Inorganica Chimica Acta, 52 (1981) 205–209
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The Crystal and Molecular Structure of Bis-aqua-2,2′,N,N′bipyridylamine Fluoro Copper(+1) Fluoride Trihydrate

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Received April 9, 1981

The crystal and molecular structure of $[Cu(H_2O)_2(bpyamine)F]F\cdot 3H_2O$ *has been determined by three-dimensional X-ray analysis and refined by least-squares methods to conventional residuals of* $R = 0.049$ *and* $R_w = 0.067$. *The lattice parameters are* a = 12.879(4), b = 6.954(4), c = 17.360(7) Å *and* $\beta = 98.06°$. *The space group is* $P2_1/n$ *with four molecular units per unit cell. A total of 2171 unique data with* $|F_o| \geq 3\sigma_F$ *were used in the structure determination. The copper ion is pentacoordinate with an oxygen atom from a water molecule, a fluoride ion and two nitrogen atoms from a bipyridylamine molecule occupying the equatorial positions of a square pyramid and an oxygen atom from a second water molecule occupying the apicial position.*

Introduction

The use of rigid or semirigid ligand molecules to stabilize the five coordinate state of copper(II) has been given a great deal of attention recently [1–6]. The ligands 2,2′bipyridine and 2,2′bipyridylamine have been successfully used to prepare a number of five coordinate complexes that are used to model intermediates in substitution reactions in which four coordinate complexes are allowed to react with ligands. The resulting five coordinate intermediates are frozen out as the result of favorable energetics of the coordination number five state of copper(II). Various halide and pseudohalide complexes have been investigated by crystallographic techniques. These complexes generally exist in the solid state as intermediate distortions between the ideal trigonal bipyramidal geometry type and the square pyramidal geometry type. This work focuses on the type of five coordinate complex formed when the fluoride ion is present along with a bipyridylamine ligand.

Experimental

Synthesis

Reagent grade copper(II) fluoride (Alpha Chemical Co.) was allowed to react with a 2:1 stoichiometric amount of bipyridylamine (Aldrich Chemical Co.) in water in a teflon beaker. Upon slow evaporation of the solvent dark green needle crystals formed which were used without further treatment. Chemical analysis for copper and fluorine gave a mol ratio of 1:2, consistent with the formulation of $Cu(bpyamine)F_2(H_2O)_5$.

Structure Solution

The crystal chosen for lattice constant determination and intensity measurements was a piece of approximate dimensions of 0.15 X 0.15 X 0.20 mm cut from a needle crystal. The crystal which was air stable for a short period of time was mounted on a glass fiber with epoxy glue and oriented on a four-circle automated diffractometer. Oscillation photographs coupled with an automatic indexing procedure [7] indicated monoclinic symmetry and the intensity data were consistent with the space group $P2_1/n$. Lattice constants obtained from the settings of twelve accurately centered reflections with 2θ angles between 30–39° are $a = 12.879(4)$, $b = 6.954(4)$, $c = 17.360(7)$ Å, and $\beta = 98.06(5)°$. Monochromated molybdenum K_α radiation was used throughout all phases of the data collection procedure ($\lambda = 0.71022$ Å). Intensity data were collected at ambient temperatures to a 2θ maximum of 50°. The data that satisfied the condition $|F_o| > 3\sigma_F$ were considered observed and the data were averaged to yield 2171 unique data. Lorentz and polarization effects were corrected for in the data reduction process. The effects of absorption were assumed to be negligible ($\mu = 15.2$ cm^{-1}). The standard deviation of a reflection was computed according to

$$\sigma_I = C_T + K_T C_B + (0.03C_T)^2 + (0.03C_B)^2$$

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where C_T and C_B represent total and background counts, K_T is a counting time factor, and 0.03 represents an estimate of non-statistical errors.

