Crystal Structure of Bis(2,2′-bipyridine)copper(I) Perchlorate

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Synopsis. The crystal structure of the title complex was determined by X-ray diffraction: Orthorhombic, space group $C222_1$, a=20.553(2) Å, b=11.210(1) Å, c=8.980(2) Å, and Z=4. The structure was solved by the direct method and was refined anisotropically by the full-matrix least-squares method: R was 0.062 for 1206 observed reflections. The $[Cu(bpy)_2]^+$ cation has a pseudo-tetrahedral arrangement (average Cu–N=2.021 Å). The interligand dihedral angle in $[Cu(bpy)_2]^+$, 75.2°, differs significantly from that previously reported $[Cu(1,10\text{-phenanthroline})_2]ClO_4$ (49.9°).

2,2′-Bipyridine(bpy) and 1,10-phenanthroline (phen) are bidentate ligands, whose π acceptor capability significantly contributes to the stabilization of their low valent metal complexes.[1,2] Regarding their complexation, it is interesting to compare these ligands with 2,9-dimethyl-1,10-phenanthroline (dmp) and 6,6′-dimethyl-2,2′-bipyridine (dmbp). Four-coordinate copper(I) cations tend to favor a regular tetrahedral arrangement[3] due to its d^{10} configuration. The interligand dihedral angles, between the mean planes defined by the metal ion and each set of bidentate nitrogen atoms, were 80.2° and 85.7° for $[Cu(dmp)_2]^+$,[4,5] and 80.7° for $[Cu(dmbp)_2]^+$,[6] indicating a pseudo-tetrahedral geometry. Recently, two interesting structures, $[Cu(phen)_2]ClO_4$ and $[Cu(phen)_2][CuBr_2]$, have been reported,[7] whose interligand dihedral angles were 49.9° and 76.8°, respectively. Although both structures have the same $[Cu(phen)_2]^+$ unit, these two angles are quite different. In the case of the $[Cu(bpy)_2]^+$ cation, the question arose as to how large is the interligand dihedral angle. In order to answer this question, an X-ray structural determination of $[Cu(bpy)_2]ClO_4$ was carried out.

Experimental

Preparations. $[Cu(bpy)_2]ClO_4$ was synthesized in the following way.[8] Under a nitrogen atmosphere, an 8-ml methanol solution of bpy(80 mM) (1 M=1 mol dm^{-3}) was added to tetrakis(acetonitrile)copper(I) perchlorate (40 mM) and stirred at 298 K. Brown prism-like crystals suitable for diffraction studies were grown from this solution in a sealed tube at 273 K.

Crystal Data. $C_{20}N_4H_{16}Cu$, ClO_4, $F.W.$ 475.35, orthorhombic, space group $C222_1$ (No. 20, systematic absences, hkl: $h+k=2n+1$ and $00l$: $l=2n+1$), a=20.553(2), b=11.210 (1), c=8.980(2) Å, D_c=1.526 g cm^{-3} for Z=4.

A crystal with approximate dimensions of 0.15×0.15×0.20 mm^3 was mounted on a Rigaku AFC-6B four-circle diffractometer with graphite-monochromatized Cu $K\alpha$ radiation ($\bar{\lambda}$=1.54178 Å). The intensity data were collected at 296 K in the θ–2θ scan mode with a 1.2° scan width, $2\theta_{max}$ of 120° ($-22\leq h\leq 22$, $0\leq k\leq 12$, $0\leq l\leq 10$), and scan rate of 4° min^{-1}. They were converted to $|F_o|$ data in the usual manner. An absorption correction was not applied (μ=2.98 mm^{-1}). Of the 1834 measured reflections, 1206 were observed ($|F_o|>3\sigma(F_o)$), where $\sigma(F_o)$ is the standard deviation estimated by countig statistics.

