The Crystal Structure of Monoaquobis(1,10-phenanthroline)-copper(II) Nitrate, $[Cu(H_2O)(phen)_2](NO_3)_2$

Hisayoshi NAKAI* and Yoshito DEGUCHI

Department of Chemistry, Faculty of Science, Osaka City University, Sugimoto-cho, Sumiyoshi-ku, Osaka 558

(Received February 28, 1975)

The crystal structure of the title compound has been determined from three-dimensional X-ray data collected on Weissenberg photographs, using Cu*Kα* radiation. The intensities were estimated visually with a standard scale. The structure was solved by the heavy-atom method and refined by the least-squares method. The final R value was 0.118 for 1835 observed reflections. The space group is C2/c, with a=22.58(2), b=7.23(1), c=16.58(2) Å, β=123.6(1)°, and Z=4. The crystal is composed of $[Cu(H_2O)(phen)_2]^{2+}$ cations with C_2-symmetry and NO_3^- anions. The copper atom is surrounded by four nitrogen atoms of the two phenanthroline ligands (average Cu–N=2.01 Å) and a water-oxygen atom (Cu–O=2.18 Å) in a distorted trigonal-bipyramidal arrangement. One oxygen atom and two nitrogen atoms of two different phenanthroline ligands are coplanar with the central copper atom, and lines linking the copper atom with each of the axial nitrogen atoms make angles of about 10°, with the normal to the basal N–N–O plane. The electronic reflectance spectrum of this complex shows a characteristic band at about 12.5×10^3 cm^{-1}, which is analogous to that of [CuI(bipy)$_2$]I.

It is well known that 1,10-phenanthroline (=phen) forms a number of bis-phenanthroline copper (II) complexes with the general formula $Cu(phen)_2X_2 \cdot nH_2O$.[1] In this case, however, the two phenanthroline molecules can not assume a square-coplanar arrangement about the copper atom because of the steric repulsions between the hydrogen atoms on the 2- and 9-carbon atoms of one molecule and the corresponding ones in the other.[2] Several investigations[3–5] have been made of the coordination geometry of these complexes, but the detailed structure has not yet been established. Jφrgensen,[3] and James *et al.*,[4] have independently suggested, from their spectral studies, that the bis-phenanthroline copper(II) complexes take a *cis*-octahedral configuration in an aqueous solution. On the other hand, Faye[5] used the elementary ligand-field theory to interpret the absorption spectra of those complexes in an acetone medium, and concluded that they probably have a trigonal bipyramidal structure.

One of the present authors (H. N.) has been attempting the crystal structure analyses of bis-bipyridine and bis-phenanthroline copper(II) complexes.[6,7] This paper will describe the crystal structure of $Cu(phen)_2(NO_3)_2 \cdot H_2O$.

Experimental

The green crystals of $Cu(phen)_2(NO_3)_2 \cdot H_2O$ were easily prepared by adding a methanol solution of 1,10-phenanthroline (20 mmol in 30 cm^3 of the solvent) to an aqueous solution of cupric nitrate (10 mmol in 30 cm^3 of water), and were recrystallized from a water–methanol mixture. Found: C, 50.80; H, 3.27; N, 14.34%. Calcd for $Cu(phen)_2(NO_3)_2 \cdot H_2O$: C, 50.93; H, 3.21; N, 14.85%.

The crystal symmetry was determined from preliminary Weissenberg photographs, which showed a Laue symmetry of $2/m$ and systematic absences of hkl for $h+k=2n+1$ and of $h0l$ for $l=2n+1$. Hence, the space group is C2/c or Cc. The centro-symmetric choice, C2/c, was initially taken on the basis of intensity statistics;[8] it was subsequently verified by the successful refinements of the derived structure. Cu*Kα* radiation (λ=1.5418 Å) was used throughout the diffraction study. The lattice parameters were obtained by the least-squares refinement of the data from the higher-angle reflections of the $h0l$ and $hk0$ Weissenberg photographs, on which aluminium powder lines were superimposed for calibration. The density was measured by the flotation technique using a mixture of benzene and bromoform. The crystal data are listed in Table 1.

