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Dimeric Iodo[1,1-di(2-pyridyl)-3-butenolato]copper(II) Bis(acetonitrile) Solvate, $[Cu_2(C_{14}H_{13}N_2O)_2I_2].2CH_3CN$

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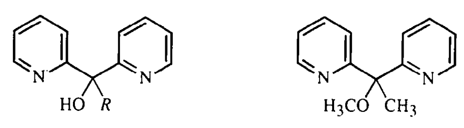
Abstract

The title compound, bis[μ-1,1-di(2-pyridyl)-3-butenolato-*N,O:N′,O*]bis[iodocopper(II)] bis(acetonitrile) solvate, was obtained from copper(I) iodide and the neutral ligand on reaction with oxygen. The olefinic function is unaffected by the oxidation. The coordination at each Cu atom is trigonal bipyramidal and the coordination polyhedra share a common edge, which is the O···O diagonal of the central Cu_2O_2 ring.

Comment

Recently, we reported (Basu, Bhaduri, Sapre & Jones, 1987; Bhaduri, Sapre & Jones, 1991) the synthesis and structures of the copper complexes of ligands HL^2 and L^3. In both cases, the mixed-valence complexes initially obtained could be fully oxidized by dioxygen to give systems with dinuclear Cu^{II} cores. Here, we describe the use of the ligand 1,1-di(2-pyridyl)-3-butenol, HL^1.

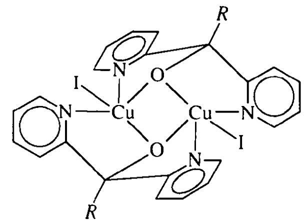


HL^1: $R = CH_2—CH{=}CH_2$
HL^2: $R = CH_3$

L^3

The object was to investigate the effect, if any, of an endogenous olefin function on the oxidation reaction. This is important in view of the proposed coordination of ethylene to copper in plant biochemistry (Thomson, Harlow & Whitney, 1983); plant metabolism of ethylene to ethylene oxide and other products is thought to involve such coordination (Beyer & Blomstrom, 1980). We wished to see if oxidation at the double bond could be effected by providing an endogenous olefin function.

Green crystals of the title complex, (1), were obtained. Although analytical data for (1) were consistent with the formulation $[Cu_2(L^1)_2I_2]$, the non-participation of the allylic double bond in the oxidation could not be inferred conclusively.



(1) $R = CH_2—CH{=}CH_2$
(2) $R = CH_3$

The structure of complex (1) (Fig. 1) is very similar to that of $[Cu_2(L^2)_2I_2]$, (2), reported earlier, although in contrast to (1), complex (2) crystallizes with exact twofold symmetry. Each ligand coordinates to one Cu atom through the O and one N atom, and to the other Cu atom through the O and the second N atom. The coordination spheres of the Cu atoms are distorted trigonal bipyramids sharing a common edge. The equatorial plane for the Cu1 atom is defined by atoms I1, O1 and N4 (deviation of Cu from this plane is 0.085 Å) and the axis is O2—Cu1—N1 [161.0 (2)°]. For Cu2, the plane is defined by atoms I2, O2 and N2 [deviation 0.067 (2) Å] and the axis is O1—Cu2—N3 [161.6 (2)°]. The shared edge is O1···O2 and the central ring is folded by 25.3 (2)° about this edge. The Cu···Cu distances in complexes (1) and (2) are 2.899 (1) and 2.830 (2) Å, respectively. The equatorial Cu—O bond lengths in (1), 2.038 (4) and 2.019 (4) Å, are somewhat longer than the axial Cu—O lengths, 1.938 (4) Å (×2). The allyl group is chemically unaltered by the oxidation, the C(7)=C(8) double-bond length being 1.312 (9) Å.

