The Crystal Structure of Bis(pyridine-2-acetamide)copper(II) Perchlorate

Masao Sekizaki, Fumiyuki Marumo,* Kazuo Yamasaki, and Yoshihiko Saito*
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya
**The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo*

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The crystal structure of bis(pyridine-2-acetamide)copper(II) perchlorate, $Cu(paaH)_2(ClO_4)_2$, was determined from three-dimensional X-ray photographic data and refined by block-diagonal least-squares methods, using 1698 independent reflections to give $R=0.12$. The crystals are monoclinic with a space group of C2/c. There are four formula units in a unit cell with dimensions of: $a=10.957$, $b=12.178$, $c=15.566$ Å, and $\beta=108.7°$. The complex is centrosymmetric and square-planar, with two ligand molecules coordinating to the copper atom in *trans* positions through the amide-oxygen and the ring-nitrogen atoms. Two perchlorate ions coordinate weakly to the central copper atom through one of the four oxygen atoms from the top and bottom of the plane containing copper, amide-oxygen, and ring-nitrogen atoms.

In the course of studies of the bivalent metal complexes of acid amides,[1–7] X-ray crystal analyses of $[Ni(H_2O)_2(piaH)_2]Cl_2$[3] and $[Ni(pia)_2]2H_2O$[4] have revealed that the former has a structure with octahedral coordination through the amide-oxygen and ring-nitrogen atoms of the ligand, while that the latter has a structure with square-planar coordination through the amide-nitrogen and ring-nitrogen atoms, where piaH denotes pyridine-2-carboxamide. On the basis of these results and also on the basis of spectral and magnetic studies, the structures of several complexes with other acid amides have been assigned.[5–7] The copper complex of pyridine-2-acetamide (abbreviated as paaH), $Cu(paaH)_2(ClO_4)_2$, has been assigned a structure similar to $[Ni(H_2O)_2(piaH)_2]Cl_2$, *e.g.*, an octahedral structure with coordination through amide-oxygen and ring-nitrogen atoms.[7] The fifth and sixth positions of the octahedron are presumably occupied by two perchlorate ions. To confirm the assigned structure, this complex was subjected to X-ray crystal analysis.

Experimental

The crystals of the complex, $Cu(paaH)_2(ClO_4)_2$, were obtained by letting a mixture of aqueous solutions of one mole of copper perchlorate and two moles of pyridine-2-acetamide stand overnight, as has been reported previously.[7] The blue prismatic crystals were elongated along the *c*-axis. The unit-cell dimensions were determined from the higher-order reflections of Weissenberg photographs ($CuK\alpha_1$, $\lambda=1.5405$ Å). The systematic absences were *hkl* for $h+k$ odd and *h0l* for *h* and *l* odd. Hence, the space group was *C2/c* or *Cc*. The former was tentatively assumed, but it was indeed verified at a later stage of the structure analysis by the calculation of the structure factors. The crystal data are given in Table 1. Equi-inclination Weissenberg photographs were taken about [010] and [1$\bar{1}$0] up to the tenth and second layers respectively. The multiple-film technique was employed, and $CuK\alpha$ radiation was used. The cross section of the specimen used for intensity measurements was about 0.3×0.2 mm. A total of 1698 independent reflections were collected. The intensities were estimated visually and were converted to $|F|$ by applying the Lorentz, polarization,and spot-shape corrections. Absorption and extinction corrections were not made.

TABLE 1. CRYSTAL DATA

trans-Bis(pyridine-2-acetamide)copper(II) perchlorate	
$Cu(C_5H_4NCH_2CONH_2)_2(ClO_4)_2$	F.W. 534.76
Monoclinic	$a=10.957\pm0.003$ Å
	$b=12.178\pm0.006$
	$c=15.566\pm0.004$
	$\beta=108.74\pm0.02°$
	$U=1967$ Å^3
Space group	*C2/c*
$Z=4$	
$D_x=1.80$ g·cm^{-3}	
$D_m=1.79$ g·cm^{-3}	

Solution and Refinement of the Structure

The general positions are eightfold for the space group *C2/c*. The copper atoms must lie on a set of fourfold special positions, since there are only four formula units in the unit cell. The complex is thus required to have a center of symmetry or a twofold axis of rotation. The coordinates of the copper and chlorine atoms were determined from the prominent peaks in the Patterson function. The copper atoms were found to lie on the centers of symmetry. A three-dimensional electron density map was then calculated with all the terms, the signs of which were calculated on the basis of the copper and the chlorine atoms. The resulting maps showed the positions of all the lighter atoms except three oxygen atoms of a perchlorate ion. One more Fourier synthesis of the electron density gave the positions of the three remaining atoms.

