The Crystal Structure of Bis(2,2′-bipyridine)nitratocopper(II) Nitrate Monohydrate $[Cu(NO_3)(bpy)_2]NO_3 \cdot H_2O$

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The crystal structure of the title compound has been redetermined from diffractometer data and refined by the least-squares method to $R=0.053$ for 2448 non-zero reflections. The crystal is triclinic, with $a=7.464(3)$, $b=10.002(5)$, $c=15.503(6)$ Å, $\alpha=111.50(5)$, $\beta=91.43(5)$, $\gamma=90.47(4)°$, space group $P\bar{1}$, and $Z=2$. The copper atom has a square-pyramidal coordination very distorted by the 4 N atoms of the bipyridine ligands and one of the O atoms of the nitrato ligand at the apical position. The disposition of the 4 N atoms at the basal plane is flattened tetrahedral. The Cu atom is displaced by 0.31 Å from the mean plane of the 4 N atoms towards the apical O atom. The Cu–O and the average Cu–N distances are 2.30 and 2.01 Å respectively. In both bipyridine molecules, the two pyridine planes are twisted slightly from each other; the interplanar angle is 2.6° in one bipyridine ligand and 6.0° in the other. The mean planes of the two bipyridine molecules make an angle of 44.6°.

The $Cu(bpy)_2^{2+}$ moiety in bis(bipyridine)copper(II) complexes has been shown to be unable to take a strictly coplanar disposition because of the interligand repulsion. Indeed, in these complexes, the planes of the two bipyridine ligands are usually twisted by 30—60° away from each other; consequently, the four nitrogen atoms are disposed tetrahedrally.[1-3] Such a situation, however, complicates the stereochemistry of penta-coordinate bis(bipyridine)copper(II) complexes; it is difficult to distinguish strictly between a trigonal-bipyramidal and a square-pyramidal structure. In the case of $[Cu(NO_3)(bpy)_2]NO_3 \cdot H_2O$, the coordination geometry of which has been reported briefly as a distorted trigonal bipyramid,[4] the reflectance spectrum is somewhat different from those of the other trigonal-bipyramidal complexes.[5]

In order to make a further investigation into the stereochemistry of bis(bipyridine)copper(II) complexes, a refinement of the crystal structure of the $[Cu(NO_3)(bpy)_2]NO_3 \cdot H_2O$ was performed using the diffractometer intensity data.

Experimental

The blue crystals of $[Cu(NO_3)(bpy)_2]NO_3 \cdot H_2O$ were prepared by Jeager's method[6] and were recrystallized from a water–methanol mixture. Found: C, 46.47; H, 3.67; N, 16.22%. Calcd for $Cu(bpy)_2(NO_3)_2 \cdot H_2O$: C, 46.38; H, 3.50; N, 16.23%.

Preliminary X-ray photographs taken with Cu $K\alpha$ radiation showed $\bar{1}$ Laue symmetry, indicating a triclinic space group. No systematic absences were observed. The space group is either $P\bar{1}$ or $P1$; the former was confirmed by a successful refinement of the structure.

A crystal with dimensions of $0.20 \times 0.20 \times 0.23$ mm was mounted on a glass fiber for data collection. The lattice constants were determined by a least-squares fit using 32 independent θ-values measured accurately on a diffractometer. Crystal data: $[Cu(NO_3)(bpy)_2]NO_3 \cdot H_2O$, $M.W.=517.9$, triclinic, $a=7.464(3)$, $b=10.002(5)$, $c=15.503(6)$ Å, $\alpha=111.50(5)$, $\beta=91.43(5)$, $\gamma=90.47(4)°$, $U=1076.4$ Å^3, $Z=2$, $D_c=1.60$, $D_m=1.60$ g·cm^{-3} (by flotation in a benzene–bromoform mixture), Mo $K\alpha$ radiation ($\lambda=0.71069$ Å), μ(Mo $K\alpha$) $=10.7$ cm^{-1}, space group $P\bar{1}$.

