Bei der abschließenden Verfeinerung wurden die Wasserstofflagen an den Imidazolringen geometrisch berechnet. Die Wasserstofflagen der Methylgruppen wurden entsprechend zwei Orientierungen aufgespalten und geometrisch streng an die C-Atome angebunden. Den beiden Sorten H-Lagen wurden jeweils gemeinsame isotrope Temperaturkoeffizienten zugeordnet. Datensammlung: Enraf-Nonius CAD-4. Gitterverfeinerung: Enraf-Nonius CAD-4. Datenreduktion: Programmsystem *SDP-Plus* (Frenz, 1978). Lösung der Struktur mit Programm: *SHELXS*86 (Sheldrick, 1985). Verfeinerung der Struktur mit Programm: *SHELX*76 (Sheldrick, 1976). Zeichenprogramm: *SCHAKAL*88 (Keller, 1988). Programme zur Berechnung der geometrische Datan und zur Erstellung der Tabellen: *KRISTALL-ST* (Tebbe, 1992), *ORFFE4* (Busing, Martin, Levy, Brown, Johnson & Thiessen, 1976), *PARST* (Nardelli, 1983).

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Die Listen der Strukturfaktoren, anisotropen Temperatur, H-Atom Koordinaten Koeffizienten und vollständigen geometrischen Daten sind bei dem British Library Document Supply Centre (Supplementary Publication No. SUP 71514: 21 pp.) hinterlegt. Kopien sind erhältlich durch: The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF Aktenzeichen: SE1026]

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Bis(2-ethoxycarbonylamino-6-methylpyridine *N*-oxide)copper(II)

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Abstract

The complex has a distorted square-planar structure with bidentate ligands chelated to Cu in a *cis* (*N*,*O*:*O*′,*N*′) arrangement. The average distance from Cu to N is 1.929 (4) Å and from Cu to O is 1.906 (4) Å. The N—Cu—N′ angle of 110.9 (1)° differs markedly from the O—Cu—O′ angle of 91.6 (1)° because of large substituents attached to N. Some measure of the deviation from idealized square-planar coordination is indicated by angles of 154.9 (1) and 157.9 (2)° between nominally *trans* N and O donor atoms spanning Cu. Molecular packing in the crystal results in parallel alignment of neighboring aromatic rings.

Comment

Several different types of coordination complexes have been isolated in an ongoing study involving the preparation of 2-substituted pyridine *N*-oxide ligands and their reaction products with various metal ions (West & Huffman 1989; West & Borowy, 1991). One series of ligands were prepared by converting an amino group at the 2 position into a urethane (Ertem, Severns & West, 1986). Subsequent reaction with copper(II) perchlorate resulted in the isolation of tetrakis complexes, $CuL_4(ClO_4)_2$, in which the ligand is presumed to be monodentate. However, reaction with copper(II) acetate resulted in deprotonation of the amino function and isolation of neutral bis complexes, CuL_2. These became of interest because the formula implied ligand chelation in the presence of a large substituent at the 2 position. Consequently, the structure determina-

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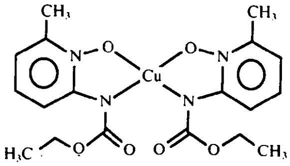
tion of the bis-copper complex shown in (I) was undertaken to establish its coordination geometry and confirm the mode of bonding.



(I)

The complex has a distorted square-planar structure with ligands chelated to Cu through the *N*-oxide O atom and the deprotonated amino N atom in a *cis* (*N,O:O′,N′*) arrangement. The two N—Cu—O 'bite' angles are very similar and average 82.8 (2)°. However, the two 'non-bite' angles differ markedly with the N—Cu—N′ angle being almost 20° larger than the O—Cu—O′ angle because of large substituents attached to N. Angles between nominally *trans* N and O donor atoms spanning Cu average 156.4 (3)°, and give an indication of the deviation from idealized square-planar coordination.

Each ligand, including Cu, but excluding the amino substituent, is nearly planar. The two ligand planes are inclined by 32.9° and result in the significant distortion from idealized square-planar coordination that is noted at Cu. The main distinction between the ligands is found in differences between the torsion angles involving the carbonyl C and amino N atoms; for C1—N2—C7—O2 the angle is 14.4 (6)°, whereas for C10—N4—C16—O5 it is 20.2 (6)°. The twisting about these bonds places the ethyl ester substituents in an *anti* conformation where they avoid each other. The packing of molecules in the crystal shows parallel alignment of neighboring aromatic rings. There are no other significant intermolecular contacts or alignments.

