Diiodotetra(pyridine-*N*)copper(II)zinc(II) Dipyridine

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Abstract

The combination of Cu^I iodide and Zn^{II} iodide in pyridine results in a mixed metal (Cu,Zn) pyridine iodide complex which is unlike the complexes formed by zinc(II), copper(I) or copper(II) with pyridine and iodide ions. The title compound, $[Cu_{0.92}Zn_{0.08}I_2(C_5H_5N)_4].2C_5H_5N$, crystallizes in the orthorhombic space group *Ccca*, with a square-planar arrangement of pyridine N atoms about the metal site and I atoms 3.460 (5) Å removed in axial positions.

Comment

Zinc(II) has been observed to form tetrahedral and trigonal bipyramidal complexes with halide and pyridine. Tetrahedral [$ZnCl_2$(pyridine)$_2$] [Zn—Cl 2.215 (2) and 2.228 (2), Zn—N 2.046 (5) and 2.052 (6) Å] (Sokolova, Atovmyan & Porai-Koshits, 1966; Steffen & Palenik, 1976) and [ZnI_2(pyridine)$_2$] [Zn—I 2.551 (2) and 2.553 (2), Zn—N 2.05 (1) and 2.06 (1) Å] (Le Quarler, Borel & Leclaire, 1977) have been reported.

Terpyridylzinc dichloride displays trigonal bipyramidal geometry with equatorial pyridine groups [Zn—N 2.09 (4)–2.24 (4) Å] and axial Zn—Cl binding [Zn—Cl 2.25 (1)–2.27 (1) Å] (Corbridge & Cox, 1956; Einstein & Penfold, 1966).

A further variation is the formation of pyridinium [$ZnBr_{1.5}Cl_{1.5}$(pyridine)] in which tetrahedral zinc is bound to pyridine and three mixed halides [Zn(halide)$_3$pyridine]$^-$, charge being balanced by a protonated pyridine molecule [Zn—N 2.073 (3), Zn—Cl 2.251 (2) and Zn—Br 2.394 (3) Å] (Villarreal-Salinas & Schlemper, 1978).

Copper(I) forms polymeric, dimeric and tetrameric complexes with pyridine and iodine: [Cu_4I_4(pyridine)$_4$] (Raston & White, 1976), [Cu_2I_2(pyridine)$_4$] (Dyason, Englehardt, Healy & White, 1984) and [CuI(pyridine)]$_x$ (Schramm, 1982), which are characterized by tetrahedral copper(I) geometry (Cu—I 2.65 Å).

Copper(II) has been observed to form polymeric [CuX_2(pyridine)$_2$], X = Br, Cl, complexes (Kupcik & Durovic, 1960; Morosin, 1975) in which copper sits at the center of a square plane linked to opposing halide [Cu—Br 2.451 (1), Cu—Cl 2.299 (2) Å] and pyri-

dine donors [Cu—N 2.004 (4) and 2.013 (5) Å], and shows long axial distances to halide atoms of neighboring square-planar copper groups [Cu⋯Br 3.240 (1), Cu⋯Cl 3.026 (2) Å].

[$Cu^{II}I_2$(imidazole)$_4$] crystallizes with a square-planar arrangement of four imidazole groups about the Cu atom (Cu—N 1.98–2.04 Å) and two axial iodide ions (Cu—I 3.42 and 3.87 Å) (Ahktar, Goodgame, Goodgame, Rayner-Canham & Skapski, 1968).

The title compound, (I), resembles the Cu^{II} iodide imidazole structure. The square-planar arrangement of pyridine N atoms about the metal site becomes octahedral with two long *M*—I bonds of 3.460 (5) Å. I—*M*—I groups are lined parallel to the *a* axis with a 5.392 Å separation between I atoms of adjacent groups.
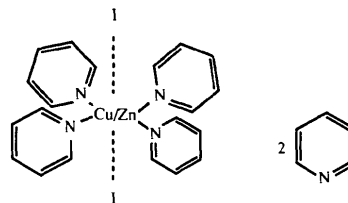
Analytical metal analysis of crystals similar to those used for data collection establishes the Cu/Zn ratio to be 92/8. Dissolution of either CuI or ZnI_2 alone in pyridine does not produce the purple rhombohedral material. The *M*—I [3.460 (5) Å] and *M*—N [average 2.037 (12) Å] distances are intermediate between those observed for Cu in [$Cu^{II}I_2$(imidazole)$_4$] (average Cu—I 3.64, Cu—N 2.01 Å) and for Zn in tetrahedral [ZnI_2(pyridine)$_2$] [Zn—I 2.552 (2), Zn—N 2.06 (1) Å].

