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The Crystal Structure of Bis(pyrazine-2-carboxamide)copper(II) Perchlorate

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The crystal structure of bis(pyrazine-2-carboxamide)copper(II) perchlorate, $Cu(pyaH)_2(ClO_4)_2$, has been determined from three-dimensional X-ray photographic data and refined by block-diagonal least-squares methods to give $R = 0.08$ for the 876 observed reflexions. The crystals are monoclinic with space group $P2_1/a$. There are two formula units in a unit cell of dimensions: $a = 10.36$, $b = 9.89$, $c = 8.77$ Å and $\beta = 110.7°$. The complex is centrosymmetric with two ligand molecules chelating to the central copper atom in *trans* positions through the amide oxygen atoms and the *ortho* nitrogen atoms of the rings. This part has a square-planar structure and the *meta* nitrogen atoms of the pyrazine ring of two neighbouring complex ions coordinate weakly to the central copper atom from the top and bottom of the coordination plane, thus completing octahedral coordination. Perchlorate ions do not coordinate to the copper atom but are bonded to the amide nitrogen atom of the ligand molecule by weak hydrogen bonds.

Introduction

In the course of studies on the bivalent metal complexes of acid amides, X-ray crystal analyses of $[Ni(pia)_2]2H_2O$ (Nawata, Iwasaki & Saito, 1967), $[Ni(H_2O)_2(piaH)_2]Cl_2$ (Masuko, Nomura & Saito, 1967), $[Cu(H_2O)_2(piaH)_2]Cl_2$ (Brown, MacSween, Mercer & Sharp, 1971) and $[Cu(ClO_4)_2(paaH)_2]$ (Sekizaki, Marumo, Yamasaki & Saito, 1971) have revealed that the first complex has a structure with square-planar coordination through the amide nitrogen and ring nitrogen atoms of the ligand, while the remaining three have a structure with octahedral or distorted octahedral coordination through the amide oxygen and ring nitrogen atoms where piaH and paaH denote pyridine-2-carboxamide and pyridine-2-acetamide respectively.

On the basis of these structure determinations and of spectral and magnetic studies (Sekizaki, Tanase & Yamasaki, 1969; Sekizaki & Yamasaki, 1969a; Sekizaki & Yamasaki, 1970) it has been proposed that bis (pyrazine-2-carboxamide)copper(II) perchlorate, $Cu(pyaH)_2(ClO_4)_2$, has a chelate structure with coordination through the amide oxygen and ring nitrogen atoms (Sekizaki & Yamasaki, 1969b). It was, however, very difficult to prove whether this complex has a square-planar structure by the coordination of pyrazine-2-carboxamide alone or a distorted octahedral

structure by the coordination of some other groups in addition to the two ligand molecules. This complex was subjected to X-ray crystal analysis in order to establish the stereochemical structure and to compare it with that of $[Cu(ClO_4)_2(paaH)_2]$.

In the present paper the nitrogen atom of the pyrazine ring at the *ortho* position with respect to the carbon atom bonded to an amide group will be called the *ortho* nitrogen, and the other nitrogen atom at the *meta* position the *meta* nitrogen.

Experimental

The complex, $Cu(pyaH)_2(ClO_4)_2$, is obtained as blue crystals on letting a mixture of aqueous solutions of one mole of copper perchlorate and two moles of pyrazine-2-carboxamide stand overnight (Sekizaki & Yamasaki, 1969b). The unit-cell dimensions were determined from higher-order reflexions on Weissenberg photographs (Cu $K\alpha_1$, $\lambda = 1.5405$ Å) The systematic absences are $h0l$ with h odd and $0k0$ with k odd. Hence the space group is $P2_1/a$. Equi-inclination integrated Weissenberg photographs were taken about the a and b axes up to the 3rd and 7th layers respectively. Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) was used. The intensities were estimated visually and were converted to $|F|$ by applying the Lorentz and polarization corrections. Absorption and extinction corrections were not made. A total of 876 independent non-zero reflexions were collected.