Table 1. Crystal data

$[Cu(H_2O)(phen)_2](NO_3)_2$
F.W.=566.0
Monoclinic
a=22.58(2) Å
b= 7.23(1)
c=16.59(2)
β=123.6(1) °
V=2256 Å^3
Z=4
D_x=1.66 g·cm^{-3}
D_m=1.65 g·cm^{-3}
μ=20.9 cm^{-1} (for Cu*Kα*)
Space group: C2/c

The intensity data of $h0l$ to $h4l$ and $hk0$ to $hk8$ were collected by the multiple-film equi-inclination technique from two cylindrically shaped crystals with approximate dimensions of 0.2×0.2×0.8 mm. The intensities of 2102 independent reflections were visually estimated by comparison with a standard scale; 267 of them were too weak to be measured and so were assumed to be zero. After the intensity data has been corrected for Lorentz-polarization, spot-extension, and absorption effects, the structure factors were placed on a common arbitrary scale by the least-squares method.

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

Structure Determination

As described above, the space group of this compound is C2/c, and the number of the complex molecules in the unit cell is four. Therefore, the copper and oxygen

---

* Address correspondence to present address: Department of Chemistry, Hyogo College of Medicine, Mukogawa-cho, Nishinomiya-shi, Hyogo 663.

TABLE 2. THE ATOMIC COORDINATES, THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS ($\times 10^4$)
The thermal parameters are of the form
$T=\exp\{-(\beta_{11}\times h^2+\beta_{22}\times k^2+\beta_{33}\times l^2+\beta_{12}\times h\times k+\beta_{13}\times h\times l+\beta_{23}\times k\times l)\}$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	5000	4001(3)	2500	14(1)	136(5)	23(1)	0	21(1)	0
O(4)	5000	7017(16)	2500	28(4)	101(27)	74(9)	0	50(10)	0
N(1)	4027(4)	4218(12)	2235(5)	14(2)	120(17)	25(4)	3(10)	20(4)	−5(14)
N(2)	5242(4)	3031(11)	3798(5)	14(2)	92(16)	20(3)	12(9)	19(4)	16(13)
C(1)	3428(5)	4850(16)	1425(7)	17(3)	139(22)	37(5)	20(13)	22(6)	20(20)
C(2)	2803(5)	5140(16)	1422(8)	15(3)	148(23)	41(6)	5(13)	23(6)	2(21)
C(3)	2791(5)	4819(16)	2204(8)	17(3)	146(23)	42(6)	−12(13)	28(7)	−20(21)
C(4)	3416(5)	4095(15)	3056(6)	15(2)	114(19)	32(5)	−8(12)	27(6)	−13(18)
C(5)	3450(5)	3649(16)	3910(7)	23(3)	144(24)	43(6)	−20(14)	44(7)	−9(20)
C(6)	4063(6)	2978(17)	4714(7)	27(3)	154(25)	41(6)	−14(15)	48(8)	−16(21)
C(7)	4686(5)	2745(15)	4692(7)	21(3)	123(21)	29(5)	−24(13)	31(6)	−8(18)
C(8)	5336(6)	2086(16)	5507(7)	27(3)	130(23)	32(5)	−13(15)	31(7)	6(19)
C(9)	5906(6)	1882(16)	5416(7)	24(3)	116(22)	33(5)	3(14)	21(7)	8(19)
C(10)	5848(5)	2366(15)	4557(6)	17(3)	117(21)	26(4)	5(12)	14(6)	11(17)
C(11)	4667(4)	3191(13)	3861(6)	14(2)	74(17)	20(4)	−1(10)	17(5)	4(15)
C(12)	4020(4)	3835(14)	3028(6)	13(2)	97(19)	24(4)	−9(11)	17(5)	−8(16)
N(3)	3428(5)	9638(13)	1586(6)	24(3)	153(21)	39(5)	−12(12)	38(6)	−35(17)
O(1)	3564(6)	9481(18)	2393(7)	58(5)	398(38)	49(5)	−10(22)	61(9)	−16(24)
O(2)	2872(6)	10495(18)	1025(9)	41(4)	368(37)	100(9)	−33(20)	54(10)	−72(30)
O(3)	3776(7)	9008(18)	1254(9)	74(6)	313(32)	123(10)	−89(24)	152(14)	−91(31)

