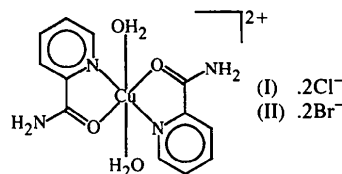North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A24, 351–359.

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# trans-Diaquabis(pyridine-2-carboxamide-$N^1$,$O$)copper(II) Dichloride and Dibromide

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## Abstract

Crystals of the title compounds, $[Cu(C_6H_6N_2O)_2(H_2O)_2]Cl_2$, (I), and $[Cu(C_6H_6N_2O)_2(H_2O)_2]Br_2$, (II), are isomorphic. The structures consist of centrosymmetric complex cations and separate chloride or bromide ions linked by hydrogen bonding. The pyridine-2-carboxamide molecules $(C_6H_6N_2O)$ are coordinated by the ring N and amide O atoms, forming the base of an elongated octahedron. Bond lengths in (I) and (II), respectively: short Cu—N of 1.960(1) and 1.965(2), Cu—O of 1.981(1) and 1.981(2), and axial Cu—$H_2O$ of 2.418(2) and 2.417(3) Å.

## Comment

The structures of pyridine-2-carboxamide complexes have not been intensively investigated. The Cambridge Structural Database (Version 5.11) (Allen & Kennard, 1993) gives information about only one $Cu^{II}$ and two $Cu^{II}$ structures with $R < 0.06$ (Castro et al., 1990; Cantarero, Amigó, Faus, Julve & Debaerdemaeker, 1988; Batsanov et al., 1986). This work presents a redetermination of the structure of trans-diaquabis(pyridine-2-carboxamide-$N^1$,$O$)copper(II) dichloride, (I), which was originally investigated by X-ray photographic methods and refined to $R = 0.13$ (Brown, MacSween, Mercer & Sharp, 1971), and the structure determination of the corresponding bromide, (II).

The structures of compounds (I) and (II) are shown in Figs. 1(a) and 1(b), respectively. The cations display inversion symmetry. Crystals of (I) and (II) are isostructural. Our investigation of (I) is not consistent with the earlier investigation, giving not only distinctly different bond lengths, but also different (but similar) unit-cell constants and unit-cell volume. The Cu atom is in an elongated octahedral environment, with four short and two long bonds. The short bonds [Cu—N 1.960(1) in (I) and 1.965(2) in (II); Cu—O 1.981(1) in (I) and 1.981(2) Å in (II)] are formed by the chelating ligand bonding through the amide O and ring N atoms. In the less symmetrical [Cu(pyridine-2-carboxamide)₂(H₂O)(NO₃)]⁺ cation (Castro et al., 1990), where pyridine-2-carboxamide in a very similar coordination mode also forms short Cu—O and Cu—N bonds, the Cu—O bonds [average 1.955(2) Å] are distinctly shorter than the Cu—N bonds [average 1.976(3) Å]. In the mononuclear [Cu(pyridine-2-carboxamide){bis(2-pyridylcarbonyl)amido}]⁺ cation (Cantarero et al., 1988), where the Cu atom is also in an elongated octahedral environment, the pyridine-2-carboxamide ligand is coordinated via the N atom of the pyridine ring and the O atom of the amide group with bond distances of 2.001(4) and 2.316(3) Å, respectively. The short Cu—N bond here is distinctly longer than in the investigated structures (I) and (II).

In compounds (I) and (II), the water molecules occupy the axial positions of the octahedron forming two long bonds of 2.418(2) in (I) and 2.417(3) Å in (II), typical for long Cu—H₂O bonds (Orpen et al., 1989). The chelate rings are not ideally planar. The deviations of the Cu and N2 atoms from the ideal plane formed by atoms N1, C2, C1 and O2 are respectively −0.135(3) and 0.028(3) Å for (I), and −0.141(4) and 0.012(5) Å for (II). The carboxamide group and Cu atom are not coplanar with the pyridine ring. The observed deviations of the C1, O2, N2 and Cu atoms from the least-squares plane of this ring are respectively 0.052(3), 0.060(3), 0.098(3) and −0.112(2) Å for (I) and 0.054(4), 0.085(5), 0.086(5) and −0.093(4) Å for (II).