The crystal data are: $Cu(C_4H_3N_2CONH_2)_2(ClO_4)_2$,

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Table 1. *Observed and calculated structure factors*

First column is l, followed by $|10F_o|$ and $10F_c$. $|F_o| > 6\cdot3$, $w = 1\cdot0$; $|F_o| \le 6\cdot3$, $w = 0\cdot5$ (marked with *).

[Table of structure factors — dense columns of numeric data not individually legible]

F.W. 508·68, monoclinic, $a = 10\cdot36 \pm 0\cdot01$, $b = 9\cdot89 \pm 0\cdot01$, $c = 8\cdot77 \pm 0\cdot01$ Å, $\beta = 110\cdot7 \pm 0\cdot1°$, $U = 840 \pm 3$ Å^3, $D_m = 2\cdot005$, $D_x = 2\cdot011$ g cm^{-3}, $Z = 2$.

Solution and refinement of the structure

The copper atom must lie on a set of twofold special positions since there are only two formula units in a unit cell. The complex is thus required to have a centre of symmetry. The coordinates of the chlorine atoms were determined from the prominent peaks in the Patterson map; those of the other atoms except hydrogens were determined from three-dimensional electron-density maps calculated with all the terms, the signs of which were calculated on the basis of the copper and chlorine atoms.

After five cycles of block-diagonal least-squares refinement with isotropic thermal parameters, the R value became 0·12. Further refinements with anisotropic thermal parameters finally reduced the R value to 0·08.

The atomic scattering factors used for the calculations were taken from *International Tables for X-ray Crystallography* (1962). The calculations were carried out on the HITAC 5020E computer at the Computer Centre of the University of Tokyo, the FACOM 230-60 computer, at the Data Processing Centre of Kyoto University and the FACOM 230-60 computer at the Computation Centre of Nagoya University using the programs of the UNICS system. The program named *ATLAS* written by A. Furusaki and others at Kwansei Gakuin University was also used for the calculation of the electron-density map. The observed and calculated structure factors are listed in Table 1, and the final atomic parameters in Table 2.

Discussion

Perspective drawings of the complex and perchlorate ions are presented in Fig. 1, together with the inter-

Table 2. *Final atomic parameters and their estimated standard deviations*

Values are given × 10⁴.
Positional parameters are expressed as fractions of the lattice parameters. The estimated standard deviations are in parentheses and refer to the last decimal positions of the respective values in this table and subsequent tables. Thermal parameters are in the form:

$$\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})].$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0	0	0	43 (1)	49 (1)	57 (1)	−42 (4)	−49 (2)	−5 (7)
Cl	3504 (1)	−62 (2)	3650 (2)	63 (1)	60 (3)	108 (3)	−0 (5)	−63 (2)	41 (10)
O(1)	−472 (3)	342 (1)	2341 (5)	43 (2)	40 (1)	68 (1)	−22 (11)	−38 (4)	2 (19)
O(2)	4674 (4)	328 (4)	2288 (7)	104 (3)	132 (8)	159 (7)	−1 (9)	102 (3)	38 (34)
O(3)	2886 (1)	1100 (3)	4640 (7)	96 (7)	102 (13)	183 (15)	−12 (18)	−86 (7)	−152 (32)
O(4)	3836 (1)	−1034 (1)	4668 (1)	193 (11)	142 (18)	295 (22)	44 (26)	−259 (4)	201 (44)
O(5)	2467 (3)	−645 (2)	3083 (3)	136 (9)	95 (7)	215 (9)	−91 (20)	−202 (12)	−46 (33)
N(1)	1589 (2)	1212 (3)	−166 (2)	48 (2)	20 (3)	51 (2)	−6 (12)	−38 (3)	−4 (22)
N(2)	4 (3)	1651 (4)	4155 (4)	50 (5)	76 (7)	59 (7)	−27 (14)	−11 (6)	−41 (27)
N(3)	3510 (1)	3017 (3)	57 (1)	40 (3)	31 (4)	78 (5)	−19 (12)	−32 (6)	21 (24)
C(1)	1484 (1)	1732 (1)	1291 (2)	31 (3)	31 (3)	57 (3)	14 (13)	−26 (5)	−6 (26)
C(2)	2438 (3)	2675 (4)	1401 (5)	56 (3)	52 (3)	65 (4)	−20 (17)	−32 (7)	9 (31)
C(4)	3645 (2)	2448(3)	−1352 (3)	41 (3)	39 (6)	89 (7)	0 (17)	−58 (4)	24 (30)
C(5)	2645 (2)	1529 (3)	−1507 (5)	38 (4)	29 (7)	87 (9)	0 (15)	−22 (4)	43 (29)
C(6)	271 (2)	1220 (3)	2671 (2)	38 (5)	17 (5)	45 (7)	40 (14)	−17 (7)	25 (26)

