(3)
H1A	0.7689	−0.3709	0.7332	0.156*
H1B	0.8829	−0.3038	0.7832	0.156*
H1C	0.8557	−0.2057	0.7220	0.156*
C2	0.7267(8)	−0.1337(11)	0.7715(3)	0.070(2)
H2A	0.6845	−0.1976	0.7987	0.085*
H2B	0.7774	−0.0346	0.7928	0.085*
C3	0.4862(8)	−0.2856(12)	0.6663(3)	0.081(2)
H3A	0.5104	−0.2363	0.6320	0.122*
H3B	0.3977	−0.3251	0.6564	0.122*
H3C	0.5407	−0.3885	0.6806	0.122*
C4	0.5011(8)	−0.1443(11)	0.7116(3)	0.069(2)
H4A	0.4848	−0.1993	0.7472	0.083*
H4B	0.4359	−0.0506	0.6991	0.083*
C5	0.6570(6)	0.0829(9)	0.6900(3)	0.0449(15)
C6	0.7794(6)	0.1717(10)	0.7026(3)	0.0540(17)
H6	0.8425	0.1342	0.7346	0.065*
C7	0.8040(6)	0.3116(9)	0.6680(3)	0.0503(16)
H7	0.8847	0.3678	0.6773	0.060*
C8	0.7143(5)	0.3756(8)	0.6190(2)	0.0386(13)
C9	0.5907(6)	0.2875(8)	0.6043(3)	0.0436(15)
C10	0.5674(6)	0.1454(8)	0.6427(3)	0.0461(15)
H10	0.4858	0.0916	0.6353	0.055*
C11	0.7480(6)	0.5230(8)	0.5850(3)	0.0441(15)
H11	0.8299	0.5737	0.5973	0.053*
C12	0.7266(5)	0.7486(9)	0.5121(3)	0.0426(14)
C13	0.8158(6)	0.7274(9)	0.4790(3)	0.0494(16)
H13	0.8478	0.6108	0.4739	0.059*
C14	0.8608(6)	0.8806(10)	0.4520(2)	0.0463(15)
C15	0.8064(6)	1.0522(9)	0.4604(3)	0.0492(17)
C16	0.7184(6)	1.0759(10)	0.4929(3)	0.0517(16)
H16	0.6857	1.1921	0.4979	0.062*
C17	0.6771(6)	0.9237(10)	0.5189(3)	0.0529(16)
H17	0.6150	0.9377	0.5414	0.064*
C18	0.9535(7)	0.8724(12)	0.4180(3)	0.067(2)
H18	0.9936	0.7606	0.4143	0.080*
C19	0.9877(8)	1.0228(12)	0.3899(3)	0.076(2)
H19	1.0485	1.0123	0.3667	0.091*
C20	0.9279(7)	1.2015(12)	0.3966(3)	0.066(2)
Cu1	0.5000	0.5000	0.5000	0.0395(4)
N1	0.6286(6)	−0.0552(8)	0.7253(2)	0.0573(15)
N2	0.6733(4)	0.5941(7)	0.5378(2)	0.0417(12)
O1	0.5005(4)	0.3319(6)	0.56031(18)	0.0549(12)
O2	0.8436(4)	1.2088(6)	0.4331(2)	0.0653(14)
O3	0.9490(5)	1.3399(8)	0.3717(2)	0.0887(19)

[a]Occupancy: 0.854(7).

[20]. So, a series of coumarin-derived Schiff bases and their complexes have a significant position in the field of modern coordination chemistry.

The crystal structure is only built up by $C_{40}H_{38}CuN_4O_6$. The Cu(II) center is four-coordinated by two N and two O atoms. The coordination geometry of the Cu(II) center can be described as square planar. The crystal structure of the Cu(II) complex is linked by C11–H11$\cdots$O3 and C16–H16$\cdots\pi_{centroid(chelate\ ring)}$ hydrogen bonds into an infinite 2D layer supramolecular structure. This linkage is further stabilized by five $\pi\cdots\pi$ stacking interactions ($\pi_{centroid(O2,C14,C15,C18–C20)}\cdots\pi_{centroid(O2,C14,C15,C18–C20)}$, $\pi_{centroid(O2,C14,C15,C18–C20)}\cdots\pi_{centroid(C12–C17)}$, $\pi_{centroid(O2,C14,C15,C18–C20)}$ $\pi_{centroid(O2,C12–C18)}$, $\pi_{centroid(C12–C17)}\cdots\pi_{centroid(O2,C12–C18)}$, and $\pi_{centroid(O2,C12–C18)}\cdots\pi_{centroid(O2,C12–C18)}$) of between the benzene (or aromatic) rings of the adjacent Cu(II) complex molecules with the centroid-centroid distances of 3.557(4)–4.272(4) Å to form a 3D supramolecular networks structure.

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