Intensity data with $2\theta \leqq 56°$ were collected at room temperature by means of the w-2θ scan technique on a Philips PW1100 four-circle diffractometer using graphite-monochromated Mo $K\alpha$ radiation. The scan speed and scan width were 0.03° s^{-1} and $(0.90+0.20\tan\theta)°$ respectively. The background was counted for 10 s at each end of the scan range. Three standard reflections (100, 040, and 002), monitored every 3 h throughout the data collection, showed no significant variation in intensity. A total of 2448 intensities with $I_{top}-2\sqrt{I_{top}}>I_{back}$ were classified as observed; I_{top} is the intensity (counts/s) measured at the top of the peak, while I_{back} is the mean background intensity (counts/s) obtained from the preliminary background measurement for 5 s on each side of the peak. The intensity data were processed with the computer program of Hornstra and Stubbe.[7] No absorption correction was made.

The reflectance spectrum of this compound was also measured, using a Hitachi 139 spectrophotometer fitted with a standard reflectance attachment.

Refinement of the Structure

The refinement of the structure was carried out by means of a block-diagonal least-squares method. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$. A weighting scheme of the type suggested by Hughes[8] was applied, using $w=1.0$ for $F_o \leqq 20.0$ and $w=(20.0/F_o)^2$ for $F_o>20.0$. The atomic scattering factors were taken from Ref. 9.

The initial parameters were those reported earlier.[4] The refinement of the atomic positions and isotropic thermal parameters gave the R value of 0.127 after three least-squares cycles. Subsequent refinement in which each atom was allowed to vibrate anisotropically reduced the value of R to 0.064. The positions of all the hydrogen atoms were obtained from the difference Fourier map calculated at this point. These hydrogen atoms were included in the final refinement, with an isotropic thermal parameter of 4.0 Å^2. The final R value was 0.053 for 2448 observed reflections. All the parameter shifts were less than 0.2σ in the final cycle of the refinement. The atomic coordinates and thermal parameters are listed in Tables 1 and 2. The observed and calculated structure factors are preserved at the Chemical Society of Japan (Document Number 8013). The computer programs used in the calculations were as follows: HBLS-V[10] (least-squares calculation), RHOMAP[10] (Fourier synthesis), and DAPH[10] (interatomic distances and angles, least-squares plane, and coordinates of the H atoms). The calculations were made on the NEAC 2200-700 and