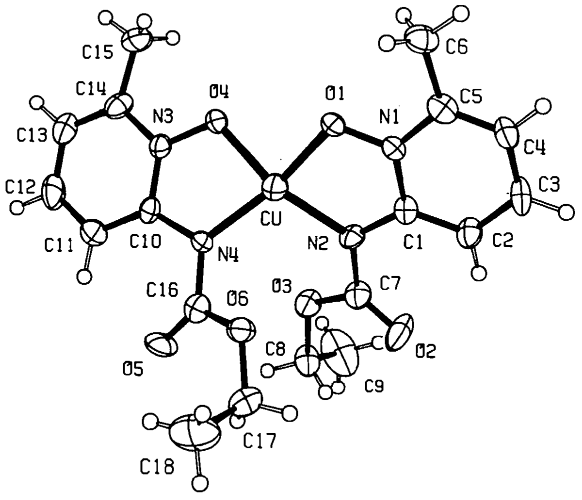


Fig. 1. *ORTEP*II plot (Johnson, 1976) of $[Cu(C_9H_{11}N_2O_3)_2]$ using 50% probability ellipsoids. H atoms are shown as small spheres of arbitrary size.

In the structure of a related complex, bis(2-dimethylaminopyridine 1-oxide)copper(II) diperchlorate, the ligands adopt a *trans* configuration and the coordination geometry is nearer square planar (West, Pavkovic & Brown, 1980). For this centrosymmetric complex, the 'non-bite' angle of 96.8° lies between the two values found for the title compound.

Experimental

Crystal data

$[Cu(C_9H_{11}N_2O_3)_2]$
M_r = 453.94
Monoclinic
$P2_1/c$
a = 17.3557 (9) Å
b = 8.5626 (4) Å
c = 14.3847 (7) Å
β = 112.686 (2)°
V = 1972.3 (4) Å^3
Z = 4
D_x = 1.53 Mg m^{-3}
D_m = 1.51 (2) Mg m^{-3}
Density measured by flotation in mixed organic solvents

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 17 reflections
θ = 32-36°
μ = 1.90 mm^{-1}
T = 292 K
Prism
0.56 × 0.45 × 0.36 mm
Green
Crystal source: evaporation of CH_3NO_2 solution

Data collection

Modified Picker FACS-I diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical corrections following φ scans with χ set at 90°
T_{min} = 0.89, T_{max} = 1.00
3892 measured reflections
2928 independent reflections

2830 observed reflections [$I > 3\sigma(I)$]
R_{int} = 0.023
θ_{max} = 60°
$h = -18 \rightarrow 17$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 16$
4 standard reflections monitored every 400 reflections intensity variation: <1%

Refinement

Refinement on F
R = 0.0628
wR = 0.0908
S = 1.5361
2830 reflections
265 parameters
H-atom parameters not refined
Calculated weights $w = 1/[\sigma^2(F) + 0.007217F^2]$

$(\Delta/\sigma)_{max}$ = 0.067
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol IV. Table 2.2B)

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}
Cu	0.24601 (3)	0.03565 (6)	0.11886 (4)	0.0357 (3)
O1	0.1642 (2)	−0.0117 (4)	−0.0106 (2)	0.034 (1)
O2	0.1235 (2)	0.3948 (4)	0.1925 (3)	0.065 (1)
O3	0.2578 (2)	0.3323 (3)	0.2428 (2)	0.037 (1)
O4	0.3316 (2)	−0.0643 (4)	0.0876 (2)	0.037 (1)
O5	0.3655 (2)	0.0661 (4)	0.4263 (2)	0.046 (1)

O6	0.2303 (2)	0.0372 (3)	0.3254 (2)	0.033 (1)
N1	0.0948 (2)	0.0722 (4)	−0.0335 (2)	0.026 (1)
N2	0.1681 (2)	0.2022 (3)	0.1120 (2)	0.028 (1)
N3	0.4008 (2)	−0.0918 (4)	0.1716 (2)	0.029 (1)
N4	0.3215 (2)	0.0001 (4)	0.2551 (2)	0.024 (1)
C1	0.0938 (2)	0.1910 (4)	0.0304 (3)	0.025 (1)
C2	0.0228 (2)	0.2818 (4)	0.0032 (3)	0.034 (1)
C3	−0.0466 (2)	0.2474 (5)	−0.0839 (3)	0.041 (1)
C4	−0.0432 (2)	0.1208 (4)	−0.1432 (3)	0.034 (1)
C5	0.0273 (3)	0.0368 (4)	−0.1200 (3)	0.032 (2)
C6	0.0372 (2)	−0.0969 (5)	−0.1810 (3)	0.039 (2)
C7	0.1766 (2)	0.3176 (4)	0.1823 (3)	0.034 (1)
C8	0.2762 (3)	0.4457 (5)	0.3242 (4)	0.042 (2)
C9	0.2868 (4)	0.6069 (6)	0.2880 (5)	0.085 (3)
C10	0.4008 (2)	−0.0555 (4)	0.2646 (3)	0.026 (1)
C11	0.4735 (3)	−0.0823 (5)	0.3480 (3)	0.039 (2)
C12	0.5412 (3)	−0.1408 (5)	0.3354 (4)	0.046 (2)
C13	0.5395 (3)	−0.1774 (5)	0.2401 (3)	0.039 (2)
C14	0.4687 (2)	−0.1513 (5)	0.1581 (3)	0.035 (2)
C15	0.4585 (3)	−0.1852 (6)	0.0526 (3)	0.049 (2)
C16	0.3112 (3)	0.0369 (4)	0.3430 (4)	0.032 (2)
C17	0.2073 (3)	0.0793 (6)	0.4080 (4)	0.041 (2)
C18	0.2118 (5)	−0.0554 (9)	0.4762 (5)	0.081 (3)