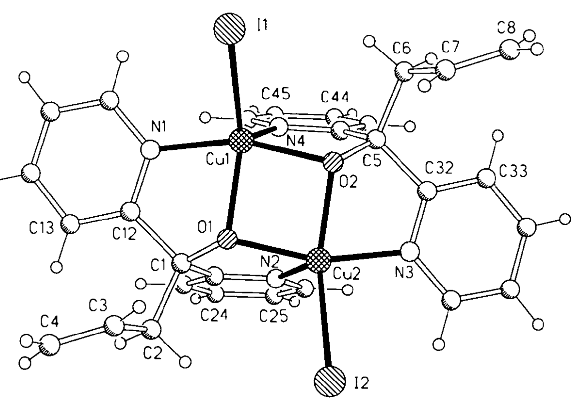


Fig. 1. The structure of the title complex in the crystal (solvent omitted). Radii are arbitrary and pyridyl rings are numbered cyclically as N*x*1—C*x*6 (*x* = 1 to 4).

Experimental

For the preparation of ligand HL^1, di-2-pyridyl ketone (1.38 g, 8 mmol) was added to an ether solution (40 ml) of allyl magnesium bromide (2.32 g, 16 mmol) over a period of 3 h.

The excess Grignard reagent was quenched with 20% NH_4Cl solution. Ether extraction followed by solvent removal gave 1,1-di(2-pyridyl)-3-butenol (HL^1) as a viscous liquid (1.7 g, 95%). IR (neat): 3350, 1645, 1590, 1575 cm^{-1}. ^1H NMR: δ 3.17 (*d*, 2H), 5.02 (*t*, 2H), 5.64 (*m*, 1H), 6.45 (*s*, 1H), 7.12–8.54 p.p.m. (*m*, 8H). For the preparation of complex (1), copper(I) iodide (0.190 g, 1 mmol) was heated with HL^1 (0.34 g, 1.5 mmol) in acetonitrile (30 ml) at 355 K for 2 h, affording a clear pale-yellow solution. After cooling to room temperature, the solution was exposed with stirring to dry dioxygen. The dioxygen-to-copper gas absorption as measured by volumetry was in the molar ratio 1:4 and was complete within 15 min. Dry diethyl ether was added to the solution and the mixture cooled at 283 K for 3 d, whereupon green crystals were obtained.

Crystal data

$[Cu_2(C_{14}H_{13}N_2O)_2I_2]$.-
  $2CH_3CN$
$M_r = 913.52$
Orthorhombic
Pbca
$a = 15.442$ (3) Å
$b = 14.865$ (4) Å
$c = 30.383$ (7) Å
$V = 6974.3$ (28) Å^3
$Z = 8$
$D_x = 1.740$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 10–11.5°$
$\mu = 3.027$ mm^{-1}
$T = 173$ (2) K
Prism
0.55 × 0.45 × 0.40 mm
Green

Data collection

Siemens *R*3 diffractometer
ω scans
Absorption correction:
  ψ scans (*XEMP*; Siemens, 1989)
  $T_{min} = 0.709$, $T_{max} = 0.855$
8133 measured reflections
6170 independent reflections
4403 observed reflections
  $[I > 2\sigma(I)]$