The copper atom was located from a sharpened Patterson map and the remaining non-hydrogen atoms were located from subsequent electron density maps. Refinement was carried out using a block diagonal least-squares procedure [8]. Anisotropic thermal parameters were used for all the non-hydrogen atoms and the quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$. At this stage hydrogen atoms were included for the pyridyl rings assuming 1.07 Å C–H bond distances and 120° bond angles. The hydrogen atom positions were not refined. Atomic scattering factors along with anomalous dispersion corrections for copper were taken from the International Tables [9]. To complete the refinement several cycles of full-matrix least-squares refinement were completed. The final conventional and weighted crystallographic residuals R and R_w are 0.049 and 0.067, respectively. During the latter stages of refinement the multiplicity parameters, the thermal parameters, then both sets of parameters together were allowed to vary for the fluorine and oxygen atoms. The results substantiate the choices of oxygen atoms and fluorine atoms based on the relative electron densities for the atoms on earlier Fourier maps. For the final refinement the multiplicity parameters were fixed at 1.0.

Discussion

Atom positional parameters for the non-hydrogen atoms are given in Table I. The anisotropic thermal parameters and the positional parameters for the hydrogen atoms are given as supplementary material. Selected bond distances and angles for the complex are given in Table II. The $[Cu(bpyamine)(H_2O)_2F]^+$ cation is best described as a somewhat distorted square pyramid (Fig. 1) with two nitrogens from the bipyridylamine group, a water oxygen, and one fluoride ion forming the base and the oxygen atom from the second water molecule occupying the apical position. This oxygen atom is slightly tipped toward the oxygen atom of the water molecule in the basal plane and thus slightly away from the other three atoms making up this plane. The Cu–N and Cu–F are within the expected range of distances found in other similar complexes [1–6, 10]; the Cu–O (apical) bond distance of 2.218(4) Å (Table II) is slightly longer than the Cu–O (basal) bond distance of 1.984(4) Å but such axial elongation is common and both distances are also well within the expected range of distances [10–14]. The two Cu–N distances are identical to within 0.001 Å indicating that there is no appreciable *trans*-influence difference between the oxygen and fluorine coordinating atoms in this complex.

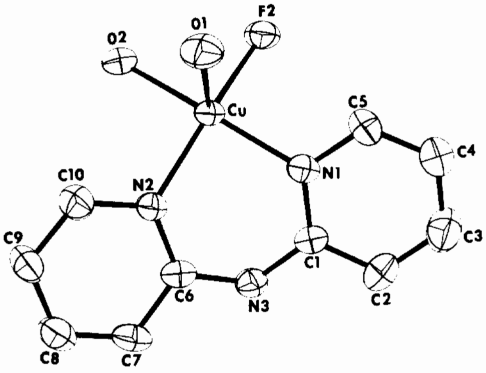

Fig. 1. Computer generated drawing of the title compound using 50% probability ellipsoids.

TABLE I. Atom Positional Parameters × 10^4.

Atom	x	y	z
Cu	1261.1(4)	655.0(9)	1081.2(3)
O1	410(3)	3162(6)	510(2)
O2	–101(2)	–625(5)	1145(2)
F1	88(2)	–4130(4)	1500(2)
F2	1277(2)	–689(4)	107(2)
N1	2703(3)	1629(6)	1042(2)
N2	1396(3)	1337(6)	2201(2)
N3	3253(3)	1112(6)	2384(2)
C1	3465(4)	1538(7)	1642(3)
C2	4513(4)	1842(9)	1546(3)
C3	4753(5)	2294(10)	813(4)
C4	3955(5)	2478(10)	203(3)
C5	2945(4)	2135(9)	329(3)
C6	2318(4)	1316(7)	2675(3)
C7	2351(4)	1507(8)	3486(3)
C8	1454(5)	1828(9)	3795(3)
C9	503(4)	1981(9)	3302(3)
C10	514(4)	1708(8)	2524(3)
O3	–1899(4)	–4629(7)	1713(3)
O4	–2626(3)	–7861(7)	822(3)
O5	–2037(4)	–6067(8)	3229(3)