atomic distances and angles and thier estimated standard deviations. The intermolecular contacts are listed in Table 3. The atomic arrangement in the crystal is shown in Figs. 2 and 3 in projection along the *b* and *c* axes respectively.

Table 3. *Intermolecular contacts less than* 3·5 Å

O(1¹)–O(3ⁱⁱ)*	3·258 (5) Å	C(2¹)–O(4ⁱⁱⁱ)	3·469 (5) Å
N(2¹)–O(5ⁱⁱ)	3·004 (4)	Cuⁱ—N(3ⁱᵛ)	2·485 (2)
Cuⁱ—N(3ⁱⁱⁱ)	2·485 (2)	Cuⁱ—C(2ⁱᵛ)	3·396 (4)
Cuⁱ—C(2ⁱⁱⁱ)	3·396 (4)	Cuⁱ—C(4ⁱᵛ)	3·305 (2)
Cuⁱ—C(4ⁱⁱⁱ)	3·305 (2)	O(1¹)–N(3ⁱᵛ)	3·040 (4)
O(1¹)–N(3ⁱⁱⁱ)	3·289 (4)	O(1¹)–C(2ⁱᵛ)	3·236 (6)
O(1¹)–C(4ⁱⁱⁱ)	3·371 (5)	N(1¹)–N(3ⁱᵛ)	3·215 (3)
O(5¹)–C(4ⁱⁱⁱ)	2·902 (3)	C(6¹)–N(3ⁱᵛ)	3·478 (3)
O(5¹)–C(5ⁱⁱⁱ)	3·138 (4)	N(2¹)–O(2ⁱᵛ)	3·481 (7)
N(1¹)–N(3ⁱⁱⁱ)	3·162 (3)	N(2¹)–O(3ⁱᵛ)	3·046 (4)
O(3¹)–O(4ⁱⁱⁱ)	3·289 (3)	C(1¹)–O(2ⁱᵛ)	3·402 (6)
N(2¹)–O(4ⁱⁱⁱ)	2·937 (4)	C(2¹)–O(2ⁱᵛ)	3·336 (7)

* The subscripts are same as those used in Fig. 2.

The complex is centrosymmetric having two ligand molecules in *trans* positions. The ligands coordinate

to the copper atom through the amide oxygen atoms, O(1), and the *ortho* nitrogen atoms of the pyrazine rings, N(1). These four coordinating atoms lie on the same plane including the central copper atom (coordination plane). All the other atoms of the complex ion lie almost on the coordination plane and their deviations from it do not exceed 0·3 Å as shown in Table 4.

Table 4. *Equation for the coordination plane and the deviations of the atoms of the complex ion from it*