TABLE 1. ATOMIC PARAMETERS($\times 10^4$) FOR THE NON-HYDROGEN ATOMS AND THEIR STANDARD DEVIATIONS
The anisotropic thermal factors are of the form: $\exp\{-(h^2B_{11}+k^2B_{22}+l^2B_{33}+hkB_{12}+hlB_{13}+klB_{23})\}$.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	1158(1)	3924(1)	2064(1)	256(2)	112(1)	43(1)	67(2)	48(1)	75(1)
N (1)	2825(7)	2776(5)	2562(3)	239(12)	104(6)	49(3)	−21(14)	3(9)	59(7)
C (1)	4431(9)	2245(7)	2230(5)	238(16)	134(9)	61(4)	21(19)	−18(12)	66(9)
C (2)	5438(11)	1422(7)	2604(5)	306(19)	116(9)	83(5)	82(20)	−62(15)	59(10)
C (3)	4750(12)	1145(8)	3358(6)	350(21)	143(10)	86(5)	3(23)	−104(17)	111(12)
C (4)	3137(11)	1723(7)	3716(5)	357(20)	143(9)	66(4)	−47(22)	−86(15)	117(11)
C (5)	2199(9)	2534(6)	3300(4)	248(15)	97(7)	45(3)	−73(16)	−31(11)	49(8)
N (2)	−187(7)	4018(5)	3172(3)	250(13)	125(7)	43(2)	−25(14)	16(9)	63(7)
C (6)	478(9)	3202(6)	3627(4)	270(16)	118(8)	43(3)	−82(18)	−10(11)	61(8)
C (7)	−457(11)	3034(8)	4351(4)	325(19)	185(11)	48(3)	−167(23)	−22(13)	97(10)
C (8)	−2043(11)	3720(9)	4607(5)	301(19)	222(13)	54(4)	−157(25)	51(14)	66(11)
C (9)	−2725(11)	4545(8)	4134(5)	288(18)	197(12)	49(4)	−74(23)	60(13)	39(10)
C (10)	−1785(9)	4658(7)	3415(4)	221(15)	145(9)	57(4)	−20(18)	46(12)	52(9)
N (3)	926(7)	5944(5)	2037(3)	203(11)	103(6)	48(3)	−10(13)	7(8)	47(6)
C (11)	337(10)	7137(7)	2704(4)	282(17)	107(8)	57(4)	13(18)	9(12)	46(9)
C (12)	351(10)	8464(7)	2622(5)	276(18)	114(8)	80(5)	46(19)	6(14)	57(10)
C (13)	1039(10)	8571(7)	1825(5)	295(18)	111(9)	83(5)	−47(20)	−47(15)	96(10)
C (14)	1698(9)	7371(7)	1146(5)	218(15)	123(8)	67(4)	−14(17)	−30(12)	89(9)
C (15)	1604(8)	6066(6)	1264(4)	172(13)	107(7)	48(3)	−42(15)	−26(10)	67(8)
N (4)	2235(7)	3575(5)	846(3)	222(11)	110(6)	46(2)	26(13)	21(9)	66(6)
C (16)	2238(8)	4713(6)	576(4)	180(13)	128(8)	43(3)	−20(16)	−1(10)	69(8)
C (17)	2822(9)	4577(7)	−296(4)	203(14)	157(9)	49(3)	−49(18)	12(11)	91(9)
C (18)	3358(9)	3265(8)	−889(4)	202(15)	199(11)	50(3)	−19(20)	33(11)	74(10)
C (19)	3321(9)	2088(8)	−618(4)	231(16)	172(10)	48(3)	19(20)	33(12)	26(9)
C (20)	2727(9)	2289(7)	258(4)	256(16)	125(8)	52(3)	39(18)	59(12)	49(9)
O (1)	−1491(7)	3165(4)	1231(3)	371(13)	108(5)	60(3)	−40(14)	−17(9)	70(6)
O (2)	−576(8)	1212(6)	1315(4)	344(15)	188(8)	114(4)	96(17)	−89(13)	152(10)
O (3)	−2903(7)	1206(5)	460(4)	282(13)	173(7)	93(4)	−109(15)	−77(11)	97(9)
N (5)	−1656(7)	1831(5)	995(3)	201(11)	131(7)	57(3)	26(14)	27(9)	86(7)
O (4)	4261(15)	5988(9)	3174(10)	787(38)	233(14)	399(16)	−213(36)	−788(44)	263(25)
O (5)	5920(15)	7652(12)	3204(8)	813(40)	427(21)	188(9)	34(46)	396(32)	232(23)
O (6)	4183(18)	8040(15)	4207(7)	956(49)	630(32)	144(8)	130(63)	214(32)	297(27)
N (6)	4772(11)	7126(9)	3471(6)	408(23)	269(14)	124(6)	66(29)	31(19)	184(16)
O(H_2O)	8102(16)	9781(14)	4750(8)	782(39)	619(30)	170(9)	−188(54)	5(29)	414(28)

TABLE 2. ATOMIC COORDINATES($\times 10^3$) OF THE HYDROGEN ATOMS AND THEIR STANDARD DEVIATIONS

Atom	x	y	z	Atom	x	y	z
H(C1)	485(6)	238(5)	158(3)	H(C12)	−9(7)	932(4)	316(3)
H(C2)	653(7)	90(5)	220(4)	H(C13)	103(7)	951(5)	179(4)
H(C3)	537(9)	61(6)	373(4)	H(C14)	199(7)	719(5)	42(3)
H(C4)	280(8)	159(5)	430(3)	H(C17)	285(6)	540(4)	−45(3)
H(C7)	3(7)	241(6)	461(3)	H(C18)	392(7)	311(6)	−154(3)
H(C8)	−282(8)	359(7)	509(3)	H(C19)	384(7)	107(5)	−105(3)
H(C9)	−384(7)	508(6)	430(3)	H(C20)	243(7)	150(5)	51(3)
H(C10)	−229(6)	526(5)	311(3)	H(H_2O)	693(18)	54(14)	517(7)
H(C11)	−11(7)	694(4)	330(3)	H(H_2O)′	785(20)	−6(17)	440(9)

ACOS-800 of Osaka University.

Results and Discussion

The crystal consists of discrete $[Cu(NO_3)(bpy)_2]^+$, NO_3^-, and H_2O. Figure 1 shows the a-axis projection of the crystal structure. The bond lengths and angles, with their estimated standard deviations, are given in Table 3.

