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Anhydrous Bis-2,2′,*N*,*N*′-bipyridylaminechloro–Copper(II) Chloride

R. A. JACOBSON

Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011, U.S.A.

and W. P. JENSEN

Department of Chemistry, South Dakota State University, Brookings, S.D. 57007, U.S.A.

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A variety of five coordinate copper(II) complexes with rigid or semi-rigid bidentate ligands have been synthesized and structurally characterized using X-ray diffraction techniques [1–5]. The geometries of these complexes range from nearly trigonal bipyramidal to nearly square pyramidal. The flexibility of the amine group in bipyridylamine is illustrated by the different structures summarized in ref. 1 where the dihedral angle described by the two pyridyl groups in a ligand molecule range from 18.2 to ~41.5°. Differences between the title compound structure and that of bis-2,2′,*N*,*N*′-bipyridylamine copper(II) chloride tetrahydrate will be discussed.

Experimental

Dark green crystals of the compound were prepared by allowing the mixture of $CuCl_2 \cdot 6H_2O$ and dipyridylamine in acetonitrile to reflux for several hours, cooling the solution slowly, and allowing normal evaporation of some of the solvent in a container open to the atmosphere. A crystal of approximate dimensions 0.1 × 0.1 × 0.15 mm was chosen for the lattice constant determination and subsequent intensity measurements. The air stable crystal was mounted on a glass fiber with epoxy glue and oriented on a four-circle automated diffractometer using standard methods. The lattice constants obtained from eleven accurately centered high angle reflections are $a = 9.704(3)$, $b = 14.493(4)$, $c = 14.704(16)$ Å, and $\beta = 97.88(5)^\circ$. Monochromatic Mo Kα ($\lambda = 0.70954$ Å by graphite monochromator) radiation was used throughout the data collection procedure.

Intensity data (8422 reflections) were collected over a hemisphere of reciprocal space to a 2θ maximum of 50° and then averaged to yield 2287 unique data where $|F_o| > 3\sigma F_o$. Monoclinic symmetry was indicated by our automatic indexing routine [6], which was subsequently verified by oscillation photographs, and the space group was determined to be $P2_1/n$ via the extinctions $0k0$, $k \neq 2n$ and $h0l$, $h + l \neq 2n$. The standard deviation of a reflection was computed as follows:

$$\sigma_I = (C_T + k_T C_B + (0.03C_T)^2 + (0.03C_B)^2)^{1/2}$$

where C_T and C_B represent total and background counts and k_T is a counting time factor. The structure was solved and refined by normal Fourier and least-squares techniques. Atomic scattering factors terms were those of Cromer and Waber [7] (hydrogen terms were taken from those of Stewart, Davidson and Simpson [8]). Copper and chlorine terms were modified using real and imaginary correction terms [9]. Anisotropic thermal parameters were used for all non-hydrogen atoms. Final residuals from a full matrix least-squares cycle were $R_w = 0.074$ and $R = 0.064$ with the shift/error ratio for positional parameters below 0.1. Final non-hydrogen atom coordinates are given in Table I*.

TABLE I. Fractional Atomic Coordinates (×10^4) for Non-hydrogen Atoms

Atom	*x*	*y*	*z*
1 Cu	2324.3(9)	0800.3(7)	2598.0(6)
2 N1	0581(6)	0483(4)	3113(4)
3 C1	−0267(8)	1144(6)	3392(5)
4 C2	−1302(8)	0864(7)	3925(5)
5 C3	−1447(9)	−0040(8)	4158(5)
6 C4	−0588(10)	−0703(7)	3863(6)
7 C5	0394(9)	−0416(6)	3353(5)
8 N10	−0167(6)	2029(4)	3182(4)
9 C6	0331(7)	2435(5)	2420(5)
10 N2	1293(6)	2007(4)	2022(4)
11 N3	4126(6)	1095(5)	2156(4)
12 C11	4818(7)	0553(5)	1656(4)
13 N11	4266(6)	−0262(4)	1283(4)
14 C12	6159(7)	0776(6)	1472(5)
15 C13	6768(8)	1578(7)	1819(6)
16 C15	4735(8)	1897(6)	2494(5)
17 C11	3396(2)	0891(2)	4083(1)
18 C19	0234(8)	−1132(6)	0690(5)
19 C17	2638(8)	−1351(6)	0610(5)
20 C9	1172(8)	3247(6)	0934(5)
21 C10	1681(7)	2414(6)	1258(5)
22 C8	0194(8)	3694(6)	1362(6)
23 N4	1899(5)	−0104(4)	1490(4)
24 C7	−0260(8)	3278(6)	2115(5)
25 C14	6052(9)	2151(7)	2357(6)
26 C16	2908(7)	−0551(5)	1104(4)
27 C18	1305(8)	−1646(6)	0398(5)
28 C12	8498(2)	3440(2)	4424(2)
29 C20	0565(8)	−0390(6)	1241(5)