Equation: $0.6034x - 0.7947y + 0.0659z = 0.0$

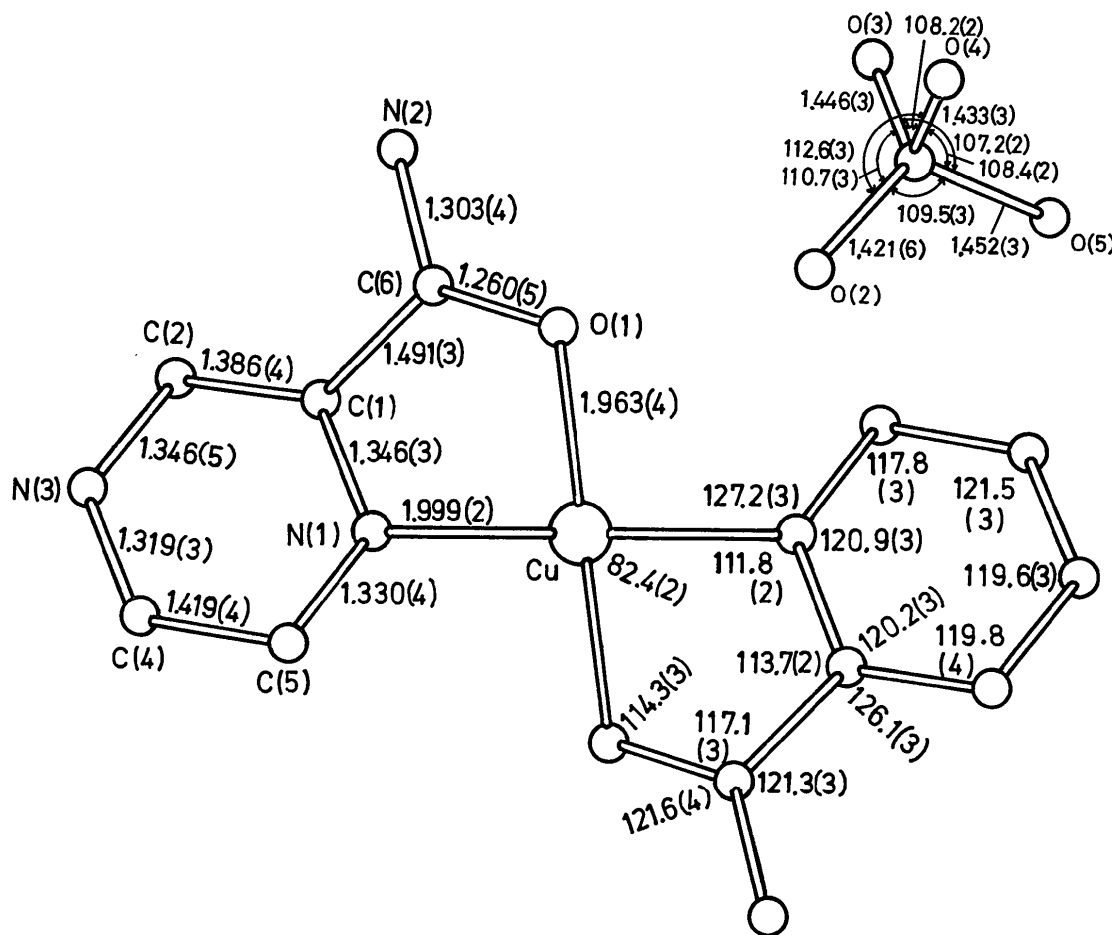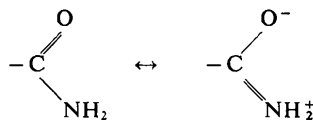|	Deviation
Cu	0·000 Å
O(1)	0·000
N(1)	−0·000
N(2)	−0·294
N(3)	−0·164
C(1)	−0·123
C(2)	−0·242
C(4)	0·028
C(5)	0·088
C(6)	−0·146

Fig. 1. Atomic arrangement, bond distances and angles with their estimated standard deviations. The estimated standard deviations are expressed in a similar way as in Table 2.

The N(3) atoms of two neighbouring complex ions coordinate to the copper atom weakly with the Cu–N(3) distance of 2·485 Å, thus completing a distorted octahedral coordination. The complex ions form a two-dimensional network through these Cu–N(3) bonds.

The perchlorate ion lies in the meshes of this network, and does not coordinate to the copper atom, because all the oxygen atoms of the perchlorate ion are more than 4 Å from the nearest copper atom. Of these oxygen atoms, however, O(4^{iii}) and O(5^{ii}) approach at 2·937 and 3·004 Å respectively, to N(2^{i}), and these oxygen atoms lie almost on the best plane of the amide group. The lines through N(2^{i}) and O(4^{iii}) and through N(2^{i}) and O(5^{ii}) make angles of about 120° with the C(6^{i})–N(2^{i}) bond. These facts suggest that O(4) and O(5) are weakly held to N(2) through hydrogen bonds.

