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The Coordination of the Perchlorate Ion. I. The Crystal and Molecular Structure of Bis(perchlorato)bis(pyrazine-2,3-dicarboxamide)copper(II)

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Bis(perchlorato)bis(pyrazine-2,3-dicarboxamide)copper(II) has been prepared, and its crystal and molecular structure has been determined by the X-ray diffraction and the infrared spectroscopic methods. The crystals are triclinic with a space group $P\bar{1}$; $a=10.959(4)$, $b=6.970(3)$, $c=7.666(3)$ Å, $\alpha=116.63(3)$, $\beta=78.14(5)$, and $\gamma=97.27(5)^\circ$, and $Z=1$. The refinement of the crystal structure has been carried out by a block-diagonal least-squares method to give $R=0.054$ for 1727 non-zero reflections. The complex is centrosymmetric, with the two bidentate ligand molecules chelating to the copper atom in *trans* positions through the amide oxygen and pyrazine nitrogen atoms to form a square-plane. The two perchlorate ions coordinate weakly to the copper atom through the oxygen atoms from the top and bottom of this plane; thus, an elongated octahedron is formed. The complex molecules are connected to one another by N–O type hydrogen bonds to form a three-dimensional network. The infrared spectrum has been compared with that of the chloride complex. The KBr region clearly show the symmetry depression of the perchlorate ion from T_d to C_{3v} on coordination.

It is well known that a perchlorate ion scarcely coordinates to the transition metal ions. However, it sometimes acts as a unidentate ligand in the presence of organic ligands.[1–4] The present investigation has been carried out in order to ascertain the structure and properties of the coordinating perchlorate ion in the copper(II) complex of pyrazine-2,3-dicarboxamide (abbreviation, pyda) by the spectroscopic and crystallographic methods.*

Experimental

Preparation of the Complexes. *Bis(perchlorato)bis(pyrazine-2,3-dicarboxamide) copper (II),* $[Cu(ClO_4)_2(pyda)_2]$: an ethanolic solution of 2.5 g of newly prepared $Cu(ClO_4)_2\cdot 6H_2O$ was added to a hot aqueous solution of 1 g of pyda (Aldrich Chem. Co.). The mixture was, then, cooled slowly. The deep blue crystals precipitated were washed with ethanol. Yield, 1.5 g. Found: Cu, 10.67; N, 18.63; C, 24.23; H, 2.22%. Calcd for $C_{12}H_{12}N_8O_{12}CuCl_2$: Cu, 10.68; N, 18.84; C, 24.23; H, 2.03%.

Pyrazine-2,3-dicarboxamidecopper(II) Chloride, $Cu(pyda)Cl_2$: Three grams of $CuCl_2\cdot 2H_2O$, dissolved in 200 cm³ of ethanol, were quickly added to 50 cm³ of a hot aqueous solution of 1 g of pyda. After the filtration of the precipitate instantaneously formed, the solution was slowly cooled to room temperature. The yellowish-green powder thus obtained was washed with ethanol. Yield, 1.2 g. Found: Cu, 21.18; N, 18.28; C, 23.67; H, 2.24%. Calcd for $C_6H_6N_4O_2CuCl_2$: Cu, 21.14; N, 18.64; C, 23.97; H, 2.01%.

Measurement of the Infrared Spectra. A JASCO DS-402G spectrometer and a Hitachi EPI-L spectrometer were used in the 200—4000 cm⁻¹ region. The samples were suspended in Nujol and HCB mulls.

Crystallographic Measurement. A crystal of 0.2×0.1×0.1 mm was selected. The intensities were measured on a Philips PW1100 automatic four-circle diffractometer with Cu $K\alpha$ radiation ($\lambda=1.5418$ Å) monochromated by a graphite plate. The θ-2θ scan technique was used at a scan rate of 0.0668°/s in θ, with a scan width of $(1.0+0.3\tan\theta)^\circ$. The intensities of the three reference reflections, monitored every 2 h, remained constant within the limits of experimental error during data collection. Of 1803 independent reflections measured up to $\theta=78^\circ$, 1727 with $|F|>3\sigma$ were used for the structure analysis. No corrections were made for absorption and extinction effects ($\mu r=0.3$). The cell dimensions were refined on the diffractometer by a least-squares method using the 2θ values of 25 reflections.