$R_{int} = 0.0233$
$\theta_{max} = 25.05°$
$h = 0 \rightarrow 18$
$k = -17 \rightarrow 4$
$l = -36 \rightarrow 6$
3 standard reflections
  monitored every 247 reflections
  intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0344$
$wR(F^2) = 0.0973$
$S = 1.072$
6165 reflections
397 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0383P)^2 + 19.4731P]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.093$
$\Delta\rho_{max} = 0.754$ e Å^{-3}
$\Delta\rho_{min} = -0.580$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^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}
Cu1	0.45491 (4)	0.30972 (5)	0.58848 (2)	0.0234 (2)
Cu2	0.37765 (4)	0.37347 (5)	0.66967 (2)	0.0235 (2)
I1	0.40393 (2)	0.19840 (3)	0.52569 (1)	0.02815 (11)
I2	0.33614 (3)	0.31172 (3)	0.74923 (1)	0.03449 (12)
C1	0.5542 (3)	0.3106 (4)	0.6672 (2)	0.0231 (12)
C2	0.5753 (4)	0.2634 (5)	0.7113 (2)	0.0333 (14)
C3	0.5663 (5)	0.1643 (5)	0.7092 (2)	0.044 (2)
C4	0.6255 (5)	0.1063 (5)	0.7202 (2)	0.054 (2)
C5	0.3176 (4)	0.4394 (4)	0.5876 (2)	0.0259 (13)
C6	0.2641 (4)	0.4231 (4)	0.5456 (2)	0.0340 (15)
C7	0.1832 (4)	0.3697 (5)	0.5534 (2)	0.039 (2)
C8	0.1052 (4)	0.3973 (5)	0.5429 (3)	0.052 (2)
O1	0.4686 (2)	0.2893 (2)	0.65445 (11)	0.0209 (8)
O2	0.3430 (2)	0.3563 (2)	0.60616 (12)	0.0234 (8)
N1	0.5790 (3)	0.2767 (3)	0.59016 (14)	0.0252 (11)
C12	0.6154 (4)	0.2803 (4)	0.6305 (2)	0.0269 (13)
C13	0.7025 (4)	0.2613 (4)	0.6363 (2)	0.0333 (14)
C14	0.7534 (4)	0.2407 (5)	0.5998 (2)	0.042 (2)
C15	0.7163 (4)	0.2391 (5)	0.5589 (2)	0.040 (2)
C16	0.6289 (4)	0.2555 (4)	0.5551 (2)	0.0339 (14)
N2	0.4886 (3)	0.4575 (3)	0.6769 (2)	0.0294 (11)
C22	0.5635 (4)	0.4134 (4)	0.6737 (2)	0.0267 (13)
C23	0.6421 (4)	0.4571 (5)	0.6768 (2)	0.042 (2)
C24	0.6438 (5)	0.5495 (5)	0.6826 (2)	0.052 (2)
C25	0.5672 (5)	0.5951 (5)	0.6855 (2)	0.047 (2)
C26	0.4908 (4)	0.5484 (4)	0.6827 (2)	0.038 (2)
N3	0.2861 (3)	0.4674 (3)	0.66464 (15)	0.0276 (11)
C32	0.2671 (3)	0.4906 (4)	0.6230 (2)	0.0266 (13)
C33	0.2061 (4)	0.5565 (4)	0.6142 (2)	0.0356 (15)
C34	0.1657 (4)	0.6003 (5)	0.6487 (2)	0.043 (2)
C35	0.1847 (4)	0.5758 (5)	0.6913 (2)	0.042 (2)
C36	0.2454 (4)	0.5091 (4)	0.6981 (2)	0.0347 (14)
N4	0.4707 (3)	0.4466 (3)	0.5707 (2)	0.0278 (11)
C42	0.3979 (4)	0.4944 (4)	0.5742 (2)	0.0252 (12)
C43	0.3966 (5)	0.5860 (4)	0.5650 (2)	0.039 (2)
C44	0.4716 (5)	0.6280 (5)	0.5528 (2)	0.048 (2)
C45	0.5472 (5)	0.5793 (4)	0.5498 (2)	0.042 (2)
C46	0.5445 (4)	0.4889 (5)	0.5588 (2)	0.040 (2)
C91	0.9158 (6)	−0.0174 (8)	0.0895 (4)	0.103 (4)
C92	0.8266 (6)	−0.0008 (6)	0.0786 (3)	0.066 (2)
N91	0.7559 (6)	0.0099 (7)	0.0697 (4)	0.110 (3)
C93	0.3667 (12)	0.7873 (16)	0.6676 (5)	0.227 (12)
C94	0.4496 (13)	0.7968 (13)	0.6491 (5)	0.158 (8)
N92	0.5165 (9)	0.7932 (9)	0.6315 (5)	0.142 (5)

Table 2. *Selected geometric parameters (Å, °)*

Cu1···Cu2	2.899 (1)	Cu2—N3	1.993 (5)
Cu1—O2	1.938 (4)	Cu2—O2	2.019 (4)
Cu1—N1	1.979 (5)	Cu2—N2	2.131 (5)
Cu1—O1	2.038 (4)	Cu2—I2	2.6639 (9)
Cu1—N4	2.120 (5)	C1—O1	1.412 (6)
Cu1—I1	2.6454 (9)	C5—O2	1.412 (6)
Cu2—O1	1.938 (3)		
O2—Cu1—N1	161.0 (2)	O1—Cu2—N3	161.6 (2)
O2—Cu1—O1	82.74 (14)	O1—Cu2—O2	83.27 (15)
N1—Cu1—O1	80.6 (2)	N3—Cu2—O2	80.0 (2)
O2—Cu1—N4	80.2 (2)	O1—Cu2—N2	79.6 (2)
N1—Cu1—N4	97.6 (2)	N3—Cu2—N2	99.6 (2)
O1—Cu1—N4	112.5 (2)	O2—Cu2—N2	112.7 (2)
O2—Cu1—I1	99.09 (11)	O1—Cu2—I2	99.70 (11)
N1—Cu1—I1	98.72 (13)	N3—Cu2—I2	98.06 (14)
O1—Cu1—I1	130.31 (11)	O2—Cu2—I2	139.46 (11)
N4—Cu1—I1	116.78 (13)	N2—Cu2—I2	107.57 (13)