We can conclude that in the $3\sigma$ range the geometrical shape of the [Cu(pyridine-2-carboxamide)₂(H₂O)₂]²⁺ complex cation is identical in the chloride and bromide salts and that the mode of (pyridine-2-carboxamide)–$Cu^{II}$ coordination may be different in the less symmetrical $Cu^{II}$ complexes (Castro et al., 1990; Cantarero et al., 1988).
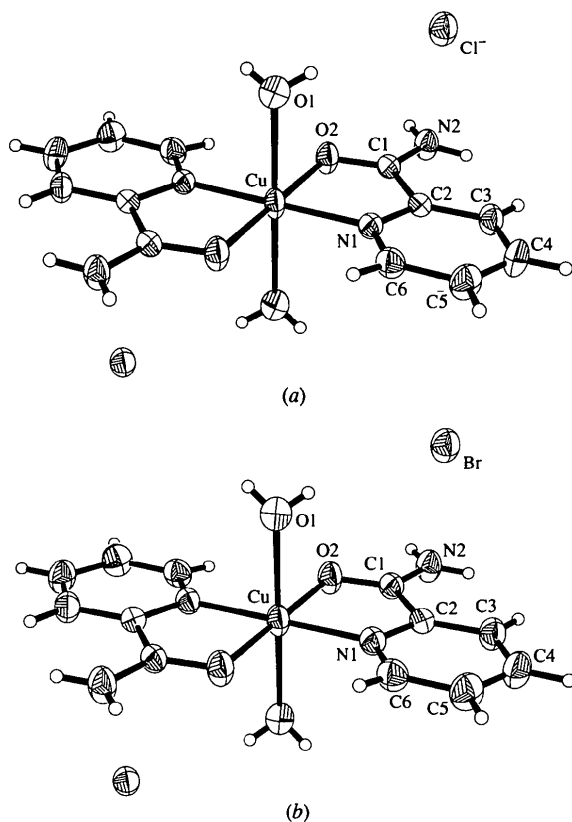
(a)



(b)

Fig. 1. (a) Centrosymmetric trans-diaquabis(pyridine-2-carboxamide)-copper(II) dichloride, (I), and (b) centrosymmetric trans-diaquabis-(pyridine-2-carboxamide)copper(II) dibromide, (II). Displacement ellipsoids are drawn at the 50% probability level.
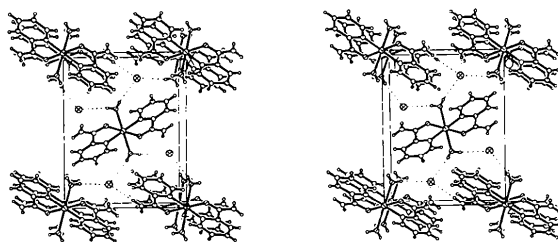


Fig. 2. Stereoview of the crystal packing of (I) viewed along [100].

The hydrogen bonds between the complex cations and chloride ions are shown in Fig. 2. Two O—H···Cl and two N—H···Cl hydrogen bonds link each Cl ion with four different complex cations, forming a three-dimensional network. The geometry of these bonds is given in Table 2, with the corresponding values for (II) in Table 4. The arrangement of the chloride/-bromide ions resembles a very irregular tetrahedron, with the H···Cl/Br···H angles ranging from 80 (1) to 145 (1)°. The distortion from a regular tetrahedron may result from packing requirements or from C—H···Cl/Br attractive interactions. In both investigated structures, two short H3···Cl/Br and H5···Cl/Br con-

tacts of 2.88 (3) and 2.82 (3) Å in (I), and of 2.88 (4) and 2.95 (4) Å in (II), with C—H···Cl/Br angles ranging from 163 (2) to 170 (3)°, are observed. There is an evident shortening from the sum of van der Waals radii ($r_H$ + $r_{Cl/Br}$) and, according to Taylor & Kennard's (1982) evidence for the existence of C—H···Cl hydrogen bonds, this may be interpreted as C—H···Cl⁻/Br⁻ attractive interactions rather than repulsive interactions.

## Experimental

The title crystals were grown from an aqueous solution of 2-pyridinecarbonitrile and copper(II) chloride or bromide, indicating the copper-assisted hydrolysis of 2-pyridinecarbonitrile to pyridine-2-carboxamide (Watanabe, Komiya & Suzuki, 1973). A pale blue solution was formed when $CuCl_2$ or $CuBr_2$ (1 mmol) was added to an aqueous solution (50 ml) containing 2-pyridinecarboxamide (2 mmol). After heating to boiling point, the solution became dark blue. After a few days, pale blue prismatic crystals of the title compounds were obtained.