Crystal Data: $Cu(ClO_4)_2\{C_4N_2H_2(CONH_2)_2\}_2$. F.W.=594.73. Triclinic, $a=10.959(4)$, $b=6.970(3)$, $c=7.666(3)$ Å, $\alpha=116.63(3)$, $\beta=78.14(5)$, $\gamma=97.27(5)^\circ$. $U=511.9(3)$ Å³. $D_x=1.929$ g cm⁻³. $Z=1$. Space group $P\bar{1}$. $\mu=47$ cm⁻¹ (Cu $K\alpha$ radiation, $\lambda=1.5418$ Å).

Determination and Refinement of the Crystal Structure

The coordinates of the copper and the chlorine atoms were determined from a Patterson map; successive Fourier syntheses gave the approximate skeletal structure. The copper atom occupies the special positions of the triclinic cell. The block-diagonal least-squares refinement was carried out based on 1727 non-zero reflections. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[5] After several cycles of refinement with isotropic temperature factors, the R-value became 0.15. Anisotropic temperature factors were, then, introduced for all the non-hydrogen atoms. The R-value was reduced to 0.058. The hydrogen atoms were obtained from the difference-Fourier synthesis. Their positional parameters were refined with isotropic temperature factors of 4.0 Å². The final R-value was 0.054.

The final atomic parameters are listed in Table 1. A list of the observed and calculated structure amplitudes has been deposited with the Chemical Society of Japan (Document No. 8108).

The refinement of the structure and the drawing of thermal ellipsoids were carried out with HBLS-IV[6] and ORTEP[7] programs respectively. The other calculations were carried out with programs written by the author. A FACOM 230-75 computer at the Computation Center of Nagoya University and a FACOM M-160 computer at the Data Processing Center of Kanazawa University were used.

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* The author has noticed a report on the crystal structure of the same complex. Its conclusion is, however, different from the present one. The details will be discussed later in the present report.

Table 1a. Final parameters of non-hydrogen atoms ($\times 10^4$)

The thermal parameters are in the form: $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$.

The estimated standard deviations are in parentheses in this table and the other subsequent tables.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0	0	0	41(01)	274(04)	231(03)	−37(03)	−80(03)	366(05)
Cl	−1786(01)	4650(02)	3544(02)	48(01)	133(03)	147(03)	−8(03)	−40(03)	138(05)
N(1)	1738(03)	1004(06)	341(06)	24(03)	136(11)	131(10)	−7(09)	−37(09)	171(17)
C(2)	2214(04)	380(07)	1483(07)	31(04)	106(12)	99(11)	7(10)	−24(10)	119(18)
C(3)	3425(04)	1086(08)	1845(07)	26(04)	157(13)	120(12)	−4(10)	−40(10)	165(20)
N(4)	4103(04)	2343(08)	1052(07)	34(04)	239(14)	190(12)	−51(11)	−63(10)	307(22)
C(5)	3605(05)	2884(10)	−91(09)	43(05)	263(18)	234(17)	−66(14)	−61(13)	392(29)
C(6)	2400(05)	2228(09)	−450(08)	43(04)	186(15)	169(14)	−25(12)	−54(12)	273(23)
C(7)	1231(04)	−979(08)	2198(08)	34(04)	155(13)	124(12)	−22(11)	−46(11)	180(20)
C(8)	4117(05)	653(09)	3170(08)	31(04)	225(16)	177(14)	−1(12)	−52(12)	266(25)
O(7)	167(03)	−1139(07)	1769(06)	28(03)	338(14)	268(12)	−76(09)	−95(09)	516(22)
N(7)	1467(04)	−1962(08)	3178(07)	43(04)	228(14)	227(13)	−56(11)	−95(11)	374(23)
O(8)	3791(04)	−816(08)	3639(07)	52(04)	379(16)	384(15)	−109(12)	−181(12)	641(27)
N(8)	5094(04)	1945(08)	3704(08)	41(04)	286(16)	240(14)	−64(12)	−123(12)	304(25)
O(1)	−659(05)	3484(10)	2847(09)	89(05)	477(22)	357(17)	269(17)	−114(15)	−117(30)
O(2)	−2497(04)	3960(07)	1964(07)	92(05)	256(13)	197(11)	−8(12)	−117(11)	192(20)
O(3)	−2530(05)	4306(08)	5167(08)	102(05)	364(17)	299(14)	−93(14)	−91(13)	542(26)
O(4)	−1466(05)	6890(07)	4239(07)	142(06)	172(12)	201(12)	−124(13)	−29(13)	148(19)