Data collection: Nicolet *P*3 software. Cell refinement: Nicolet *P*3 software. Data reduction: *XDISK* (Siemens, 1991). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: FG1121). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Diperchlorato[(1*RS*,4*RS*,5*SR*,7*RS*,8*SR*,11*SR*,-12*RS*,14*SR*)-(5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane)]copper(II)

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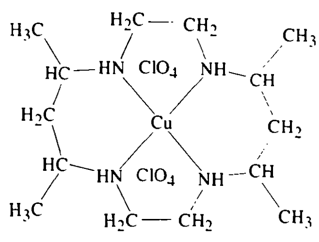
Abstract

The Cu^{II} ion of $[Cu(C_{14}H_{32}N_4)(ClO_4)_2]$ is sixfold coordinated in a distorted octahedral environment with the four N atoms of the macrocyclic ligand equatorial and the two O atoms of the perchlorate ion axial. The quadridentate ligand adopts its most stable conformation with the two six-membered rings in chair forms and the two five-membered rings in *gauche* forms. The complex has a 1*RS*,4*RS*,8*SR*,11*SR* configuration for the four chiral N-atom centres and a 5*SR*,7*RS*,12*RS*,14*SR* configuration for the four chiral C-atom centres.

Comment

There is a great deal of interest in transition metal complexes of 14-membered tetraaza macrocycles because of their particular stereochemistry (Boeyen & Dobson, 1987; Bosnich, Poon & Tobe, 1965). This paper reports the crystal structure of the copper(II) complex of 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane, (I).



(I)

The coordination around the Cu^{II} ion is distorted octahedral with the four N atoms of the macrocyclic ligand equatorial and the two O atoms of the perchlorate ions axial. This structure is similar to that of diperchlorato(1,4,8,11-tetraazacyclotetradecane)copper(II) (Tasker & Sklar, 1975). The quadridentate ligand adopts its most stable conformation with the two six-membered rings in chair forms and the two five-membered rings in *gauche* forms. The Cu—N distances range from 2.023 (3) to 2.030 (3) Å. The long Cu—O bond of 2.539 (2) Å is the result of the Jahn–Teller effect. The four methyl groups occupy equatorial positions. The complex has a 1*RS*,4*RS*,8*SR*,11*SR* configuration for the four chiral N-atom centres and a 5*SR*,7*RS*,12*RS*,14*SR* configuration for the four chiral C-atom centres.

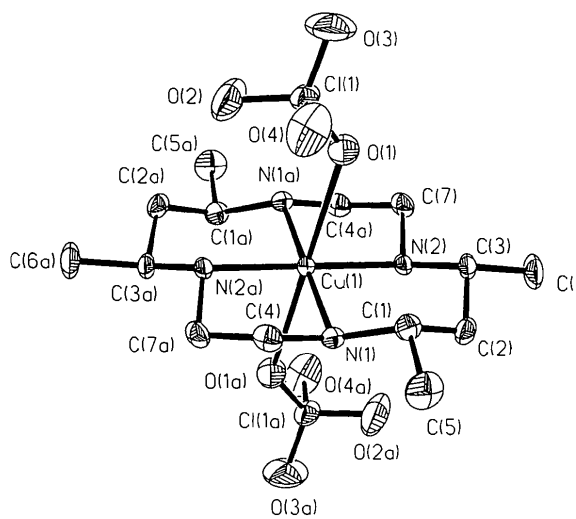


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of a single molecule with displacement ellipsoids scaled to 30% probability. H atoms are not shown.