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Instrumental Achievements

Crystal Structure of (2,2′-Dipyridyl)-(2-hydroxynaphthaldehydato)copper(II) Perchlorate

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Because of their preparative accessibility and structural variability, a great number of Schiff base complexes of copper have been subjected to extensive studies. In comparison with organic molecules, metal complexes offer a wider variety of structures, with comparable or, in some cases, higher environmental stability and a much greater diversity of tunable electronic properties, as a result of the coordinated metal center.[1] We report here the results of the reaction of copper(II) with the ligand 2-hydroxynaphthalene-1-carbaldehyde and 2,2′-dipyridyl, to form a monomeric five-coordinated copper(II) complex (Fig. 1).

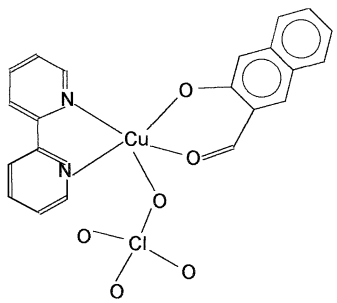

Fig. 1 Structural chemical diagram.

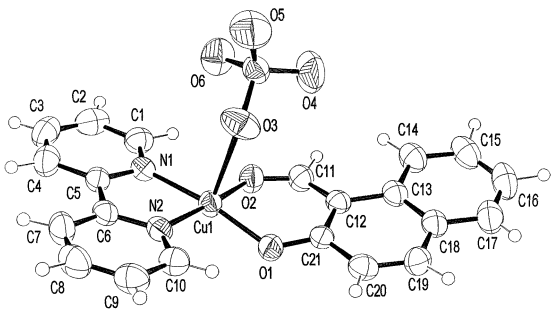

Fig. 2 The molecular structure of the title compound, showing the atom labeling scheme and 50% probability level displacement ellipsoids.

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The X-ray diffraction data were collected by a graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). The crystal structure was solved by direct methods.[2] All the non-hydrogen atoms were refined anisotropically. H atoms bonded to C atoms were refined using a riding model (C–H = 0.93 Å) and H atom displacement parameters were restricted to be 1.2 U_{eq} of the parent atom. Table 1 shows the crystal and experimental data, while final atomic parameters are given in Table 2. The bond distances and angles are shown in Table 3.

The Cu(II) atom adopts a (4+1) distorted square-pyramidal geometry, with two donor O atoms of the naphthaldehyde ligand and two N atoms of 2,2′-dipyridyl ligand in the basal plane. The Cu–N and Cu–O distances are quite normal. Examination of the main metal-ligand distances shows that the Cu–N distances are longer than the Cu–O distances, as observed in the title complex and in many salicylaldehydate complexes.[3] The apical coordination site is occupied by the O3 atom of perchlorate, with a Cu1–O3 distance of 2.504(4)Å. The apical distance is the most variable in this class of complex. For example, the distance from the metal to the apical O atom from the nitrate ion is [2.239(2)Å],[3] while it is 2.496(3)Å for the unsubstituted phenanthroline.[4]

The angle between the two least square planes of the planar ligands is inclined at 15.32(14)°. The angle between the planes

Table 1 Crystal and experimental data

Formula: $C_{21}H_{15}ClCuN_3O_5$	
Formula weight: 488.35	
Crystal system: triclinic	
Space group: $P\bar{1}$	Z = 2
a = 9.255(2)Å	α = 85.18(1)°
b = 9.939(1)Å	β = 82.43(1)°
c = 10.774(1)Å	γ = 81.35(1)°
V = 969.2(2)Å^3	
D_x = 1.673 g/cm^3	
R = 0.062	wR = 0.145
$(\Delta/\sigma)_{max}$ = 0.001	
$(\Delta\rho)_{max}$ = 0.558 eÅ^{-3}	
$(\Delta\rho)_{min}$ = –0.470 eÅ^{-3}	
No. of reflections used = 3809	
Measurements: Enraf-Nonius CAD-4 diffractometer	
Program system: CAD-4 EXPRESS Software	
Structure determination: SHELXS-97	
Refinement: full-matrix least-squares (MolEN)	