Table 1b. Positional parameters of the hydrogen atoms ($\times 10^3$)

	x	y	z
H-C(5)	417(07)	377(12)	−78(12)
H-C(6)	200(07)	256(12)	−131(12)
Ha-N(7)	86(07)	−290(13)	346(12)
Hb-N(7)	222(07)	−170(12)	356(12)
Ha-N(8)	502(07)	332(12)	492(12)
Hb-N(8)	585(07)	168(13)	300(12)

Results and Discussion

Crystal Analysis. The molecular structure of the complex is shown in Fig. 1, with anisotropic thermal ellipsoids of the non-hydrogen atoms. The bond lengths are also shown in this figure. The bond angles are listed in Table 2.

The complex is centrosymmetric, with two ligand molecules in *trans* positions. Each of the ligand molecules acts as bidentate through one of the pyrazine nitrogen atoms and the oxygen atom of the *ortho* amide group, thus forming a five-membered chelate ring. The four coordinating atoms form a square-plane around the copper atom. The distances of the coordination bonds are similar to those of the other copper amide complexes.[2,8,9]

The oxygen atom of the perchlorate ion lies on the normal line of this plane passing through the copper atom. The distance between the copper and the oxygen atom is 2.495 Å. This value is larger than those of the usual coordination-bond lengths on the square-plane. However it is smaller than those of the other perchloratocopper(II) complexes (2.61 Å for $[Cu(ClO_4)_2(en)_2]$[1] or 2.52 Å for $[Cu(ClO_4)_2(paaH)_2]$,[2] where paaH denotes 2-pyridylacetamide).

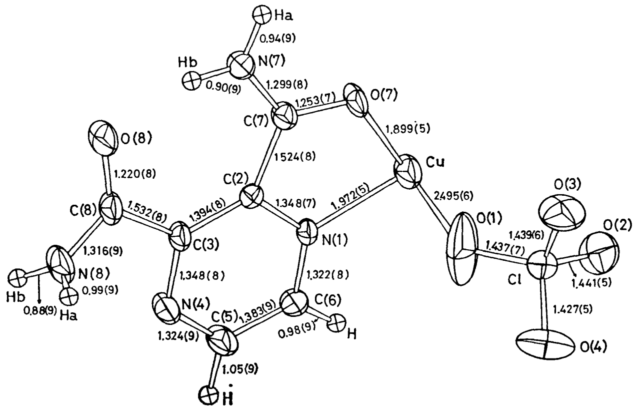

Fig. 1. Structure of the asymmetric unit with the bond lengths (l/Å) and the e.s.d.'s.
Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are drawn as spheres with a diameter of 0.2 Å.

Thus, the complex forms a distorted octahedron elongated to the perchlorate oxygen atoms.

The complex molecule is arranged as shown in Fig. 2, with the copper atom occupying the special position of the triclinic unit cell. The hydrogen bonds are listed in Table 3.

The uncoordinated amide group is hydrogen-bonded to that of the neighboring molecule through $O(8)\cdots N(8)^{i}$ to form a column in the [101] direction. The perchlorate ions connect these columns by the hydrogen bonds through $O(4)\cdots N(7)^{iv}$, $O(2)^{ii}\cdots N(8)$, and $O(3)^{ii}\cdots N(8)$. The van der Waals interactions shorter than 3.2 Å are also observed around the anion. The [101] columns are thus combined with one another by these interactions through the perchlorate ions, thus forming a three-dimensional network.