The equatorial atoms O2–F2–N1–N2 are coplanar to within 0.08 Å as indicated in Table III. The copper atom almost resides in this plane, being displaced by only 0.194 Å toward the apical oxygen. As might be expected the plane described by Cu–O1 and N3 is essentially perpendicular to the basal plane, the dihedral angle being 91.1°. The dihedral angle between the two aromatic rings in the dipyridylamine ligand in various complexes has been reported [15]. The molecule is shown to be rather flexible and the angle varies from 9.8° to 41.41°. The dihedral angle for the aromatic rings in this structure (least squares planes 2 & 3, Table III) is 23.9°, close to the 23.0° angle reported for the trigonal bipyramidal complex $[Cu(bpyamine)_2Cl]Cl\cdot 4H_2O$. The four equatorial

TABLE II. Selected Distances and Interatomic Angles.

Distances

Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
Cu	O1	2.218(4)	C4	C5	1.369(8)
Cu	F2	1.934(3)	C1	N3	1.385(6)
Cu	O2	1.984(4)	N3	C6	1.377(6)
Cu	N1	1.986(4)	N2	C6	1.346(6)
Cu	N2	1.985(4)	N2	C10	1.361(6)
N1	C1	1.330(6)	C6	C7	1.409(7)
N1	C5	1.364(7)	C7	C8	1.360(8)
C1	C2	1.399(7)	C8	C9	1.397(8)
C2	C3	1.387(9)	C9	C10	1.366(8)
C3	C4	1.374(9)			

Interatomic Angles

Atom 1	Atom 2	Atom 3	Angle (°)	Atom 1	Atom 2	Atom 3	Angle (°)
O1	Cu	O2	89.6(2)	C1	C2	C3	119.1(5)
O1	Cu	F2	93.1(1)	C2	C3	C4	119.2(6)
O1	Cu	N1	97.0(2)	C3	C4	C5	119.1(6)
O1	Cu	N2	102.7(2)	C4	C5	N1	122.2(5)
F2	Cu	O2	87.1(1)	C1	N1	C5	119.1(4)
F2	Cu	N1	90.6(2)	C1	N3	C6	128.0(4)
F2	Cu	N2	164.0(2)	C2	C1	N3	117.6(4)
N1	Cu	N2	89.9(1)	N3	C6	C7	118.1(4)
N1	Cu	O2	173.1(2)	N3	C6	C7	118.1(4)
N2	Cu	O2	90.6(2)	C6	N2	C10	117.8(4)
Cu	N1	C1	123.2(3)	N2	C6	C7	120.7(4)
Cu	N1	C5	116.9(3)	C6	C7	C8	120.1(5)
Cu	N2	C6	123.0(3)	C7	C8	C9	119.4(5)
Cu	N2	C10	119.0(3)	C8	C9	C10	117.8(5)
N1	C1	N3	121.2(4)	N2	C10	C9	124.0(5)
N1	C1	C2	121.2(5)				

TABLE III. Least Square Planes.

Plane 1 (plane determined by atoms O2, F2, N1 & N2)

$$-0.3854X + 0.84687Y - 0.36838Z + 1.01483 = 0$$

Atom	Distance from LS plane (Å)
O2	0.078
F2	-0.080
N1	0.076
N2	-0.076
Cu	0.194

Plane 2 (plane determined by atoms N1, C1–C5)

$$-0.13509X + 0.96958Y + 0.20414Z - 1.04801 = 0$$

Atom	Distance from LS plane (Å)
N1	-0.020
C1	0.016
C2	0.002
C3	-0.016
C4	0.013
C5	0.005

Plane 3 (plane determined by atoms N2, C6–C10)

$$0.14137X + 0.98453Y - 0.10352Z - 0.72679 = 0$$

Atom	Distance from LS plane (Å)
N2	-0.025
C6	0.028
C7	-0.007
C8	-0.016
C9	0.020
C10	0.000

ligand atoms F_2, O_2, N_1 and N_2 are nearly coplanar (see least squares plane 1, Table III), again indicating that this structure is closer to the idealized C_{4v} symmetry type than to the idealized D_{3h} symmetry type typical of so many amine halide structures.