At this stage it appeared that the ligand coordinates to the central atom through the ring-nitrogen and one atom of the amide group. However, it was not pos-

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Table 2. Final atomic parameters and their estimated standard deviations

Positional parameters are expressed as fractions of the lattice parameters. The estimated standard deviations are in parentheses and refer the last decimal positions of the respective values.
Thermal parameters are in the form: $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.2500	0.2500	0.0000	0.0027(02)	0.0005(02)	0.0022(01)	−0.0008(03)	0.0006(02)	0.0008(02)
Cl	0.2156(03)	0.2968(03)	0.2268(02)	0.0105(04)	0.0023(03)	0.0021(02)	−0.0033(04)	0.0047(04)	−0.0008(03)
O(1)	0.4280(07)	0.1929(07)	0.0480(06)	0.0030(07)	0.0014(06)	0.0037(04)	−0.0009(10)	0.0004(08)	0.0019(08)
O(2)	0.2322(20)	0.2357(12)	0.1569(10)	0.0469(38)	0.0085(13)	0.0074(09)	−0.0013(36)	0.0323(33)	−0.0031(17)
O(3)	0.0841(16)	0.3463(15)	0.1851(17)	0.0144(21)	0.0117(18)	0.0238(24)	0.0114(31)	−0.0010(35)	0.0109(33)
O(4)	0.1961(11)	0.2326(09)	0.2985(07)	0.0149(14)	0.0062(10)	0.0053(06)	0.0053(18)	0.0112(15)	0·0060(12)
O(5)	0.2771(20)	0.3905(12)	0.2475(12)	0.0374(36)	0.0059(13)	0.0096(11)	−0.0220(34)	0.0054(31)	−0.0005(18)
C(1)	0.2475(10)	0.0088(09)	0.0304(07)	0.0045(10)	0.0007(09)	0.0024(05)	−0.0022(13)	0.0031(12)	0.0020(10)
C(2)	0.1962(13)	−0.0976(10)	0.0114(09)	0.0083(14)	0.0009(10)	0.0042(07)	−0.0016(17)	0.0047(16)	0.0003(12)
C(3)	0.0866(12)	−0.1178(10)	−0.0642(09)	0.0057(11)	0.0021(11)	0.0037(07)	−0.0037(16)	0.0037(14)	−0.0022(12)
C(4)	0.0272(12)	−0.0294(10)	−0.1185(08)	0.0068(12)	0.0002(09)	0.0029(06)	−0.0022(14)	0.0030(13)	−0.0008(10)
C(5)	0.0792(11)	0.0707(10)	−0.0969(08)	0.0047(11)	0.0038(11)	0.0024(06)	−0.0023(16)	0.0006(12)	0.0005(11)
C(6)	0.3634(11)	0.0306(09)	0.1094(07)	0.0056(11)	0.0001(09)	0.0022(05)	−0.0016(13)	0.0003(12)	0.0016(09)
C(7)	0.4585(10)	0.1064(10)	0.0902(07)	0.0031(09)	0.0031(10)	0.0020(05)	0.0011(14)	−0.0003(11)	0.0004(10)
N(1)	0.1833(08)	0.0954(07)	−0.0248(05)	0.0046(09)	0.0006(07)	0.0013(04)	0.0003(11)	0.0014(09)	−0.0008(07)
N(2)	0.5795(10)	0.0764(09)	0.1201(09)	0.0043(10)	0.0024(09)	0.0064(08)	0.0004(13)	−0.0018(14)	0.0028(12)

sible to distinguish between the oxygen and nitrogen atoms of the amide group. Therefore, the atomic scattering factor of oxygen was applied to these atoms in the initial block-diagonal least-squares refinement. The R-value obtained was 0.32; the coordinating atom of the amide group showed a reasonable isotropic temperature factor compared with those of the other atoms of the ligand, whereas the atom of the amide group not bonded to the copper atom showed about four times as large a temperature factor as the other atoms in the ligand. Therefore, it is not appropriate to assign oxygen to the non-coordinating atom of the amide group, and subsequent refinements have been continued on the assumption of the amide-oxygen coordination.