The perchlorate ion is almost a regular tetrahedron.

Table 2. Bond angles (φ/°)

N(1)-Cu-O(7)	81.9(2)	C(3)-N(4)-C(5)	118.9(6)	C(3)-C(8)-O(8)	121.8(6)
N(1)-Cu-O(1)	87.5(2)	N(4)-C(5)-C(6)	121.5(7)	C(3)-C(8)-N(8)	114.7(6)
O(1)-Cu-O(7)	90.6(3)	C(5)-C(6)-N(1)	119.2(6)	O(8)-C(8)-N(8)	123.5(7)
Cu-N(1)-C(2)	115.0(4)	C(3)-C(2)-C(7)	132.4(5)	O(1)-Cl-O(2)	110.0(4)
Cu-N(1)-C(6)	123.6(4)	N(1)-C(2)-C(7)	109.2(5)	O(1)-Cl-O(3)	110.4(4)
Cu-O(1)-Cl	133.7(4)	C(2)-C(7)-O(7)	116.6(5)	O(1)-Cl-O(4)	108.9(4)
Cu-O(7)-C(7)	116.8(4)	C(2)-C(7)-N(7)	122.7(6)	O(2)-Cl-O(3)	109.4(4)
C(2)-N(1)-C(6)	121.4(5)	O(7)-C(7)-N(7)	120.7(6)	O(2)-Cl-O(4)	110.0(3)
N(1)-C(2)-C(3)	118.3(5)	C(2)-C(3)-C(8)	126.7(5)	O(3)-Cl-O(4)	108.1(4)
C(2)-C(3)-N(4)	120.6(5)	N(4)-C(3)-C(8)	112.7(5)		

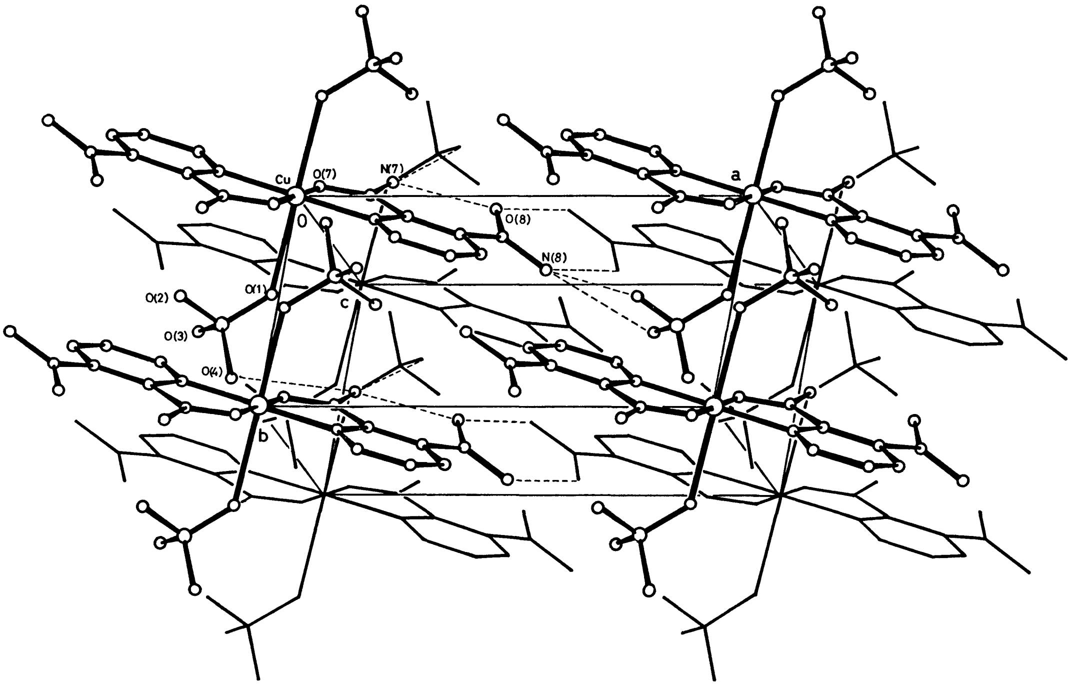

Fig. 2. Crystal structure. Dashed lines exhibit hydrogen bonds.