While the $Cu(LL)_2X$ structures [15] where LL represent a bidentate nitrogen-containing ligand generally demonstrate coordination polyhedra that are closer to an idealized trigonal bipyramid, the present structure is clearly closer to the idealized

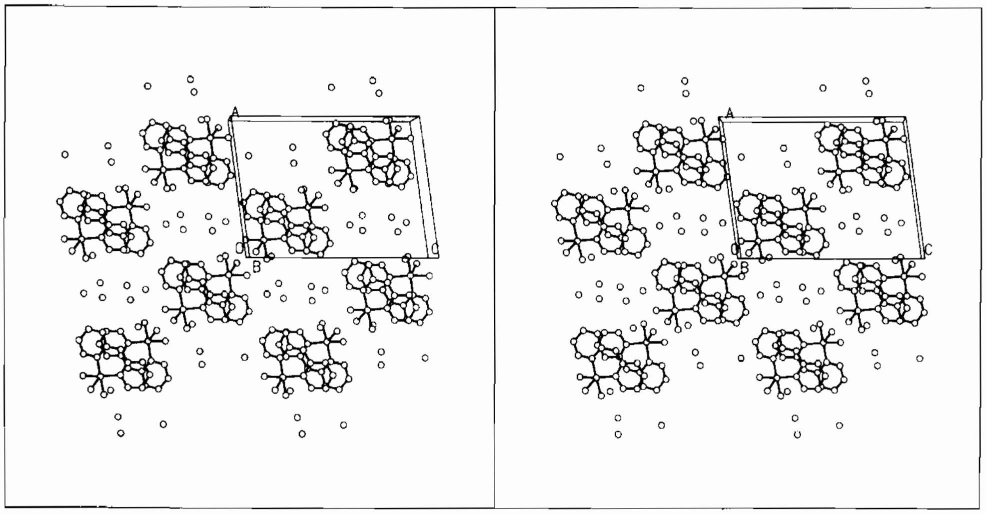

Fig. 2. A stereoscopic view of the unit cell.

TABLE IV. Probable Hydrogen Bonding Interactions.

Atoms	Distances
$O1_1$*–F1	2.621 Å
O2–F1	2.517
O3–F1	2.659
O3–O4	2.813
O3–O5	2.844
$O3–O5_2$	2.839
$O4–O5_3$	2.841
Related angles	
O4–O3–F1	106.3°
O5–O3–F1	111.1
O5′–O3–F1	111.7
O4–O3–O5	99.7
O4–O3–O5′	126.3
O5–O3–O5′	100.4
O3–O4–O5′	112.0
O3–O5–O4	123.4
O3–O5–O3′	115.6
O4–O5–O3	107.2
O1–F1–O2	123.6
O2–F1–O3	104.0
Cu–O2–F1	112.9
Cu–O1–F1	113.1

*Subscripts indicate symmetry operation: 1 = (x, y − 1, z); 2 = (−1/2 − x, 1/2 + y, 1/2 − z); 3 = (−1/2 − x, −1/2 + y, 1/2 − z).

square pyramid configuration. It is not possible to say whether this difference is due to the fact that only one bidentate ligand is present in the complex, or due to some inherent difference related to the effect of the fluoride ion. We are currently attempting to obtain structural data on other fluoride-containing complexes to help resolve this question.

The crystal packing of this compound is also of interest. As is shown in Fig. 2, the cations pack in planes containing the *ac* cell diagonal and the *b* cell axis. Although the hydrogen atoms associated with the water molecules could not be located with any certainty, examination of the pertinent distances (Table IV) indicate that the water molecules of hydration serve to link these planes and the F1 anion together via hydrogen bonds. In particular F1 is hydrogen bonded to three oxygens, O1, O2, and O3. Oxygen O3 in turn is also hydrogen bonded to O4, O5, and an additional O5. The corresponding angles all appear close to the tetrahedral angle. This type of packing is consistent with the observation that the crystals decompose into a light green powder within a few weeks if they are allowed to equilibrate with the atmosphere.

Acknowledgement

This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Materials Sciences Division, Budget Code KC-02-03-01 under contract W-7405-ENG-82.

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