Although the two chelate rings composed of Cu and the bpy have substantially the same structure, two Cu–N bonds in each ring are significantly different in length; the average value of the longer bond lengths is 2.034(5) Å, while that of the shorter ones is 1.983(5)

Å. The nitrato group is coordinated virtually as a unidentate ligand through the O(1) atom(Cu–O(1)= 2.299(5) Å), but one more oxygen atom, O(2), is located at a distance of 2.818(7) Å from the copper atom. The copper atom is thus five-coordinate, but the coordination polyhedron around the copper atom seems to be intermediate between a trigonal bipyramid and a square pyramid.

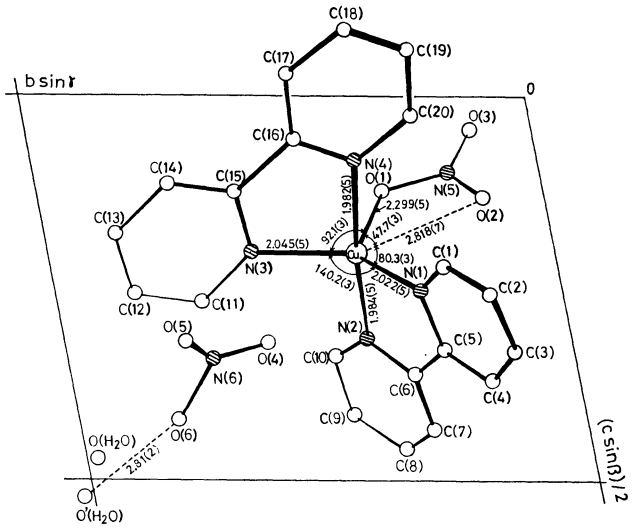


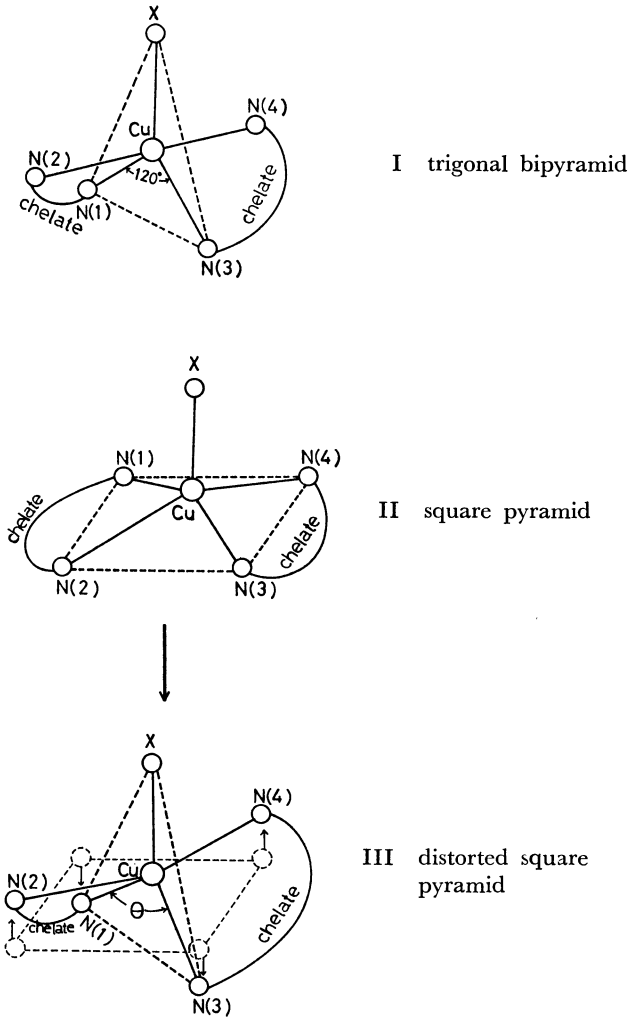
Fig. 1. The crystal structure viewed down the a axis.

If this complex is regarded as assuming a trigonal–bipyramidal structure, I, the N(2) and N(4) atoms can be said to occupy the axial positions, while the Cu, O(1), N(1), and N(3) atoms form an equatorial plane. However, in $[CuX(bpy)_2]^{n+}$-type complexes (X=I, NH_3, Cl, $CS(NH_2)_2$, and Cu^ICl_2) which have been classified as trigonal–bipyramidal structures on the bases of the spectral and X-ray studies,[5,11–15] it has been found that the axial Cu–N distances are significantly (0.06—0.12 Å) shorter than the equatorial ones except for the case of $[CuI(bpy)_2]^+$,[11] and also that the N–Cu–N angle in the equatorial plane is in the 109—123° range, which is close to the angle (120°) in the regular trigonal bipyramid. In the present complex, the difference between the axial and equatorial Cu–N bond distances is 0.038 Å, a little smaller than those in the trigonal–bipyramidal complexes mentioned above. Besides, the angle of N(1)–Cu–N(3) in the equatorial plane is 140.2(3)°; this value is considerably outside the range of 109—123°.