Table 3. Hydrogen bonds

A	H	$D^{a)}$	A-D(l/Å)	A-H(l/Å)
O(8)	Hb	$N(7)^{b)}$	2.618(8)	1.76(9)
O(8)	Ha	$N(8)^{i}$	2.993(8)	2.98(9)
$O(2)^{ii}$	Hb	N(8)	3.164(8)	2.50(9)
$O(3)^{ii}$	Ha	N(8)	3.034(8)	2.71(9)
O(3)	Hb	$N(7)^{iii}$	2.930(8)	2.50(9)
O(4)	Ha	$N(7)^{iv}$	3.239(7)	2.49(9)

a) A, Hydrogen acceptor; D, Hydrogen donor.

b) Key to symmetry operation.

No mark	x	y	z
i	$1-x$	$-y$	$1-z$
ii	$1+x$	y	z
iii	$-x$	$-y$	$1-z$
iv	x	$1+y$	z

The thermal vibrations of the oxygen atoms are larger than those of the other atoms; especially, the coordinated oxygen atom shows a large anisotropy normal to the coordination bond.

Infrared Spectra. The spectrum in the 700—4000 cm^{-1} region has given only poor results because of too many unassignable bands. But that in the 200—700 cm^{-1} region has given important information on the coordination of the perchlorate ion. It is shown in Fig. 3, together with some tentative assignments.[10,11] Those of the free ligand and the chloride complex are also shown for the sake of comparison.

Most of the bands of the free ligand are also observed in both the complexes. On coordination, some new peaks appear; they are marked with e in Fig. 3. Furthermore, the perchlorato complex gives a broad doublet at *ca.* 580 cm^{-1} and two weak bands at 462 and 431 cm^{-1} (marked with f). They must be due to the unidentately coordinating perchlorate ion. Of the four normal vibrations of the free perchlorate ion, two exist in this region (*ca.* 460 and 610 cm^{-1});[12,13] the latter is infrared-active. If the symmetry is lowered to C_{3v} on coordination, the former becomes infrared-active and the latter splits into two bands. The 580 cm^{-1} doublet is assigned a split band, and either of the two bands at 462 and 431 cm^{-1} corresponds to the former.

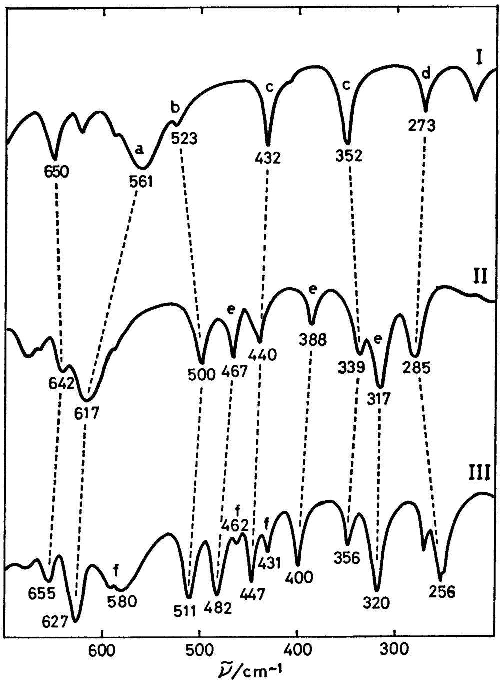

Fig. 3. Infrared spectra of free pyda(I), Cu(pyda)-Cl_2(II), and $[Cu(ClO_4)_2(pyda)_2]$ (III).
a: C–O in-plane bending, b: C–O out-of-plane bending, c: pyrazine ring deformation ,d: pyrazine-amide torsion, e: skeletal vibrations due to octahedral coordination, f: normal vibrations of the perchlorate ion.