After six cycles of block-diagonal least-squares refinements with isotropic thermal parameters, the R-value decreased to 0.22; further refinements with anisotropic thermal parameters finally reduced the R-value to 0.12. The final results show that the distance between the carbon atom, C(7), and the coordinating atom is 1.23 Å, and that the distance between C(7) and the other atom attached to C(7) is 1.31 Å (Fig. 1 and Table 3). These values correspond, respectively, to the C=O and C–N bond distances found in the related molecules.[3,4,8,9] This fact proves that the assumption of the amide-oxygen coordination is correct and that the ligand coordinates to the copper atom through the ring-nitrogen and amide-oxygen atoms. This result is in agreement with that presumed from the infrared spectral data.[7]

The final three-dimensional electron density map showed more ill-defined and lower peaks at the atomic positions of the perchlorate ion than at those of the complex cation. Moreover, the temperature factors of the atoms of the perchlorate ion are several times larger than those of the others (Table 2). These facts indicate a larger thermal motion and/or positional disorder for the former. Clearly the uncertainty in atomic positions of the perchlorate ion is responsible for the comparatively high R-value. The atomic scattering factors used for the calculations were taken from the "International Tables for X-ray Crystallography." The calculations were carried out on the FACOM 270-30 computer at the Institute for Solid State Physics, the University of Tokyo, and on the HITAC 5020E computer at the Computing Center of the University of Tokyo, using the programs of the UNICS System. The final atomic parameters are listed in Table 2. The table of the observed and calculated structure factors is kept by the Chemical Society of Japan.[10]

Description of the Structure and Discussion

The interatomic distances and angles are listed in Tables 3 and 4. The structures of the complex ion and the perchlorate ion are illustrated in Figs. 1 and 2, together with the interatomic diatances and angles. The atomic arrangement in the crystal is shown in Fig. 3 in projection along the b-axis. The complex is centrosymmetric, having two ligand molecules in *trans* positions. The copper atom is surrounded by a distorted octahedron of six coordinating atoms, four of which are the amide-oxygen atoms and the ring-nitrogen atoms of the pyridine-2-acetamide molecules. These four coordinating atoms lie on the same plane with the central copper atom. The other two weakly

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[10] The F_o-F_c table is kept as Document No. 7108 at the office of the Bulletin of the Chemical Society of Japan. A copy may be secured by citing the document number and by remitting, in advance, ¥200 for photoprints. Payment may be made by check or money order payable to: Chemical Society of Japan.

Table 3. Interatiomic distances and angles

The estimated standard deviations are in parentheses and refer to the last decimal positions of the respective values.

Cu-O(1)	1.98(1) Å	Cu-N(1)-C(1)	120.5(6)
Cu-N(1)	2.01(1)	Cu-N(1)-C(5)	121.7(7)
Cu-O(2)	2.52(2)	C(2)-C(1)-C(6)	121.2(10)
N(1)-C(1)	1.40(2)	C(1)-C(6)-C(7)	114.4(10)
C(1)-C(6)	1.48(2)	C(6)-C(7)-O(1)	123.3(10)
C(6)-C(7)	1.49(2)	C(6)-C(7)-N(2)	116.7(10)
C(7)-O(1)	1.23(2)	O(1)-C(7)-N(2)	120.0(11)
C(7)-N(2)	1.31(2)	Cu-O(1)-C(7)	124.7(8)
C(1)-C(2)	1.41(2)	C(5)-N(1)-C(1)	117.8(9)
C(2)-C(3)	1.41(2)	N(1)-C(1)-C(2)	118.5(10)
C(3)-C(4)	1.39(2)	C(1)-C(2)-C(3)	120.9(11)
C(4)-C(5)	1.34(2)	C(2)-C(3)-C(4)	118.6(11)
C(5)-N(1)	1.35(1)	C(3)-C(4)-C(5)	118.2(11)
Cl-O(2)	1.38(2)	C(4)-C(5)-N(1)	125.9(11)
Cl-O(3)	1.50(2)	Cu-O(2)-Cl	143.1(10)
Cl-O(4)	1.43(1)	O(2)-Cl-O(3)	103.1(10)
Cl-O(5)	1.31(2)	O(2)-Cl-O(4)	114.3(9)
		O(2)-Cl-O(5)	118.4(10)
N(1)-Cu-O(1)	89.9(3)°	O(3)-Cl-O(4)	101.1(8)
N(1)-Cu-O(2)	89.1(5)	O(3)-Cl-O(5)	95.9(10)
O(1)-Cu-O(2)	89.1(5)	O(4)-Cl-O(5)	118.5(9)