Table 3. Interatomic distances(l/Å) and angles(φ/°), with their estimated standard deviations in parentheses

Cu-N(1)=2.022(5)	C(16)-C(17)=1.390(9)	O(1)-Cu-N(4)=85.5(3)	C(6)-C(7)-C(8)=119.5(7)
Cu-N(2)=1.984(5)	C(17)-C(18)=1.367(11)	N(1)-Cu-N(2)=81.1(3)	C(7)-C(8)-C(9)=119.8(8)
Cu-N(3)=2.045(5)	C(18)-C(19)=1.389(11)	N(1)-Cu-N(3)=140.2(3)	C(8)-C(9)-C(10)=118.9(8)
Cu-N(4)=1.982(5)	C(19)-C(20)=1.382(10)	N(1)-Cu-N(4)=100.0(3)	N(2)-C(10)-C(9)=121.9(7)
Cu-O(1)=2.299(7)	N(5)-O(1)=1.251(7)	N(2)-Cu-N(3)=103.6(3)	C(11)-N(3)-C(15)=118.4(5)
Cu···O(2)=2.818(7)	N(5)-O(2)=1.222(8)	N(2)-Cu-N(4)=170.9(3)	N(3)-C(11)-C(12)=122.7(7)
N(1)-C(1)=1.350(9)	N(5)-O(3)=1.231(8)	N(3)-Cu-N(4)=81.4(3)	C(11)-C(12)-C(13)=118.2(7)
N(1)-C(5)=1.347(8)	N(6)-O(4)=1.119(18)	O(2)···Cu-O(1)=47.7(4)	C(12)-C(13)-C(14)=119.9(7)
C(1)-C(2)=1.385(11)	N(6)-O(5)=1.162(15)	O(2)···Cu-N(1)=80.3(4)	C(13)-C(14)-C(15)=118.8(7)
C(2)-C(3)=1.405(12)	N(6)-O(6)=1.264(18)	O(2)···Cu-N(2)=81.8(4)	N(3)-C(15)-C(14)=121.9(6)
C(3)-C(4)=1.379(12)	C(1)-H(C1)=1.12(5)	O(2)···Cu-N(3)=139.5(4)	N(3)-C(15)-C(16)=114.8(5)
C(4)-C(5)=1.391(10)	C(2)-H(C2)=1.06(6)	O(2)···Cu-N(4)=89.5(4)	C(14)-C(15)-C(16)=123.3(6)
C(5)-C(6)=1.467(9)	C(3)-H(C3)=1.02(6)	O(4)···Cu-N(1)=72.6(8)	Cu-N(3)-C(11)=128.4(5)
N(2)-C(6)=1.349(9)	C(4)-H(C4)=0.99(6)	O(4)···Cu-N(2)=95.3(8)	Cu-N(3)-C(15)=113.0(5)
N(2)-C(10)=1.354(9)	C(7)-H(C7)=0.93(6)	O(4)···Cu-N(3)=67.6(8)	Cu-N(4)-C(16)=115.0(4)
C(6)-C(7)=1.397(10)	C(8)-H(C8)=1.01(7)	O(4)···Cu-N(4)=93.6(8)	Cu-N(4)-C(20)=124.6(4)
C(7)-C(8)=1.366(12)	C(9)-H(C9)=0.98(5)	Cu-O(1)-N(5)=109.3(5)	C(16)-N(4)-C(20)=119.9(5)
C(8)-C(9)=1.382(12)	C(10)-H(C10)=0.96(5)	Cu···O(2)-N(5)=84.3(6)	C(15)-C(16)-N(4)=115.4(5)
C(9)-C(10)=1.370(11)	C(11)-H(C11)=1.07(5)	C(1)-N(1)-C(5)=119.0(6)	C(15)-C(16)-C(17)=123.9(6)
N(3)-C(11)=1.347(9)	C(12)-H(C12)=1.02(6)	N(1)-C(1)-C(2)=122.4(7)	N(4)-C(16)-C(17)=120.7(6)
N(3)-C(15)=1.357(8)	C(13)-H(C13)=0.96(6)	C(1)-C(2)-C(3)=118.0(7)	C(16)-C(17)-C(18)=119.3(7)
C(11)-C(12)=1.379(11)	C(14)-H(C14)=1.10(5)	C(2)-C(3)-C(4)=119.7(8)	C(17)-C(18)-C(19)=120.1(7)
C(12)-C(13)=1.389(12)	C(17)-H(C17)=0.94(6)	C(3)-C(4)-C(5)=118.9(7)	C(18)-C(19)-C(20)=118.1(7)
C(13)-C(14)=1.378(11)	C(18)-H(C18)=1.06(6)	N(1)-C(5)-C(4)=121.9(6)	N(4)-C(20)-C(19)=122.0(6)
C(14)-C(15)=1.384(9)	C(19)-H(C19)=1.07(5)	N(1)-C(5)-C(6)=114.7(6)	O(1)-N(5)-O(2)=118.2(6)
C(15)-C(16)=1.474(9)	C(20)-H(C20)=1.03(5)	C(4)-C(5)-C(6)=123.4(6)	O(1)-N(5)-O(3)=118.7(6)
N(4)-C(16)=1.349(8)	O(6)···O'(H_2O)[a]=2.81(2)	Cu-N(1)-C(1)=127.1(5)	O(2)-N(5)-O(3)=123.1(6)
N(4)-C(20)=1.337(9)		Cu-N(1)-C(5)=113.8(5)	O(4)-N(6)-O(5)=128.1(13)
		Cu-N(2)-C(6)=114.6(4)	O(4)-N(6)-O(6)=122.6(13)
O(1)-Cu-N(1)=127.8(3)	C(5)-C(6)-N(2)=115.2(6)	Cu-N(2)-C(10)=125.4(5)	O(5)-N(6)-O(6)=109.2(12)
O(1)-Cu-N(2)=86.7(3)	C(5)-C(6)-C(7)=124.4(6)	C(6)-N(2)-C(10)=119.4(6)	
O(1)-Cu-N(3)=92.1(3)	N(2)-C(6)-C(7)=120.5(6)		