It is not unexpected to find copper and zinc sharing a metal site. Their radii are similar (Cu^{II} 0.73, Zn^{II} 0.74 Å) for hexacoordination. Mixed Cu/Zn sites have been reported in the literature. The methods of determining site occupancy have varied. In tetrakis[μ_3-methoxo-(2,4,6-trichlorophenoxo)methanol(Cu^{II},Zn^{II})], occupancies of specific metal sites were not determined, overall composition being based on the relative stoichiometries of the synthetic starting materials (Yablokov, Simonov, Yampol'skaya, Dvorkin, Matuzenko, Voronkova & Mosina, 1980).

In [(Cu,Zn)(formate)$_2$].2H$_2$O (Ogata, Taga & Osaki, 1977) and (Cu,Zn)bis(pyridine-3-sulphonate) hydrate (Walsh & Hathaway, 1980), occupancy factors for mixed metal sites, *M*, were calculated by comparing the amount of axial distortion observed in *M*—O distances with the non-distorted distances seen in the zinc-only analogs and the greater distortions seen in the copper-only complexes.

Application of this approach to the determination of mixed-site occupancy in the title structure is inconclusive due to the lack of a well determined value for the axial Cu^{II}—I distance.
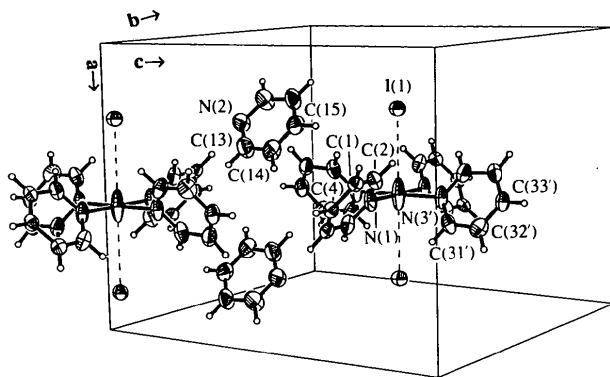
Fig. 1. View of the title compound. Displacement ellipsoids are plotted at the 50% probability level.

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($\mathring{A}^2$)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

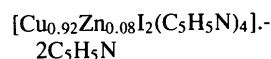|	x	y	z	U_{eq}
I(1)	0.7810 (1)	3/4	1/4	0.067 (1)
Cu(1)†	1/2	3/4	1/4	0.131 (3)
Zn(1)‡	1/2	3/4	1/4	0.131 (3)
N(1)	1/2	0.6185 (7)	1/4	0.074 (5)
C(1)	0.4227 (11)	0.4841 (7)	0.2086 (7)	0.057 (5)
C(2)	0.4246 (12)	0.5736 (9)	0.2101 (7)	0.071 (5)
C(4)	1/2	0.4382 (9)	1/4	0.061 (6)
N(2)	1/4	1/2	0.0499 (10)	0.097 (10)
C(13)	0.1789 (14)	0.4557 (12)	0.0071 (8)	0.106 (8)
C(14)	0.1747 (13)	0.4519 (11)	−0.0749 (9)	0.095 (7)
C(15)	1/4	1/2	−0.1129 (14)	0.091 (11)
N(3)	1/2	3/4	0.1261 (7)	0.074 (5)
C(31)	0.4229 (13)	0.7893 (8)	0.0844 (8)	0.074 (6)
C(32)	0.4184 (14)	0.7902 (10)	0.0018 (10)	0.082 (6)
C(33)	1/2	3/4	−0.0401 (11)	0.077 (7)

† Occupancy of 0.92.
‡ Occupancy of 0.08.