The geometry of the amide group is compared with that of the free ligand and of the other amide compounds in Table 5. The difference between C=O and C–N bond distances in the present complex is much smaller than those observed in other compounds as well as in the free ligand. Such a small difference suggests that the resonance,

$$-C\overset{\displaystyle O}{\underset{\displaystyle NH_2}{\Big\diagdown}}\quad \leftrightarrow\quad -C\overset{\displaystyle O^-}{\underset{\displaystyle NH_2^+}{\Big\diagup}}$$

is more predominant in the present complex than in the other compounds listed in Table 5.

Melsom, 1969), etc. in which either the coordination or the hydrogen bonding does not occur.

When the structures of [Cu(ClO$_4$)$_2$(paaH)$_2$] and Cu(pyaH)$_2$(ClO$_4$)$_2$ are compared, the following points are to be noted:

(1) Both complexes have a distorted octahedral structure with the coordination of two ligand molecules in *trans* positions through amide oxygen and ring nitrogen atoms.

(2) The pyridine ring of the former complex is tilted at an angle of about 33° with respect to the coordination plane in the Cu–N(1) direction, whereas the pyrazine ring and the coordination plane of the latter are almost coplanar.

(3) Above and below the coordination plane, a perchlorate ion coordinates to the central atom through one of the oxygen atoms in the former complex, whereas the two neighbouring complex ions coordinate through the *meta*-nitrogen atoms of their ligands in the latter complex. The perchlorate ions in the latter are held only with weak hydrogen bonds.

(4) The perchlorate ion is considerably distorted in the former, whereas its shape is almost regular tetrahedral in the latter.

Table 5. *The* C=O *and* C–N *distances of some amide compounds*

	C=O	C–N	Reference
piaH	1·24 Å	1·33 Å	1
[Ni(H$_2$O)$_2$(piaH)$_2$]Cl$_2$	1·24	1·31	2
[Cu(H$_2$O)$_2$(piaH)$_2$]Cl$_2$	1·26	1·36	3
[Cu(ClO$_4$)$_2$(paaH)$_2$]	1·23	1·31	4
CH$_2$ \\ CHCONH$_2$ CH$_2$ /	1·26	1·33	5
α-pyaH	1·31	1·24	6
β-pyaH	1·33	1·23	7
Cu(pyaH)$_2$(ClO$_4$)$_2$	1·26	1·30	Present work

References 1. Takano, Sasada & Kakudo (1966)
2. Masuko, et al. (1967)
3. Brown, et al. (1971)
4. Sekizaki, et al.(1971)
5. Long, Maddox & Trueblood (1969)
6. Takaki, Sasada & Watanabé (1960)
7. Rø & Sørum (1972)

The bond distances and angles of the perchlorate ion are 1·42–1·45 Å and 107·2–112·6° (Fig. 1). These values indicate that the perchlorate ion is only slightly distorted and its shape is almost that of a regular tetrahedron. Such a small distortion is observed in KBrO$_4$ (Siegel, Tani & Appelman, 1969), KBF$_4$ (Brunton, 1969), Cu(pyridine N-oxide)$_4$(ClO$_4$)$_2$ (Lee, Brown &
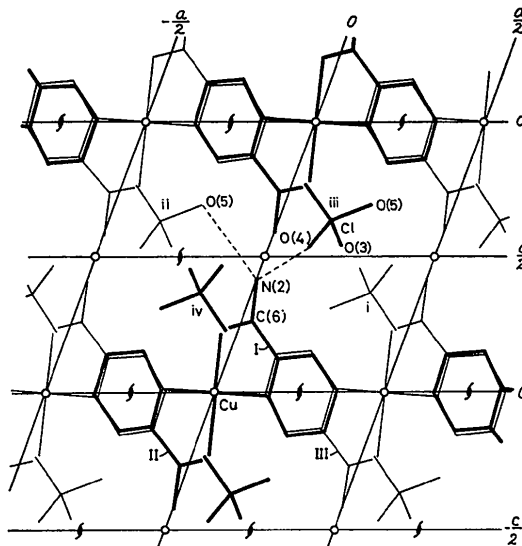
Fig. 2. Projection of the structure along the *b* axis.