Structure Solution and Refinement. The structure was solved by a direct method (*MULTAN* 78),[9] and refined by full-matrix least-squares calculations with anisotropic thermal parameters, including isotropic H atoms located on a difference Fourier synthesis. The final R and R_w values were 0.062 and 0.060, respectively. The atomic parameters of non-hydrogen atoms are given in Table 1.#

The atomic scattering factors[10] and anomalous dispersion[11] terms for all atoms were obtained from International Tables for X-Ray Crystallography, Vol. IV. All computation were performed on a FACOM M-382 computer at the Data Processing Center, Kyoto University using the program system KPPXRAY.[12]

Results and Discussion

The view of the cation in Fig. 1 shows that the central copper atom, with a pseudo-tetrahedral geometry, is coordinated to two bpy molecules via the pyridine nitrogens. Selected bond lengths and angles are also given in Fig. 1. A perchlorate anion does not coordi-

Table 1. Atomic Coordinates of Non-hydrogen Atoms, with Estimated Standard Deviations in Parentheses and Equivalent Isotropic Temperature Factors

Atom	x	y	z	B_{eq}[a]/Å^2
Cu	0.0	0.0918(3)	0.2500	7.41
Cl	0.1316(2)	0.5000	0.5000	8.15
C1	0.1350(5)	0.0656(10)	0.1952(11)	4.71
C2	0.1973(6)	0.0236(13)	0.2090(15)	7.10
C3	0.2120(7)	−0.0769(14)	0.2964(15)	8.88
C4	0.1622(7)	−0.1280(13)	0.3778(15)	7.92
C5	0.1031(7)	−0.0841(12)	0.3561(14)	7.43
C6	0.1161(5)	0.1675(10)	0.1077(12)	5.07
C7	0.1573(6)	0.2311(12)	0.0156(21)	7.27
C8	0.1339(8)	0.3262(13)	−0.0696(15)	8.82
C9	0.0692(7)	0.3526(11)	−0.0689(15)	6.75
C10	0.0310(6)	0.2867(11)	0.0233(18)	6.95
N1	0.0876(4)	0.0116(9)	0.2690(13)	6.44
N2	0.0505(5)	0.1956(9)	0.1068(12)	6.10
O1	0.1704(6)	0.4022(12)	0.4947(26)	17.43
O2	0.0887(7)	0.5158(23)	0.3957(18)	22.18

a) Equivalent isotropic temperature factor defined by Hamilton.[20]

Tables of thermal parameters of non-hydrogen atoms, fractional coordinates of hydrogen atoms, and the observed and calculated structure factors are being kept at the Chemical Society of Japan, Document No. 8734.

nate to the copper because the closest Cu···O contact is 5.26 Å. The bpy ligand is planar within 0.04 Å, with the twisting about the Cl–C6 bond (dihedral angle is 2.2°). The Cu–N lengths are slightly shorter than that of $[Cu(dmbp)_2]BF_4$,[6] indicating that the steric interaction between copper atom and methyl group is unexpectedly little. On the other hand, a steric effect of the methyl group has been found in $[Cu(phen)_2]^+$ and $[Cu(dmp)_2]^+$, and the Cu–N length for the former is clearly shorter than that for the latter (Table 2). The interligand dihedral angle, α, of the present complex is of particular interest. The angle 75.2° is slightly smaller (by 5.7°) than that in $[Cu(dmbp)_2]^+$, and an apparent difference between two complexes is not appreciated; this indicates that there are no marked substituent effects. Table 2 shows that α of $[Cu(phen)_2]NO_3$ differs by 27° from that of $[Cu(phen)_2][CuBr_2]$.

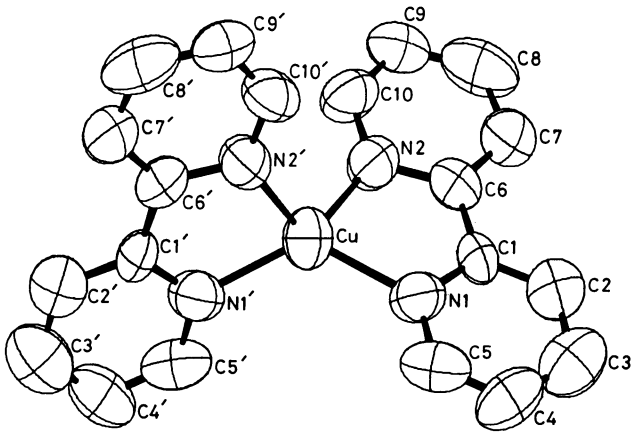

Fig. 1. View of the $[Cu(bpy)_2]^+$ cation. Thermal ellipsoids are drawn at 50% probability level: Hydrogen atoms are omitted. The labeling scheme used for the atom in the molecule is also shown. The primed atom notes the atom translated by two-fold axis. Selected bond lengths (Å) and angles (deg.) are as follows: Cu–N1=2.020(9); Cu–N2=2.021 (11); Cl–C6=1.440(15); Cl–N1=1.325(14); C6–N2= 1.385(15); N1–Cu–N1′=127.1(4); N1–Cu–N2′=131.3 (4); N1–Cu–N2=81.5(4); N2–Cu–N2′=109.7(4); C6–Cl–N1=115.9(9); Cl–C6–N2=116.5(9); Cu–N1–Cl= 114.2(8); Cu–N1–C5=127.3(8); Cu–N2–C6=111.4(8); Cu–N2–C10=130.3(9).