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

Cu—O1	1.899 (3)	N3—C10	1.375 (5)
Cu—O4	1.912 (3)	N3—C14	1.365 (5)
Cu—N2	1.941 (3)	N4—C10	1.411 (5)
Cu—N4	1.916 (3)	N4—C16	1.380 (6)
O1—N1	1.330 (4)	C1—C2	1.381 (5)
O2—C7	1.189 (5)	C2—C3	1.394 (6)
O3—C7	1.345 (5)	C3—C4	1.395 (6)
O3—C8	1.459 (5)	C4—C5	1.346 (6)
O4—N3	1.357 (4)	C5—C6	1.493 (6)
O5—C16	1.231 (6)	C8—C9	1.512 (7)
O6—C16	1.327 (5)	C10—C11	1.384 (5)
O6—C17	1.438 (5)	C11—C12	1.353 (6)
N1—C1	1.376 (5)	C12—C13	1.396 (7)
N1—C5	1.374 (5)	C13—C14	1.354 (6)
N2—C1	1.372 (5)	C14—C15	1.486 (6)
N2—C7	1.380 (5)	C17—C18	1.496 (8)
O1—Cu—O4	91.6 (1)	C1—N2—C7	118.4 (3)
O1—Cu—N2	82.2 (1)	O4—N3—C10	119.7 (3)
O4—Cu—N2	154.9 (1)	O4—N3—C14	117.1 (3)
O1—Cu—N4	157.9 (2)	C10—N3—C14	123.2 (3)
O4—Cu—N4	83.3 (1)	Cu—N4—C10	114.2 (3)
N2—Cu—N4	110.9 (1)	Cu—N4—C16	128.4 (3)
Cu—O1—N1	113.0 (2)	C10—N4—C16	117.0 (3)
Cu—O4—N3	111.7 (2)	N1—C1—N2	111.9 (3)
O1—N1—C1	118.5 (3)	N1—C1—C2	117.9 (3)
O1—N1—C5	118.7 (3)	N2—C1—C2	130.2 (3)
C1—N1—C5	122.8 (3)	N3—C10—N4	110.4 (3)
Cu—N2—C1	113.5 (2)	N3—C10—C11	117.6 (3)
Cu—N2—C7	127.8 (3)	N4—C10—C11	131.9 (4)

Cell-constant data were collected by + and -2θ scans and parameters were determined from least-squares calculations that accounted for $K(\alpha_1-\alpha_2)$ splitting. All H atoms were found in subsequent difference Fourier maps. During refinement the H atoms were fixed in positions of idealized geometry with C—H = 0.95 Å and U(H) = 0.04, 0.05 and 0.06 Å^2 for the aromatic, methylene and methyl H atoms, respectively. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71602 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1043]

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Polyol Metal Complexes. V.† Structure of (2,2′-Bipyridyl-κ^2N,N')[*meso*-oxolane-3,4-diolato(2−)-κ^2O,O']palladium(II) 6.5-Hydrate

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Abstract

In the title compound, [Pd($C_4H_6O_3$)($C_{10}H_8N_2$)].6.5H_2O, an oxolanediolato ligand forms a chelate complex with palladium(II). The dianion is formed by double deprotonation of anhydroerythritol in alkaline aqueous solution. The square-planar [(2,2′-bipyridyl)Pd($C_4H_6O_4$)] complex acts as a multiple acceptor in a hydrogen-bond system *via* its alkoxide and ether O atoms. A special feature of the hydrogen-bond system is a homodromic helix, formed by four of the 6.5 water molecules of the asymmetric unit.

Comment

Multiply charged polyolato ligands derived from simple polyalcohols or carbohydrates are formed in alkaline aqueous solution by deprotonation in the presence of copper(II) ions (Habermann, Klaassen & Klüfers, 1993; Habermann, Jung, Klaassen & Klüfers, 1992; Klaassen & Klüfers, 1993; Fuchs, Habermann & Klüfers, 1993). Diols are deprotonated twice in such solutions to form

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† Part IV: Fuchs, Habermann & Klüfers (1993).