Complex ion				
I	at	x,	y,	z
II		$-x$,	$-y$,	$-z$
III		$\frac{1}{2}-x$,	$-\frac{1}{2}+y$,	$-z$
IV		$-\frac{1}{2}+x$,	$\frac{1}{2}-y$,	z
Perchlorate ion				
i	at	x,	y,	z
ii		$-x$,	$-y$,	$1-z$
iii		$\frac{1}{2}-x$,	$\frac{1}{2}+y$,	$1-z$
iv		$-\frac{1}{2}+x$,	$\frac{1}{2}-y$,	z

goniometers and some computation programs of his laboratory. Part of the expenses of the present study were met by a grant from the Matsunaga Science Foundation, to which the author's thanks are due.
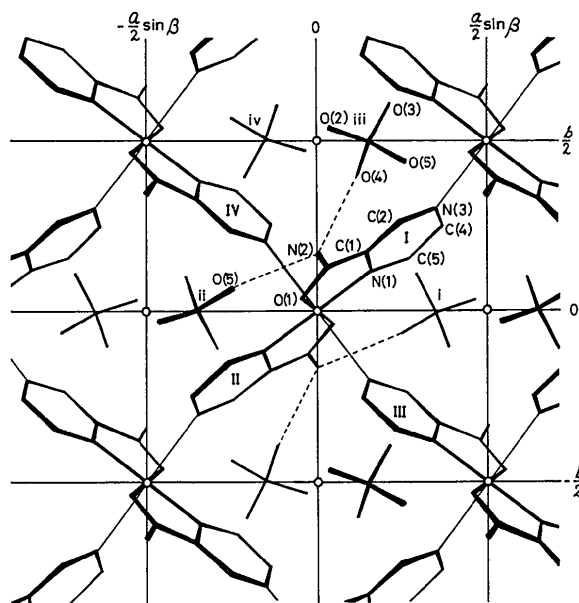

Fig. 3. Projection of the structure along the c axis. The molecules are numbered in a similar way as those in Fig. 2.

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The Crystal Structure of Phenyl Phosphorodiamidate

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Crystals of phenyl phosphorodiamidate, $C_6H_5O.PO(NH_2)_2$, are orthorhombic, $a = 7·99$, $b = 34·02$, $c = 5·97$ Å, space group $Pbca$, 8 molecules in the unit cell. The crystal structure has been determined from X-ray diffractometer intensity data and refined by least squares to $R = 0·045$ for 1457 reflexions. There is a significant difference between the lengths of the two P–N bonds (1·604, 1·628 Å), which results from the nitrogen atoms having different hydrogen-bond environments (respectively trigonal and tetrahedral). The shortness of the P–N bonds suggests that they have considerable π character. The P=O length is 1·482 Å and that of P–O(C_6H_5) 1·598 Å. A network of weak hydrogen bonds, NH $\cdots$ O (lengths 2·93–3·08 Å) and NH $\cdots$ N (3·20 Å), links the molecules in double sheets. The 'doubly bonded' oxygen atom forms three NH $\cdots$ O bonds whose spatial arrangement resembles that in the phosphoric triamide and urea crystals.

Introduction

Current theories of the bonding in cyclic phosphazenes and in phosphates (Craig & Paddock, 1962; Cruickshank, 1961a) allow for participation of all the atoms attached to phosphorus in molecular π-bond systems. Attached amino groups are considered to be involved as a result of donation of electrons from nitrogen to vacant $3d$ orbitals of phosphorus. This is supported by the observation of short bonds between phosphorus and such groups in a number of amino-substituted cyclic phosphazenes, the exocyclic P–N bond length being 1·62–1·68 Å (see for example Ahmed & Pollard, 1972 or Bullen, 1962) as compared to the accepted length of a P–N single bond, 1·77 Å. In phosphoric triamide, $PO(NH_2)_3$, the P–N bonds are again short (Bullen, Stephens & Wade, 1969) and it has been estimated that they have about 30 % π-bond order, a value