The small angle for the former is not necessarily due to a counter anion because of no coordination of the anion; the angle is associated with the intermolecular interaction from a crystal packing, rather than the intramolecular interaction inherent in copper(I). The α of 49.9° is close to that of a copper(II) complex, $[Cu(bpy)_2]^{2+}$.[14] In the copper(II) complex, the small angle α is reasonable since the copper(II) cation prefers a near square-planar structure to a tetrahedral one.[15] According to Table 2, α for the methyl complex, $[Cu(dmbp)_2]^+$, is about 81°, larger by ca. 6° than that for methyl group-free complexes. On the other hand, it is surprising to find that α for $[Cu(tmbp)_2]^+$ is smaller than that for the present complex in spite of the dmbp analog.[16] These facts suggest that α for tetrahedral copper(I) complexes with the bidentate ligand *in the solid state* depends on the crystal packing dominating over the steric effect of methyl groups. The effect of the methyl group should be considered, especially in the case of a square-planar arrangement, rather than a tetrahedral arrangement. The near neighboring methyl groups probably play an important role in inhibiting the deformation toward a square-planar geometry. This role is advantageous for copper(I) complexes. In fact, dmp favors a copper(I) ion rather than a copper(II) ion: the stability con-

Table 2. Comparison of Average Bond Parameters in Some $[Cu(biL)_2]X_n$ Type Complexes

biL	Oxidation Number of Copper (n)[a]	X	Bond Length (Å) Cu–N[b]	Angles (deg.)		Reference	Redox Potential $E_{1/2}$ (V. vs. NHE)
				N–Cu–N[b]	Dihedral[c]		
2,2′-Bipyridine (bpy)	+1 (1)	ClO_4^-	2.021 (11)	81.5 (4)	75.2	Present work	0.12[d], 0.254[e]
6,6′-Dimethyl-2,2′-bipyridine (dmbp)	+1 (1)	BF_4^-	2.034 (1)	81.9 (1)	80.7	(6)	0.574[e]
4,4′,6,6′-Tetramethyl-2,2′-bipyridine (tmbp)	+1 (1)	ClO_4^-	2.057 (10)	80.6 (4)	68	(14)	
1,10-Phenanthroline (phen)	+1 (1)	ClO_4^-	2.049 (9)	81.4 (3)	49.9	(7)	0.174[d]
1,10-Phenanthroline (phen)	+1 (1)	$CuBr_2^-$	2.039 (8)	82.2 (3)	76.8	(7)	
2,9-Dimethyl-1,10-phenanthroline (dmp)	+1 (1)	NO_3^-	2.071 (8)	82.7 (3)	80.2	(4)	0.603[f]
2,9-Dimethyl-1,10-phenanthroline (dmp)	+1 (1)	NO_3^- [g]	2.063	83.4	85.7	(5)	
2,2′-Bipyridine (bpy)	+2 (2)	PF_6^-	1.985 (11)	83.0 (7)	44.6	(14)	

a) Number of counter ions. b) Bond lengths and intraligand N–Cu–N angle. Two values are averaged. c) An interligand dihedral angle. d) Ref. 1. e) Present work. Obtained from cyclic voltammograms of acetone solution at 25 °C. f) Ref. 18. g) Dihydrate.

stant $10^{19.1}$ of $[Cu(dmp)_2]^+$ is very much larger than that, $10^{11.7}$, of $[Cu(dmp)_2]^{2+}$.[17] This is also well-illustrated in terms of the redox properties of the copper complexes of dmp and dmbp since both $[Cu(dmp)_2]^+$ and $[Cu(dmbp)_2]^+$ have higher redox potentials of copper than the corresponding complexes without methyl substituents (Table 2).[1,18,19] These facts indicate that the steric interaction of the methyl groups in the 2 and 9 positions of phen and in the 6 and 6′ positions of bpy favor the tetrahedral geometry of the copper(I) complex *in solution* since there is no effect owing to closed packing, forcing the copper(II) complex to avoid a square planar geometry.

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