Experimental

The title copper–zinc pyridine diiodo complex was prepared by mixing copper iodide and zinc iodide (1:1) in pyridine in air. The solution was heated to boiling until all solid dissolved. It was then allowed to stand at room temperature for several days. Large purple rhombohedral crystals formed on slow evaporation of the solvent.

Crystal data

[Cu$_{0.92}$Zn$_{0.08}$I$_2$(C$_5$H$_5$N)$_4$].-   Mo $K\alpha$ radiation
2C$_5$H$_5$N $\lambda = 0.71073$ $\mathring{A}$
$M_r = 792.11$ Cell parameters from 41
Orthorhombic   reflections
$Ccca$ $\theta = 9.84–24.82°$
$a = 12.313$ (1) $\mathring{A}$ $\mu = 2.700$ mm^{-1}
$b = 15.335$ (2) $\mathring{A}$ $T = 298$ K
$c = 16.616$ (2) $\mathring{A}$ Rhombohedron
$V = 3137.4$ (7) $\mathring{A}^3$ $0.2 \times 0.2 \times 0.2$ mm
$Z = 4$ Purple
$D_x = 1.676$ Mg m^{-3}

Data collection

Syntex $P4$ four-circle $R_{int} = 0.0176$
  diffractometer $\theta_{max} = 22.5°$
$\theta/2\theta$ scans $h = -1 \rightarrow 13$
Absorption correction: $k = -1 \rightarrow 16$
  semi-empirical $l = -1 \rightarrow 17$
  $T_{min} = 0.12$, $T_{max} = 0.37$ 3 standard reflections
1348 measured reflections   frequency: 97 min
1034 independent reflections   intensity variation: 11.11%
492 observed reflections
  [$F > 4.0\sigma(F)$]

Refinement

Refinement on F $(\Delta/\sigma)_{max} = 0.010$
$R = 0.0316$ $\Delta\rho_{max} = 0.86$ e $\mathring{A}^{-3}$
$wR = 0.0394$ $\Delta\rho_{min} = -0.89$ e $\mathring{A}^{-3}$
$S = 0.98$ Atomic scattering factors
1348 reflections   from *International Tables*
97 parameters   *for Crystallography* (1992,
H atom parameters not   Vol. C, Tables 4.2.6.8 and
  refined   6.1.1.4)
$w = 1/[\sigma^2(F) + 0.0008F^2]$

Table 2. *Selected geometric parameters* ($\mathring{A}$, °)

Cu(1)—I(1)	3.460 (5)	N(3)—C(31^{iii})	1.321 (16)
Cu(1)—N(3)	2.058 (12)	C(33)—C(32)	1.368 (19)
Cu(1)—N(1)	2.016 (11)	C(33)—C(32^{iii})	1.368 (19)
Cu(1)—N(3^i)	2.058 (12)	N(2)—C(13)	1.316 (19)
Cu(1)—N(1^i)	2.016 (11)	N(2)—C(13^{iv})	1.316 (19)
C(1)—C(2)	1.373 (17)	C(15)—C(14)	1.343 (19)
C(1)—C(4)	1.370 (14)	C(15)—C(14^{iv})	1.343 (19)
C(2)—N(1)	1.333 (15)	C(13)—C(14)	1.364 (20)
C(4)—C(1^{ii})	1.370 (14)	C(31)—C(32)	1.374 (19)
N(3)—C(31)	1.321 (16)	N(1)—C(2^{ii})	1.333 (15)
N(3)—Cu(1)—N(1)	90.0	C(13)—N(2)—C(13^{iv})	114.7 (17)
C(2)—C(1)—C(4)	119.6 (12)	C(14)—C(15)—C(14^{iv})	123.8 (21)
C(1)—C(2)—N(1)	122.5 (12)	N(2)—C(13)—C(14)	125.9 (16)
C(1)—C(4)—C(1^{ii})	118.0 (13)	C(15)—C(14)—C(13)	114.9 (16)
C(31)—N(3)—C(31^{iii})	116.7 (15)	N(3)—C(31)—C(32)	123.9 (14)
C(32)—C(33)—C(32^{iii})	118.9 (19)	C(33)—C(32)—C(31)	118.3 (15)

Symmetry codes: (i) $x, \frac{3}{2} - y, \frac{1}{2} - z$; (ii) $1 - x, y, \frac{1}{2} - z$; (iii) $1 - x, \frac{3}{2} - y, z$; (iv) $\frac{1}{2} - x, 1 - y, z$.