### Compound (I)

*Crystal data*

| | |
|---|---|
| [Cu(C₆H₆N₂O)₂(H₂O)₂]Cl₂ | Mo $K\alpha$ radiation |
| $M_r = 414.73$ | $\lambda = 0.71073$ Å |
| Monoclinic | Cell parameters from 29 |
| $P2_1/n$ | reflections |
| $a = 6.2976 (7)$ Å | $\theta = 3.8-13.1°$ |
| $b = 10.0596 (14)$ Å | $\mu = 1.701$ mm⁻¹ |
| $c = 12.8122 (11)$ Å | $T = 293 (2)$ K |
| $\beta = 93.316 (8)°$ | Prism |
| $V = 810.3 (2)$ Å³ | $0.67 \times 0.15 \times 0.15$ mm |
| $Z = 2$ | Pale blue |
| $D_x = 1.700$ Mg m⁻³ | |
| $D_m = 1.69$ Mg m⁻³ | |
| $D_m$ measured by flotation in a CH₃I/benzene mixture | |

*Data collection*

| | |
|---|---|
| Siemens P3 diffractometer | $\theta_{max} = 26°$ |
| $\omega/2\theta$ scans | $h = -1 \rightarrow 8$ |
| Absorption correction: none | $k = -1 \rightarrow 13$ |
| 2273 measured reflections | $l = -16 \rightarrow 16$ |
| 1587 independent reflections | 3 standard reflections |
| 1472 reflections with | every 96 reflections |
| $I > 2\sigma(I)$ | intensity decay: 1.2% |
| $R_{int} = 0.0115$ | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $\Delta\rho_{max} = 0.446$ e Å⁻³ |
| $R(F) = 0.0234$ | $\Delta\rho_{min} = -0.347$ e Å⁻³ |
| $wR(F^2) = 0.0655$ | Extinction correction: |
| $S = 1.129$ | SHELXL93 (Sheldrick, |
| 1587 reflections | 1993) |
| 139 parameters | Extinction coefficient: |
| All H atoms refined | 0.013 (2) |
| $w = 1/[\sigma^2(F_o^2) + (0.0387P)^2 + 0.3133P]$ | Scattering factors from International Tables for |
| where $P = (F_o^2 + 2F_c^2)/3$ | Crystallography (Vol. C) |
| $(\Delta/\sigma)_{max} < 0.001$ | |

Table 1. *Selected geometric parameters (Å, °) for (I)*

| | | | |
|---|---|---|---|
| Cu—O1 | 2.418 (2) | N1—C2 | 1.343 (2) |
| Cu—O2 | 1.981 (1) | N1—C6 | 1.335 (2) |
| Cu—N1 | 1.960 (1) | N2—C1 | 1.308 (2) |
| O2—C1 | 1.250 (2) | C1—C2 | 1.500 (2) |
| O1—Cu—O2 | 91.40 (6) | N1—C6—C5 | 121.7 (2) |
| O1—Cu—N1 | 88.76 (6) | N2—C1—C2 | 120.0 (2) |
| O2—Cu—N1 | 82.30 (6) | C1—O2—Cu | 113.5 (1) |
| O2—C1—N2 | 121.9 (2) | C2—N1—Cu | 113.9 (1) |
| O2—C1—C2 | 118.0 (1) | C6—N1—Cu | 126.6 (1) |
| N1—C2—C1 | 112.0 (1) | C2—N1—C6 | 119.5 (2) |
| N1—C2—C3 | 121.9 (2) | C1—C2—C3 | 126.1 (2) |