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*Further information is available, see 'Supplementary Material'.

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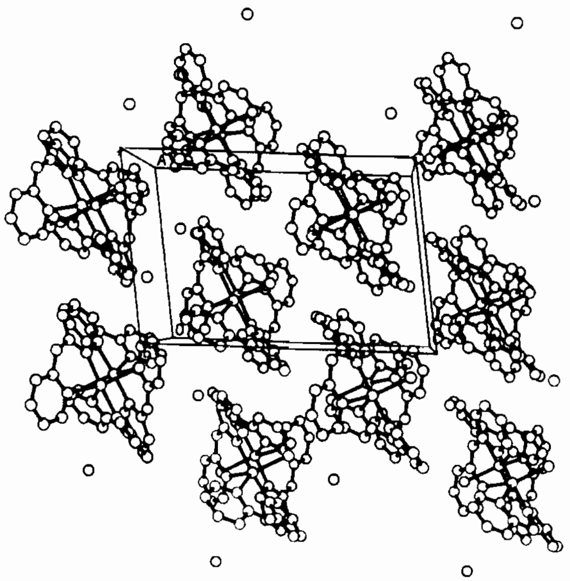

Fig. 1. The packing of [Cu(bpyamine)$_2$Cl]Cl.

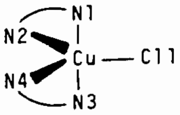

Fig. 2. The coordination of the Cu(II) ion.

Discussion

The coordination about the copper atom is that of a highly distorted trigonal bipyramid (Figs. 1 and 2). Pertinent bond distances and angles are given in Table II along with those of the tetrahydrate salt.

As can be seen from Table II, the most striking differences between the anhydrous complex (this work) and the tetrahydrate complex are observed in the equatorial plane angles (e.g., Cl1–Cu–N4, 142.7 *vs.* 159.0°) representing different degrees of distortion from a regular trigonal bipyramid and in the twist angles of the ligands as observed in the intraligand pyridyl ring dihedral angles. These differences must arise from different packing arrangements of the two compounds.

Supplementary Material

Hydrogen atom coordinates and anisotropic thermal parameters are available from the authors on request.

TABLE II. Selected Distances (Å) and Angles (°)

	[Cu(bpyamine)$_2$Cl]Cl	[Cu(bpyamine)$_2$Cl]Cl·4H$_2$O^a
Cu–N1	1.999(6)	2.004(6)
Cu–N2	2.133(6)	2.172(6)
Cu–N3	1.994(6)	2.001(6)
Cu–N4	2.088(6)	2.028(6)
Cu–Cl1	2.290(3)	2.334(4)
Cu–N10	3.213(6)	
Cu–N11	3.263(6)	
N2–Cu–Cl1	117.3(2)	104.4(2)
N2–Cu–N4	99.9(2)	97.5(2)
Cl1–Cu–N4	142.7(2)	158.0(2)
N1–Cu–N2	87.9(2)	87.2(2)
N1–Cu–Cl1	87.1(2)	88.5(2)
N1–Cu–N4	93.7(2)	91.7(2)
N3–Cu–Cl1	89.7(2)	90.5(2)
N3–Cu–N2	94.6(3)	99.7(2)
N1–Cu–N3	176.6(2)	173.0(2)
Intraligand pyridyl angles	25.2, 18.2	23.0, 37.5

^{a}Atoms relabeled.

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