A variable scan rate was used with a scan width of 0.6° below $K\alpha_1$ and 0.6° above $K\alpha_2$ to a maximum 2θ value of 45°. Refinement was completed using full-matrix least-squares methods.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXS86*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BR1084). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Aqua(glycinato)(3,4,7,8-tetramethyl-1,10-phenanthroline)copper(II) Nitrate

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Abstract

In the title compound, $[Cu(C_2H_4NO_2)(C_{16}H_{16}N_2)(H_2O)]NO_3$, Cu^{II} displays distorted square-pyramidal coordination where the water molecule is in the apical position and the base is defined by the N and one of the O atoms from the glycinate ligand, and both phenanthroline N atoms. The phenanthroline chelate-ring plane (N1, C12, C11, N2, Cu) is slightly distorted from planarity, whereas the five-membered ring formed by the glycinate ligand (defined by atoms N3, C18, C17, O1 and Cu), presents a distorted half-chair conformation.

Comment

In the context of a study on the anticancer properties of several mixed substituted phenanthroline and amino acid complexes, we have determined the structure of the title compound, (I).
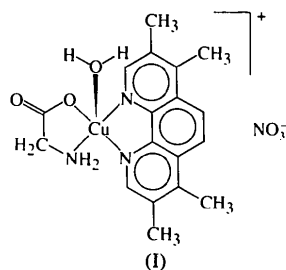

(I)

Fig. 1 shows a view of the structure with the atom-numbering scheme. Cu^{II} is surrounded by five ligand atoms in an N_3O_2-type distorted square-pyramidal coordination mode. The water molecule is in the apical position. The N and one of the O atoms from the glycinate moiety, and both phenanthroline N atoms lie in a slightly tetrahedrally distorted plane. The distances to the least-squares plane defined by atoms N1, N2, N3 and O1 are −0.082(2) for N1, 0.087(2) for N2, 0.081(2) for N3 and −0.087(2) Å for O1. Cu^{II} is 0.160(2) Å out of this plane. The Cu—N distances are longer than the Cu—O1 distance, as reported for many related complexes (Aoki & Yamasaky, 1980; Antolini, Marcotrigiano, Menabue & Pellacani, 1983; Antolini, Marcotrigiano, Menabue, Pellacani, Saladini & Sola, 1985; Antolini, Battaglia, Corradi, Marcotrigiano, Menabue, Pellacani, Saladini & Sola, 1986; Solans, Ruiz-Ramírez, Gasque & Briansó, 1987; Mendoza-Diaz, Martínez-Aguilera, Pérez-Alonso, Solans & Moreno-Esparza, 1987; Solans, Ruiz-Ramírez, Martínez, Gasque & Briansó, 1988; Solans, Aguiló, Gleizest, Faus, Julve & Verdaguer, 1990; Solans, Ruiz-Ramírez, Martínez, Gasque & Moreno-Esparza, 1992, 1993; Mendoza-Diaz, Martínez-Aguilera, Moreno-Esparza, Pannell & Cervantes Lee, 1993).

The Cu—OW1(aqua) bond is longer than those observed in some related complexes: 2.355(4) Å for this complex and 2.294(6) Å for the L-glutamate complex (Antolini, Marcotrigiano, Menabue & Pellacani, 1983) and 2.213(10) Å for the L-phenylalaninato complex (Solans, Ruiz-Ramírez, Gasque & Briansó, 1987).

The chelate ring formed by atoms N1, C12, C11, N2 and Cu is slightly distorted from planarity, whereas the chelate ring formed by atoms N3, C18, C17, O1 and Cu shows a distorted half-chair conformation, the asymmetry parameter $\Delta C_2(O1)$ being 9.3(4)°, as defined by Duax, Weeks & Roher (1976). The angle between the two chelate-ring mean planes is 9.9(2)°.

The nitrate ion is not involved in the Cu coordination sphere. The nearest atom, O41(1−x, −y,