atoms in the complex cation $[Cu(H_2O)(phen)_2]^{2+}$ must be situated at a special position, and the two phenanthroline ligands as well as the two nitrate ions are equivalent.

The position of the copper atom was readily determined from a three-dimensional Patterson map, which lies on the two-fold axis. The Fourier synthesis phased with the Cu atom gave positions of about a half of the lighter atoms; the remaining non-hydrogen atoms were obtained from the subsequent Fourier and difference Fourier maps. The structure was refined by the block-diagonal least-squares method, using the HBLS-IV program.[9] The weighting scheme used was:

$$w = 0.2 \text{ when } F_0 = 0$$

and

$$w = 1.0 \text{ when } F_0 > 0.$$

The atomic scattering curves were taken from the International Tables for X-ray Crystallography, Vol. III,[10] the real part of the anomalous dispersion correction ($\Delta f' = -2.1$) being applied for the neutral copper atom. Three cycles of refinements with anisotropic thermal parameters for the copper atom and isotropic for the remainder reduced the R value to 0.15 for 1835 non-zero reflections. A further two cycles of refinements with anisotropic thermal parameters for all the non-hydrogen atoms improved the R value to 0.118. In the last cycle of the calculations, the shift in any parameter was less than one-tenth of its estimated standard deviation. The final atomic coordinates and temperature factors are listed in Table 2. A comparison of the observed and calculated structure factors is given in Table 3**.

Results and Discussion

The crystal consists of the $[Cu(H_2O)(phen)_2]^{2+}$ cations and the nitrate anions. Figure 1 shows the b-axis projection of the crystal structure. The bond lengths and bond angles, with their estimated standard deviations, are given in Table 4.

Figure 2 shows a schematic drawing of the complex cation $[Cu(H_2O)(phen)_2]^{2+}$, where only two nitrogen atoms of each phenanthroline ligand are shown. As is shown in Fig. 2, the complex cation has a two-fold axis passing through the oxygen atom O(4) of the coordi-

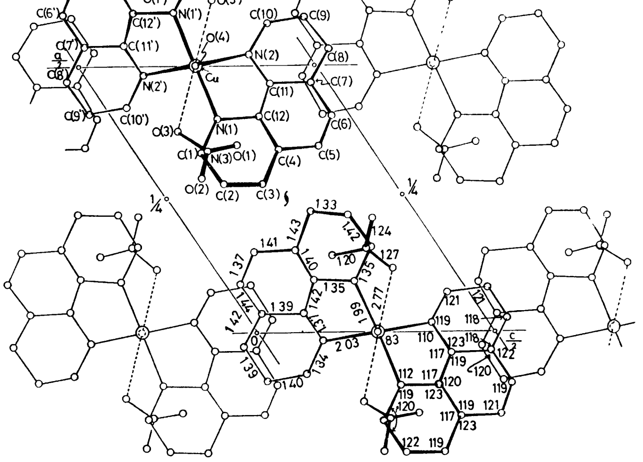

Fig. 1. The b-axis projection of the structure of $[Cu(H_2O)(phen)_2](NO_3)_2$.