Table 3. *Selected geometric parameters (Å, °) for (II)*

| | | | |
|---|---|---|---|
| Cu—O1 | 2.417 (3) | N1—C2 | 1.343 (3) |
| Cu—O2 | 1.981 (2) | N1—C6 | 1.335 (3) |
| Cu—N1 | 1.965 (2) | N2—C1 | 1.301 (3) |
| O2—C1 | 1.255 (3) | C1—C2 | 1.496 (3) |
| O1—Cu—O2 | 91.62 (9) | N1—C6—C5 | 122.0 (3) |
| O1—Cu—N1 | 88.79 (9) | N2—C1—C2 | 120.2 (2) |
| O2—Cu—N1 | 82.25 (8) | C1—O2—Cu | 113.3 (2) |
| O2—C1—N2 | 121.7 (2) | C2—N1—Cu | 113.9 (2) |
| O2—C1—C2 | 118.2 (2) | C6—N1—Cu | 127.0 (2) |
| N1—C2—C1 | 112.0 (2) | C2—N1—C6 | 119.1 (2) |
| N1—C2—C3 | 121.8 (2) | C1—C2—C3 | 126.2 (2) |

Table 2. *Hydrogen-bonding geometry (Å, °) for (I)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| O1—H1···Cl | 0.75 (4) | 2.53 (4) | 3.270 (2) | 171 (3) |
| O1—H2···Cl$^i$ | 0.68 (3) | 2.55 (3) | 3.216 (2) | 168 (3) |
| N2—H7···Cl$^{ii}$ | 0.78 (3) | 2.50 (3) | 3.271 (2) | 171 (2) |
| N2—H8···Cl$^{iii}$ | 0.85 (3) | 2.44 (3) | 3.282 (2) | 171 (2) |

Symmetry codes: (i) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $x-1, y, z$; (iii) $-x, 1-y, -z$.

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| O1—H1···Br | 0.77 (6) | 2.68 (6) | 3.379 (3) | 154 (7) |
| O1—H2···Br$^i$ | 0.75 (4) | 2.60 (4) | 3.331 (3) | 165 (4) |
| N2—H7···Br$^{ii}$ | 0.78 (4) | 2.64 (4) | 3.410 (3) | 169 (3) |
| N2—H8···Br$^{iii}$ | 0.84 (4) | 2.61 (4) | 3.421 (3) | 164 (3) |

Symmetry codes: (i) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $x-1, y, z$; (iii) $-x, 1-y, -z$.

## Compound (II)

### Crystal data

$[Cu(C_6H_6N_2O)_2(H_2O)_2]Br_2$
$M_r = 503.65$
Monoclinic
$P2_1/n$
$a = 6.3722$ (6) Å
$b = 10.2962$ (8) Å
$c = 13.1279$ (14) Å
$\beta = 94.400$ (8)°
$V = 858.78$ (14) Å$^3$
$Z = 2$
$D_x = 1.948$ Mg m$^{-3}$
$D_m = 1.95$ Mg m$^{-3}$
$D_m$ measured by flotation in
    a $CH_3I$/benzene mixture

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 46
    reflections
$\theta = 3.8$–20.2°
$\mu = 5.947$ mm$^{-1}$
$T = 293$ (2) K
Prism
$0.70 \times 0.26 \times 0.17$ mm
Pale blue

### Data collection

Siemens $P3$ diffractometer
$\omega/2\theta$ scans
Absorption correction:
    empirical *via* $\psi$ scan
    (North, Phillips &
    Mathews, 1968)
    $T_{min} = 0.046$, $T_{max} = 0.104$
2160 measured reflections
1988 independent reflections

1764 reflections with
    $I > 2\sigma(I)$
$R_{int} = 0.0242$
$\theta_{max} = 28.06°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 13$
$l = -17 \rightarrow 17$
3 standard reflections
    every 96 reflections
    intensity decay: 1.3%

### Refinement

Refinement on $F^2$
$R(F) = 0.0286$
$wR(F^2) = 0.0746$
$S = 1.138$
1988 reflections
139 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2 + 0.1218P]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.806$ e Å$^{-3}$
$\Delta\rho_{min} = -0.428$ e Å$^{-3}$
Extinction correction:
    *SHELXL93* (Sheldrick,
    1993)
Extinction coefficient:
    0.0076 (12)
Scattering factors from
    *International Tables for
    Crystallography* (Vol. C)

The title structures were solved by the conventional Patterson method and refined by full-matrix least-squares calculations. All non-H atoms were refined anisotropically. All H atoms were located from a difference synthesis and refined isotropically.

For both compounds, data collection: Siemens $P3$ software; cell refinement: Siemens $P3$ software; data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1990); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *XP* in *SHELXTL/PC*; software used to prepare material for publication: *SHELXL93*.

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