Comment on the Report by Mondal and Ray[14)]

In the course of this investigation, Mondal and Ray reported the crystal structure of the same complex by the photographic method. According to them, the crystal is triclinic with the space group of $C\bar{1}$ and $Z=2$; the structure is square-planar without any coordination of the ClO_4^- ion.

The space group $C\bar{1}$ can be converted to $P\bar{1}$ by means of the following formula on the unit-cell vectors:

$$\boldsymbol{a} = \boldsymbol{c}_r,$$

$$\boldsymbol{b} = (\boldsymbol{a}_r+\boldsymbol{b}_r)/2,$$

and

$$\boldsymbol{c} = (\boldsymbol{b}_r-\boldsymbol{a}_r)/2,$$

where $\boldsymbol{a}_r$, *etc.* are as defined by Mondal and Ray. The lattice constants thus converted are: $a=11.06$, $b=6.80$, $c=7.58$ Å, $\alpha=116.06$, $\beta=76.68$, and $\gamma=97.33°$, which are approximately coincident with the results of the present investigation.

The ClO_4^- ion indeed seems to be non-coordinated, because the atomic parameters given by them certainly show that the anion is far from the complex cation. However the contact between the cation (x,y,z) and the anion $(x-1/2, y-1/2, z)$ is short so that one of the oxygen atoms of the latter approaches the copper atom with the distance of 2.46 Å, which undoubtedly indicates the weak coordination of the anion. Furthermore, although they have stated that there are no hydrogen bonds around the anion, some short contacts are observed between the anion and the neighboring complex molecules. Perhaps they might have forgotten the discussion of the intermolecular interaction in the unit cell of $C\bar{1}$. A set of the XDC[15)] converts the positional parameters of the anion so that the anion is near the complex cation. The bond distances and angles less than 2.5 Å calculated by these parameters agree with the results of the present investigation within the limits of experimental error, including the Cu–O weak coordination bond. It is regrettable that, although Mondal and Ray obtained correct data by means of a troublesome photographic method, they gave an incorrect conclusion as to the molecular structure.

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References

1) A. Pajunen, *Suomen Kemistilehti, Sect. B*, **40**, 32 (1967).
2) M. Sekizaki, F. Marumo, K. Yamasaki, and Y. Saito, *Bull. Chem. Soc. Jpn.*, **44**, 1731 (1971).
3) M. Sekizaki, K. Yamasaki, and K. Hayashi, *Nippon Kagaku Zasshi*, **91**, 1191 (1970).
4) M. Sekizaki, *Ionics*, Ionics Co., Ltd., Tokyo, **6**, 23 (1980).
5) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV.
6) T. Ashida, "Universal Crystallographic Computation Program System (UNICS)," ed by T. Sakurai, The Crystallographic Society of Japan, Tokyo (1967).
7) C. K. Johnson, Oak Ridge National Laboratory Report ORNL-3794 (1965); K. Sasaki, "ORTEP-II(NUNICS)," Library Program of the Computation Center of Nagoya University.
8) M. Sekizaki, *Acta Crystallogr., Sect. B*, **29**, 327 (1973).
9) M. Sekizaki, *Bull. Chem. Soc. Jpn.*, **47**, 1447 (1974).
10) M. Sekizaki and K. Yamasaki, *Spectrochim. Acta, Part A*, **25**, 475 (1969).
11) M. Sekizaki and K. Yamasaki, *Revue de Chimie Minérale*, **6**, 255 (1969).
12) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley-Intersc. (1970), p. 106.
13) M. Procter, B. J. Hathaway, and P. Nicholls, *J. Chem. Soc., A*, **1968**, 1678.
14) M. Mondal and S. Ray, *Acta Crystallogr., Sect. B*, **33**, 2297 (1977).
15) Cambridge Crystallographic Data Base, TOOL-IR Crystallographic Data Centre (XDC), The University of Tokyo.