

METAL-ORGANIC COMPOUNDS

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**Bis(di-2-pyridyl-*N*-amine)(propionato-*O*)-
copper(II) Chloride Monohydrate**

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Abstract

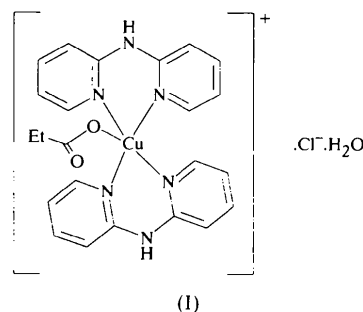
The CuN₄O₂ chromophore in [Cu(C₁₀H₉N₃)₂(C₃H₅O₂)]Cl·H₂O exhibits trigonal distorted square-pyramidal stereochemistry around the metal centre, with the second O atom of the propionate group occupying a sixth coordinating position at a longer distance of 2.640 (4) Å, to give (4+1+1*)-type coordination. The Cl⁻ ion participates in N—H···Cl hydrogen bonding.

Comment

The [Cu^{II}(chelate)₂(OXO)]⁺ cations, where chelate is di-2-pyridyl or 1,10-*o*-phenanthroline and OXO is [ONO]⁻, [CH₃CO₂]⁻ or [HCO₂]⁻, have been characterized (Hathaway, 1984) as having fluxional copper(II) stereochemistries (Fitzgerald *et al.*, 1981; Simmons *et al.*, 1983*a,b*, 1987; Fitzgerald & Hathaway, 1985; Hill *et al.*, 1997) in which the copper(II) coordination sphere varies in geometry, as a function of co-anion and temperature, from square pyramidal (monodentate O-bonded nitrite or carboxylate) to *cis*-distorted octahedral (bidentate chelating O-bonded nitrite or carboxylate). Only a few crystal structures have been determined, although the fluxional behaviour of the corresponding dpyam (di-2-pyridylamine) complexes has been reported (Aduldecha *et al.*, 1991; Youngme *et al.*, 1998). To obtain more information on complexes containing the more flexible nitrogen-chelate ligand, the crystal structure of [Cu(dpyam)₂(O₂CCH₂CH₃)]Cl·H₂O, (I), has been determined.

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The asymmetric unit of (I) is made up of a [Cu(C₁₀H₉N₃)₂(C₃H₅O₂)]⁺ cation, a Cl⁻ anion and a water molecule. In the CuN₄O₂ chromophore, the metal centre adopts distorted square-pyramidal stereochemistry with atoms N1, N2, N4 and O1 forming the basal plane, and O1—Cu—N2 as the basal angle positioned opposite the elongated Cu—N5 direction. The Cu^{II} centre is displaced out of the basal plane by 0.235 (3) Å in the direction of N5. The basal plane has a slight trigonal distortion with a τ value ($\tau = [\{N1-Cu-N4\} - \{N2-Cu-O1\}]/60$) (Addison *et al.*, 1984) of 0.22, which is relatively close to that of an ideal square-pyramidal chromophore ($\tau = 0$). The second O atom (O2) of the propionate group occupies a sixth coordinating position at a longer distance of 2.640 (4) Å, to give (4+1+1*)-type coordination. Although O2 lies well off the *z* axis of the square pyramid, it is close enough to be involved in off-axis weak coordination to the Cu^{II} ion (Hathaway, 1973; Hathaway *et al.*, 1980). However, the bidentate coordination of the propionate group is highly asymmetric with a $\Delta_{O_{1,2}}$ value of 0.648 (3) Å, giving an extremely asymmetric *cis*-distorted octahedral stereochemistry to the CuN₄O₂ chromophore. Hence, the geometry may be considered to be intermediate between asymmetric *cis*-distorted octahedral geometry and distorted square-based-pyramidal five-coordinate geometry, plus an additional long bond to the sixth ligand (O2), giving (4+1+1*)-type coordination (Fitzgerald & Hathaway, 1981; Hathaway *et al.*, 1980). This type of coordination is best described as square-pyramidal *cis*-distorted octahedral (4+1+1*) (Hathaway, 1973), which has been reported for the corresponding dpyam complexes [Cu(dpyam)₂(O₂CCH₃)]NO₃, (II), [Cu(dpyam)₂(O₂CH)]BF₄, (III), and [Cu(dpyam)₂(O₂CCH₂CH₃)]NO₃, (IV) (Aduldecha *et al.*, 1991; Youngme *et al.*, 1998). The $\Delta(Cu-O)_{eq}$ and $\Delta(Cu-N)_{eq}$ difference plot has been used to suggest a structural pathway for these fluxional CuN₄O₂ chromophores (Simmons *et al.*, 1987; Fitzgerald & Hathaway, 1985). These differences for (I) are consistent with fluxional behaviour of the CuN₄O₂ chromophore and the dpyam complexes may