** Table 3 has been deposited at the Office of the Chemical Society of Japan, Document No. 7520.

TABLE 4. BOND DISTANCES AND ANGLES WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES[a)]

Distances (d/Å)	
Cu-N(1)=1.99(1)	C(6)-C(7)=1.44(2)
Cu-N(2)=2.03(1)	C(7)-C(8)=1.42(2)
Cu-O(4)=2.18(1)	C(8)-C(9)=1.39(2)
N(1)-C(1)=1.35(2)	C(9)-C(10)=1.40(2)
N(1)-C(12)=1.35(1)	C(11)-C(12)=1.42(1)
N(2)-C(11)=1.37(1)	C(7)-C(11)=1.39(1)
N(2)-C(10)=1.34(1)	C(4)-C(12)=1.40(2)
C(1)-C(2)=1.42(2)	N(3)-O(1)=1.20(2)
C(2)-C(3)=1.33(2)	N(3)-O(2)=1.24(2)
C(3)-C(4)=1.43(2)	N(3)-O(3)=1.27(2)
C(4)-C(5)=1.42(2)	
C(5)-C(6)=1.37(2)	O(3)···O(4)=2.77(2)
Angles[b)] (φ/°)	
N(1)-Cu-N(2)=83.0(4)	C(1)-C(2)-C(3)=122(1)
N(1)-Cu-N(2′)=100.1(4)	C(2)-C(3)-C(4)=119(1)
N(1)-Cu-N(1′)=171.0(4)	C(3)-C(4)-C(5)=123(1)
N(2)-Cu-N(2′)=139.6(4)	C(3)-C(4)-C(12)=117(1)
O(4)-Cu-N(1)=85.5(4)	C(5)-C(4)-C(12)=119(1)
O(4)-Cu-N(2)=110.0(4)	C(4)-C(5)-C(6)=121(1)
Cu-N(1)-C(12)=112.0(7)	C(4)-C(12)-C(11)=120(1)
Cu-N(2)-C(11)=110.0(7)	C(5)-C(6)-C(7)=119(1)
C(1)-N(1)-C(12)=119(1)	C(6)-C(7)-C(8)=122(1)
C(10)-N(2)-C(11)=119(1)	C(6)-C(7)-C(11)=120(1)
N(1)-C(1)-C(2)=120(1)	C(7)-C(11)-C(12)=119(1)
N(1)-C(12)-C(4)=123(1)	C(7)-C(8)-C(9)=118(1)
N(1)-C(12)-C(11)=117(1)	C(8)-C(7)-C(11)=118(1)
N(2)-C(10)-C(9)=121(1)	C(8)-C(9)-C(10)=121(1)
N(2)-C(11)-C(7)=123(1)	O(1)-N(3)-O(2)=114(1)
N(2)-C(11)-C(12)=117(1)	O(2)-N(3)-O(3)=118(1)
	O(1)-N(3)-O(3)=128(1)

a) Estimated standard deviations, shown in parentheses, are right-adjusted to the last digit of the preceding number. b) Atoms with primes are related by two-fold symmetry to the corresponding unprimed atoms (see Fig. 1 for labelling of atoms).

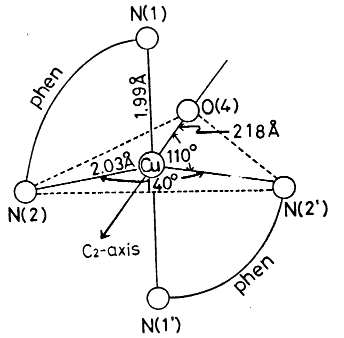

Fig. 2. A schematic drawing of the complex cation $[Cu(H_2O)(phen)_2]^{2+}$.