Table 2 Final atomic coordinates and equivalent isotropic thermal parameters

Atom	*x*	*y*	*z*	B_{eq} (Å^2)
C1	0.3193(6)	-0.1565(5)	-0.2970(5)	4.16(4)
C2	0.3653(7)	-0.2561(6)	-0.3794(6)	5.03(2)
C3	0.2648(8)	-0.2988(6)	-0.4443(5)	5.00(2)
C4	0.1187(7)	-0.2375(5)	-0.4288(5)	4.65(2)
C5	0.0788(5)	-0.1352(4)	-0.3446(4)	3.32(2)
C6	-0.0707(5)	-0.0636(4)	-0.3191(4)	3.33(2)
C7	-0.1880(6)	-0.0841(6)	-0.3786(5)	4.47(2)
C8	-0.3223(6)	-0.0070(6)	-0.3498(5)	4.91(2)
C9	-0.3389(6)	0.0853(6)	-0.2614(5)	4.51(2)
C10	-0.2190(5)	0.1027(5)	-0.2021(5)	3.80(3)
C11	0.3039(5)	0.1315(5)	-0.0255(4)	3.67(3)
C12	0.2018(5)	0.2382(4)	0.0275(4)	3.14(3)
C13	0.2572(5)	0.3382(4)	0.0934(4)	3.53(2)
C14	0.4063(6)	0.3488(6)	0.0923(5)	4.50(4)
C15	0.4489(7)	0.4475(6)	0.1581(6)	5.14(2)
C16	0.3493(8)	0.5369(6)	0.2260(5)	5.31(2)
C17	0.2034(7)	0.5304(6)	0.2289(5)	4.90(2)
C18	0.1537(6)	0.4338(4)	0.1610(4)	3.66(2)
C19	0.0009(6)	0.4308(5)	0.1584(5)	4.13(3)
C20	-0.0492(6)	0.3416(5)	0.0920(5)	3.81(2)
C21	0.0497(5)	0.2428(4)	0.0250(4)	3.20(2)
N1	0.1791(4)	-0.0964(4)	-0.2793(3)	3.29(1)
N2	-0.0864(4)	0.0285(4)	-0.2310(3)	3.18(1)
O1	-0.0081(3)	0.1568(3)	-0.0308(3)	3.64(1)
O2	0.2783(4)	0.0404(3)	-0.0906(3)	3.92(1)
Cu1	0.09441(5)	0.041706(5)	-0.15580(5)	3.26(2)
O3	0.1343(4)	0.2431(4)	-0.3047(4)	5.62(2)
O4	0.3306(6)	0.3503(5)	-0.2732(5)	7.37(2)
O5	0.2441(7)	0.3688(5)	-0.4693(4)	7.54(2)
O6	0.3670(4)	0.1616(4)	-0.3969(4)	5.88(3)
Cl1	0.2700(1)	0.2844(1)	-0.3615(1)	3.74(3)

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.

formed by the metal and the coordinated atoms, Cu1/N1/N2 and Cu1/O1/O2, is 6.20(27)˚. The Cu1 atom is 0.048(1)Å above the best N_2O_2 plane. The bond distances and angles of 2,2′-dipyridyl molecule are quite normal. The 2,2′-dipyridyl molecule is nearly planar [the largest deviation of atoms from the mean plane is 0.042(5)˚].

Table 3 Bond distances (Å) and angles (˚)

N1 – Cu1	1.989(3)
N2 – Cu1	1.978(4)
O1 – Cu1	1.906(3)
O2 – Cu1	1.923(3)
O3 – Cu1	2.504(4)
O1 – Cu1 – O2	91.55(13)
O1 – Cu1 – N2	93.16(14)
O2 – Cu1 – N2	175.13(14)
O1 – Cu1 – N1	171.87(13)
O2 – Cu1 – N1	93.70(14)
N2 – Cu1 – N1	81.48(15)
O1 – Cu1 – O3	36.90(13)
O2 – Cu1 – O3	36.62(13)
N1 – Cu1 – O3	94.94(14)
N2 – Cu1 – O3	52.50(14)

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