a) $1-x$, $2-y$, $1-z$.



The electronic reflectance spectrum of this complex in the range of 11.5—20.0×10³ cm⁻¹ shows a single peak at 13.2×10³ cm⁻¹. The peak position is considerably different from those for the trigonal-bipyramidal Cu–bpy complexes,[5] in which the spectra have been known to show a single characteristic band with a maximum at 12.0—12.5×10³ cm⁻¹. These structural and spectral features are not compatible with those of the trigonal-bipyramidal copper(II) chelates of the bpy.

On the other hand, if the coordination polyhedron of this complex is regarded as a square pyramid, II, the four nitrogen atoms should be taken as forming

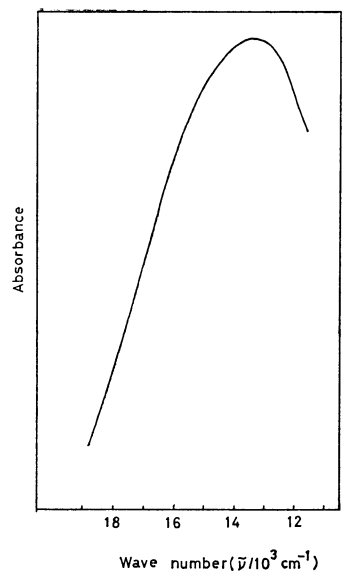


Fig. 2. Electronic reflectance spectrum of $[Cu(NO_3)(bpy)_2]NO_3 \cdot H_2O$.