nated water molecule. The coordination geometry about the copper atom is a distorted trigonal bipyramid; the axial positions are occupied by N(1) and N(1′), while the Cu, N(2), N(2′), and O(4) atoms lie on the trigonal plane. The axial Cu–N bonds are 1.99 Å long and are slightly shorter than the equatorial Cu–N bonds (2.03 Å). The N(1)–Cu–O(4) angle is 85.5°; thus, the axial Cu–N bonds are not perpendicular to the trigonal plane. The angles between those axial bonds and that normal to the trigonal plane are about 10°. The angles of O(4)–Cu–N(2) and N(2)–Cu–N(2′) in the trigonal plane are 110.0 and 139.6° respectively. The N–Cu–N angles in chelate rings are 83.0°, normal for metal-phenanthroline complexes.[11–15)] An analogous stereochemistry with the chromophore $[CuN_4O]$ has been found in $[Cu(NO_3)(bipy)_2]NO_3\cdot H_2O$, where the bipy is the 2,2′-bipyridine molecule. Although these two complexes have such an analogous stereochemistry and both have the general formula of $Cu(chelate)_2(NO_3)_2\cdot H_2O$ (chelate=phen or bipy), it must be noted that the coordinating group in the fifth position is different.

The phenanthroline ligands are planar within a maximum deviation of 0.04 Å (Table 5). The dihedral angle between the best planes of these two phenanthro-

TABLE 5. THE DEVIATIONS OF THE ATOMS FROM THE LEAST-SQUARES PLANE

(X, Y, and Z are coordinates in Å along the a, b, and c* axes respectively)

Best plane through phenanthroline ligand			
$0.122X+0.938Y+0.324Z=4.74$			
N(1)	0.02 Å	C(6)	0.02 Å
N(2)	−0.04	C(7)	0.01
C(1)	0.03	C(8)	0.00
C(2)	0.00	C(9)	0.01
C(3)	−0.04	C(10)	−0.01
C(4)	−0.01	C(11)	−0.01
C(5)	0.00	C(12)	0.01
Distance from the above plane			
Cu	−0.19 Å		
Best plane through nitrate anion			
$0.456X+0.852Y+0.256Z=9.36$			
N(3)	−0.006 Å	O(1)	0.004 Å
O(2)	0.003	O(3)	0.004
Plane formed by Cu, N(1), and N(2)			
$0.006X+0.930Y+0.366Z=4.01$			

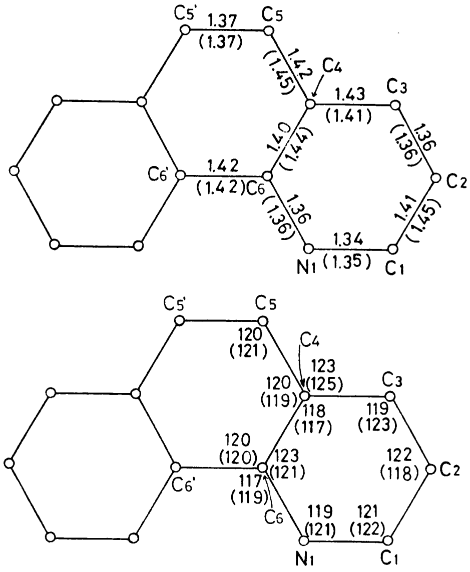

Fig. 3. Average bond lengths and bond angles in the phenanthroline ligand (values in parentheses are corresponding ones in $[Cu(phen)_3](ClO_4)_2$).

line ligands is about 40°. The bond lengths in the phenanthroline ligands range from 1.33 (2) to 1.44 (2) Å in C–C and from 1.34 (1) to 1.37 (1) Å in C–N (Fig. 1 and Table 4). Assuming that the phenanthroline ligand has a C_{2v}-symmetry, the average bond lengths and bond angles are as given in Fig. 3, where the values in parentheses are the corresponding ones in $[Cu(phen)_3](ClO_4)_2$.[11] As is shown in Fig. 3, the C(2)–C(3) and C(5)–C(5′) bond lengths are shorter than the others by 0.3—0.7 Å; the same trend has been observed in $[Cu(phen)_3](ClO_4)_2$. All the average bond lengths and angles are in good agreement with those in the $[Cu(phen)_3]^{2+}$ in view of the standard deviations.