Table 4. Intermolecular contacts less than 3.5 Å

Molecule				
I	at	x,	y,	z
II		$1/2+x$,	$-1/2+y$,	z
III		$1/2-x$,	$1/2+y$,	$1/2-z$
IV		x,	$-y$,	$1/2+z$
V		$1-x$,	y,	$1/2-z$
VI		$1/2+x$,	$1/2-y$,	$1/2+z$

C(6)$^{\rm I}$-O(3)$^{\rm II}$	3.23(2) Å
N(2)$^{\rm I}$-O(3)$^{\rm II}$	2.97(2)
N(2)$^{\rm I}$-O(5)$^{\rm II}$	3.31(2)
N(2)$^{\rm I}$-O(4)$^{\rm V}$	3.04(2)
O(4)$^{\rm I}$-C(2)$^{\rm III}$	3.49(2)
O(4)$^{\rm I}$-C(3)$^{\rm IV}$	3.10(2)
O(5)$^{\rm I}$-C(4)$^{\rm VI}$	3.32(2)
O(5)$^{\rm I}$-C(5)$^{\rm VI}$	3.45(2)

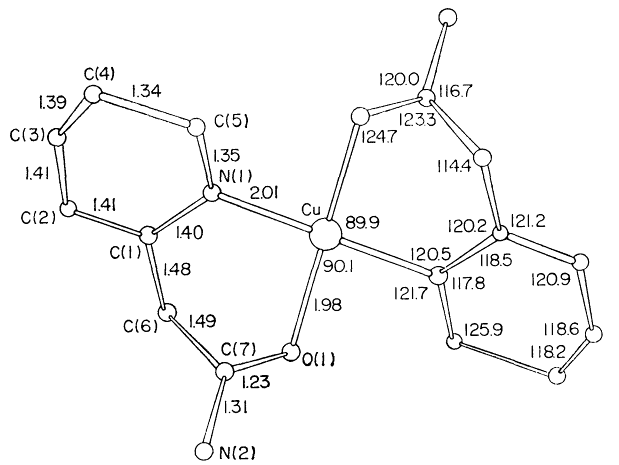

Fig. 1. Atomic arrangement, bond distances and angles of the complex ion.

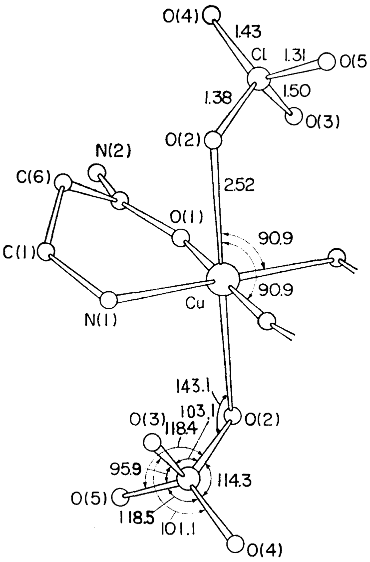

Fig. 2. Atomic arrangement, bond distances and angles of the perchlorate ion.