the basal plane, and the O(1) atom, as occupying the apical position. In this case, however, the nitrogen atoms can not take a planar disposition because of the interligand repulsion, and so presumably have a flattened tetrahedral arrangement, as is shown in III. The scaled model indicates that the N(1)–Cu–N(3)(=θ) and X–Cu–N(1)(=X–Cu–N(3)) angles in III (X= a donor atom in the fifth position) are 140—160° and 100—110° respectively. In the present complex, however, the O(1)–Cu–N(1) angle (127.8°), which corresponds to the X–Cu–N(1) angle in III, is larger than the expected value of about 110°, since the N(1)–Cu–N(3) angle corresponding to θ is 140.2°. On examining the significance of this observation in detail, it should be noted that the O(2) atom of the nitrato group almost lies on the plane, "A", defined by the Cu, O(1), N(1), and N(3) atoms (Fig. 1) and has short contacts with the atoms of the chelate rings: 3.178(8) Å to N(1), 3.205(8) Å to N(2), and 2.66(5) Å to H(C20). The steric interactions with the bipyridine ligands appear to prevent bidentate coordination of the nitrato group. Moreover, the O(2) atom results in the enlargement of the O(1)–Cu–N(1) angle by 35.7° as compared with the O(1)–Cu–N(3). On the basis of the structural features described above, the coordination geometry about the copper atom should

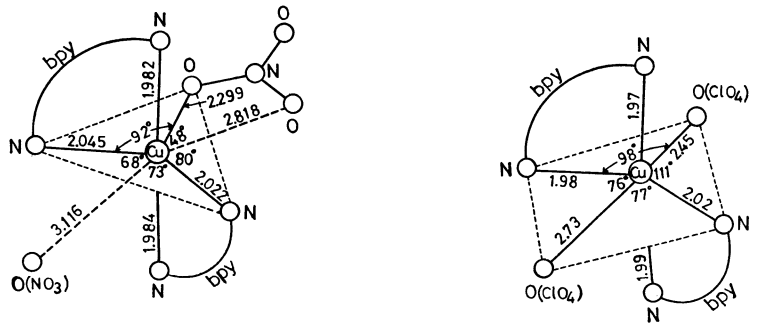


Fig. 3. The resemblance between the stereochemistries of $[Cu(NO_3)(bpy)_2]NO_3 \cdot H_2O$ and $[Cu(ClO_4)(bpy)_2]ClO_4$.

be regarded as a distorted square pyramid.

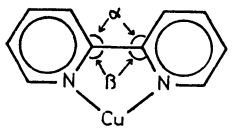
The copper atom is displaced by 0.31 Å towards the apical O(1) atom from the mean plane of the 4 N atoms. The Cu–N bond distances are 2.008 Å, on the average. The dihedral angle between the $\begin{matrix}\nearrow N(1)\\ Cu\\ \searrow N(2)\end{matrix}$ and $\begin{matrix}\nearrow N(3)\\ Cu\\ \searrow N(4)\end{matrix}$ planes is 42.8°. The structure of the present complex is thought to be related to that of the distorted *trans*-octahedral $[Cu(ClO_4)(bpy)_2]ClO_4$.[1] This is illustrated in Fig. 3, which shows a schematic drawing of these two complexes. Although the O(4) atom of the uncoordinated NO_3^- ion is situated nearly at the sixth position in an octahedral coordination, it is 3.12 Å apart from the copper atom.

Table 4. Equation of the least-squares plane[a] and deviations of atoms from the planes(l/Å)