The nitrate anions are planar (Table 5) and are linked to the water molecule in $[Cu(H_2O)(phen)_2]^{2+}$ by hydrogen bonds, which are indicated by the dotted lines in Fig. 1 (O(3)···O(4)=2.77 Å). This value is comparable to the $O(NO_3^-)\cdots O(H_2O)$ distance (2.79 Å) found in $Cu(NO_3)_2\cdot 5/2H_2O$.[16]

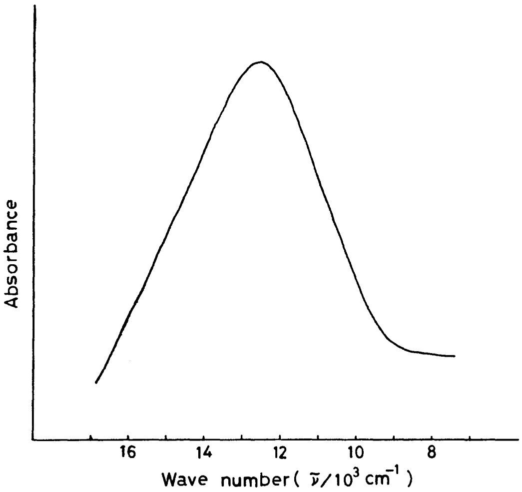

Fig. 4. Electronic reflectance spectrum of $[Cu(H_2O)(phen)_2](NO_3)_2$.

The electronic reflectance spectrum of this compound was also measured at room temperature (Fig. 4); it shows a single peak at 12.5×10^3 cm^{-1}. This is quite similar to those of $[CuI(bipy)_2]I$ and $[Cu(NH_3)(bipy)_2]X_2$ ($X=ClO_4$ or BF_4), but is clearly different from the spectrum of the trigonal-bipyramidal $[Cu(NO_3)(bipy)_2]^+$.[17] On examining the crystal structure of $[Cu(NO_3)(bipy)_2]NO_3\cdot H_2O$ in detail,[6] we can recognize, however, two more oxygen atoms at a distance of 2.8—3.0 Å from the copper atom.

The authors wish to express their thanks to Professor Hisao Kuroya and Dr. Shun'ichiro Ooi for their kind discussions throughout the present work.

References

1) C. M. Harris, T. N. Locker, and H. Waterman, *Nature*, **192**, 424 (1961).

2) F. P. Dwyer, H. A. Goodwin, and E. C. Gyarfas, *Austr. J. Chem.*, **16**, 544 (1963).

3) C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955).

4) B. R. James, M. Parris, and R. J. P. Williams, *J. Chem. Soc.*, **1961**, 4630.

5) G. H. Faye, *Can. J. Chem.*, **44**, 2165 (1966).

6) H. Nakai, S. Ooi, and H. Kuroya, This Bulletin, **43**, 577 (1970).

7) H. Nakai, *ibid.*, **44**, 2412 (1971).

8) H. Lipson and W. Cochran, "The Determination of Crystal Structures," G. Bell and Sons, London, England (1957), pp. 32—41.

9) "The Universal Crystallographic Computing System (I)," Japanese Crystallographic Association (1967).

10) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham (1962), p. 202.

11) O. P. Anderson, *J. Chem. Soc., Dalton*, **1973**, 1237.

12) P. S. Shetty and Q. Fernando, *J. Amer. Chem. Soc.*, **92**, 3964 (1970).

13) G. P. Khare and R. Eisenberg, *Inorg. Chem.*, **9**, 2211 (1970).

14) C. G. Pierpont and R. Eisenberg, *ibid.*, **9**, 2218 (1970).

15) K. R. Butler and M. R. Snow, *J. Chem. Soc., A*, **1971**, 565.

16) B. Morosin, *Acta Crystallogr.*, **B26**, 1203 (1970).

17) B. J. Hathaway, I. M. Procter, R. C. Slade, and A. A. G. Tomlinson, *J. Chem. Soc., A*, **1969**, 2219.