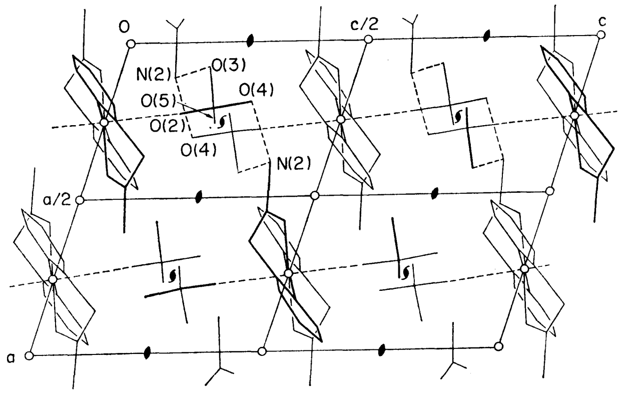

Fig. 3. Projection of the structure along the b-axis.

coordinating atoms are the oxygen atoms of the perchlorate ions, which lie on the normal through the copper atom. This general feature of the structure is completely coincident with that presumed from the spectral and magnetic data in the previous paper.[7] The equations of the coordination plane and the best-plane through the pyridine ring and the deviations of various atoms therefrom are given in Table 5. The six-membered chelate ring is not planar, but is in a boat form, a methylene carbon atom (C(6)) being off the coordination plane at 1.33 Å. On the contrary, the five-membered chelate ring and the pyridine ring in $[Ni(H_2O)_2(piaH)_2]Cl_2$, which has no methylene group, are almost perfectly coplanar.[3] The pyridine ring in the present complex does not lie on the coordination plane, but is tilted at an angle of about 33° with respect to the coordination plane in the Cu-N(1)-C(3) direction. This distortion of the ligand molecule is certainly due to an additional methylene group. The coordinate bond distances of this complex (Cu-O, 1.98; Cu-N, 2.01 Å) are not very different from those observed in $[Ni(H_2O)_2(piaH)_2]Cl_2$ (Ni-O, 2.045; Ni-N, 2.022 Å).[3]

The perchlorate ion forms a distorted tetrahedron with Cl-O distances of 1.31—1.50 Å and O-Cl-O

TABLE 5. EQUATIONS FOR THE COORDINATION PLANE AND THE BEST PLANE OF THE PYRIDINE RING AND THE DEVIATIONS OF THE ATOMS FROM THEM

(A) Coordination plane
$0.39881X+0.04916Y-0.91571Z=1.24215$
(B) The best-plane of the pyridine ring
$0.80595X-0.14657Y-0.57735Z=1.77402$
where $X=ax+cz\cos\beta$, $Y=by$ and $Z=cz\sin\beta$; x, y, and z are the fractional coordinates referred to the crystal axes.

	Deviations from (A)	Deviations from (B)
Cu	0.00 Å	—
O(1)	0.00	—
N(1)	−0.00	0.02
C(1)	0.63	−0.02
C(2)	0.62	0.01
C(3)	−0.06	−0.00
C(4)	−0.69	0.00
C(5)	−0.65	−0.01

angles of 95.9—118.5° (Fig. 2 and Table 3). One of the oxygen atoms, O(2), lies on a line through the copper atom and almost perpendicular to the coordination plane. The Cu–O(2) distance is 2.52 Å, which is comparable with the distances found for the other complexes in which a tetrahedral anion coordinates weakly as a unidentate ligand, *e.g.*, Cu–O, 2.60 Å for $Cu(en)_2(ClO_4)_2$,[11] Cu–F, 2.56 Å for $Cu(en)_2(BF_4)_2$,[12] and Cu–O, 2.62 Å for $Cu(histamine)_2(ClO_4)_2$[13]. These values support the weak coordination of the perchlorate ion in this case. Consequently, it may be appropriate to express this complex as $[Cu(ClO_4)_2(paaH)_2]$ rather than as $[Cu(paaH)_2](ClO_4)_2$. Such a weak coordination is sometimes called "semi-coordination," which means an intermediate between bonding and non-bonding states. This result supports the presence of interaction between the perchlorate ion and the copper atom presumed in the infrared spectral studies previously reported.[7]

All the complex entities are oriented in a O(2)···Cu···O(2) direction nearly parallel to the plane (010). The short contacts between N(2) and O(3) and between N(2) and O(4) are 2.97 and 3.04 Å respectively (Fig. 3 and Table 4). These contacts appear to be intermolecular hydrogen bonds of the N–H···O type. No other strong interaction seems to be present between the perchlorate and the complex ions. All the complex entities are linked with each other by these hydrogen bonds, forming layers parallel to the plane (102). These layers are connected with the semi-coordination bond of Cu–O(2).

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