Pyridine ring I					
$-0.4432X-0.6450Y-0.6226Z+4.0435=0$					
N (1)	0.013	C (1)	−0.008	C (2)	−0.005
C (3)	0.013	C (4)	−0.009	C (5)	−0.004
Pyridine ring II					
$-0.4594X-0.6094Y-0.6462Z+4.1600=0$					
N (2)	−0.010	C (6)	−0.002	C (7)	0.010
C (8)	−0.007	C (9)	−0.005	C (10)	0.013
Bipyridine ligand I					
$-0.4550X-0.6260Y-0.6333Z+4.1181=0$					
N (1)	0.049	C (1)	0.013	C (2)	−0.019
C (3)	−0.020	C (4)	−0.025	C (5)	0.014
C (6)	0.006	C (7)	0.037	C (8)	0.011
C (9)	−0.016	C (10)	−0.018	N (2)	−0.031
Pyridine ring III					
$-0.8970X-0.0257Y-0.4414Z+1.9320=0$					
N (3)	0.008	C (11)	−0.011	C (12)	0.003
C (13)	0.008	C (14)	−0.012	C (15)	0.005
Pyridine ring IV					
$-0.9268X-0.0897Y-0.3646Z+2.1974=0$					
N (4)	−0.014	C (16)	0.009	C (17)	−0.001
C (18)	−0.003	C (19)	−0.001	C (20)	0.010
Bipyridine ligand II					
$-0.9121X-0.0641Y-0.4050Z+2.0784=0$					
N (3)	0.069	C (11)	0.060	C (12)	0.018
C (13)	−0.049	C (14)	−0.082	C (15)	−0.004
C (16)	−0.007	C (17)	0.050	C (18)	0.063
C (19)	0.015	C (20)	−0.040	N (4)	−0.079
Nitrato group					
$0.6082X+0.1645Y-0.7766Z+1.6931=0$					
O (1)	−0.001	O (2)	−0.001	O (3)	−0.001
N (5)	0.004				
Uncoordinated nitrate ion					
$-0.6632X+0.5074Y-0.5502Z+2.3854=0$					
O (4)	−0.004	O (5)	−0.004	O (6)	−0.004
N (6)	0.013				
Plane through N(1), N(2), N(3), and N(4)					
$-0.6884X-0.4547Y-0.5651Z+3.7622=0$					
N (1)	−0.293	N (2)	0.374	N (3)	−0.462
N (4)	0.560	Cu[b]	0.312		
Plane through Cu, N(1), N(3), and O(1)					
Cu	0.004	N (1)	−0.002	N (3)	−0.001
O (1)	−0.001	O (2)[b]	0.201	O (4)[b]	−0.131
Plane formed by Cu, N(1), and N(2)					
$-0.4800X-0.6873Y-0.5452Z+3.8742=0$					
Plane formed by Cu, N(3), and N(4)					
$-0.8885X-0.0910Y-0.4499Z+2.2572=0$					

a) Planes are defined as $AX+BY+CZ+D=0$, where X, Y, and Z are Cartesian coordinates which are related to the triclinic cell coordinates(x, y, z) by these transformations: $X=xa+yb\cos\gamma+zc\cos\beta$, $Y=yb\sin\gamma-zc\cos\alpha^*\sin\beta$, and $Z=zc\sin\alpha^*\sin\beta$. b) Atoms not used to define the least-squares plane.

The bipyridine ligands are not planar, but the individual pyridine moiety is planar within ±0.014 Å. The pyridine moieties of the bipyridine molecule are slightly twisted from each other about the 2,2′-carbon bond; the twist angle is 2.6° for the molecule comprising N(1) and N(2) and 6.0° for the other. Furthermore, the bond angle of α is larger than that of β by about 9°. A similar difference in these angles



(5—10°) has also been observed in the crystal structure of the 2,2′-bipyridine molecule[16] and its copper(II) complexes.[1] The bond lengths in the bipyridine ligands range from 1.37(1) to 1.41(1) Å in the aromatic C–C bond, and from 1.34(1) to 1.36(1) Å in C–N, while the 2,2′-carbon bonds are about 1.47 Å long (Table 3). The bond angles of C–C–C, C–N–C, and C–C–N in pyridine rings are 119.1, 119.2, and 121.8° respectively, on the average. The H(C1)---H(C20) and H(C10)---H(C11) distances between the bipyridine chelates are 2.37(7) and 2.27(7) Å. These values are not very different from the sum of the van der Waals radii of the hydrogen atoms.

The nitrato group is planar and acts as a unidentate ligand through the O(1) atom; another O(2) atom is located at the distance of 2.818(7) Å from the copper atom. The angle of Cu–O(1)–N(5) is 109.3(5)°. This mode of coordination of the nitrato group has also been found in the complexes[17] containing unidentate nitrato groups (ex. $[Cu(NO_3)_2(phen)]$[18] and $[Cu(NO_3)(dach)_2]NO_3 \cdot [Cu(H_2O)(dach)_2](NO_3)_2$[19] (dach=1,4-diazacycloheptane)). The N(5)–O(1) bond distance is a little longer (0.02—0.03 Å) than the remaining N(5)–O(2) and N(5)–O(3) ones, and the O(2)–N(5)–O(3) angle is greater (4—5°) than those of O(1)–N(5)–O(2) and O(1)–N(5)–O(3). The dihedral angle between the nitrato plane and the "A" plane is about 10°.

The uncoordinated nitrate ion is linked to the water-oxygen atom, $O'(H_2O)[1-x, 2-y, 1-z]$, through O–H---O hydrogen bonding ($O'(H_2O)$---O(6)=2.81Å).

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