have fluxional CuN₄O₂ stereochemistries, as previously reported for (II)–(IV)

The pyridine rings form dihedral angles of 23.1 (1) and 17.1 (1)° for the ligands defined by N1/N2 and N4/N5, respectively. The Cl[−] ion participates in both inter- and intramolecular N—H···Cl hydrogen bonds (Table 2) and the water O atom has short contacts of 2.734 (7) and 3.202 (6) Å to the O2 and Clⁱⁱⁱ atoms, respectively [symmetry code: (iii) *x*, *y* − 1, *z*]. Although the water H atoms were not found, the presence of the hydrogen bonding can be confirmed from the angle of 115.5 (2)° subtended at the water O atom by these short contacts.

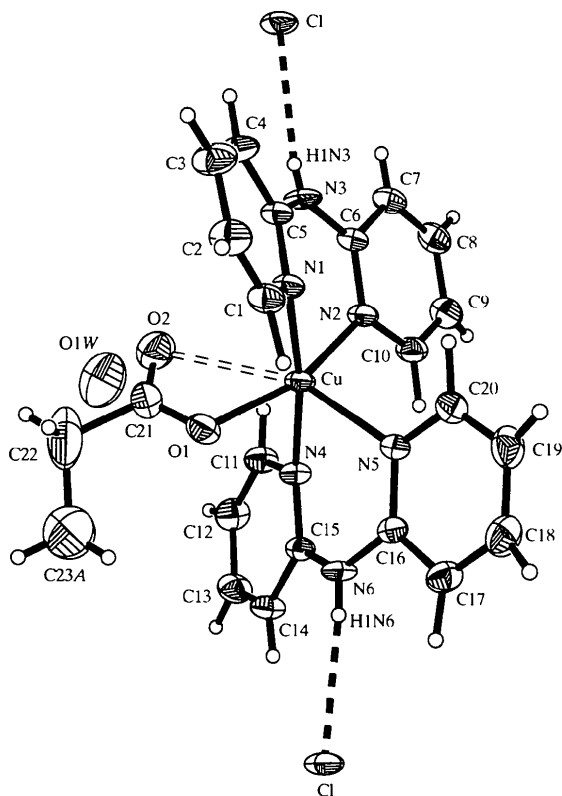


Fig. 1. The structure of the title compound showing 30% probability displacement ellipsoids and the atom-numbering scheme. For clarity, only the major (66%) component of the disorder affecting C23 is shown. [Symmetry code: (i) *x* − 1, *y* − 1, *z*.]

Experimental

The complex [Cu(dpyam)₂(O₂CCH₂CH₃)]Cl·H₂O was prepared by adding a boiling solution containing CuCl₂·2H₂O (0.34 g, 2.0 mmol) in water (40 ml) to a warm solution of dpyam (0.68 g, 4.0 mmol) in ethanol (60 ml), after which CH₃CH₂COONa (0.38 g, 4.0 mmol) was added. Dark-green crystals of the product were obtained on slow evaporation over a period of a few weeks.

Crystal data

[Cu(C₁₀H₉N₃)₂(C₃H₅O₂)]Cl·H₂O
M_r = 532.488
 Triclinic
P $\bar{1}$
a = 9.2751 (17) Å
b = 10.3900 (16) Å
c = 14.080 (2) Å
 α = 98.503 (12)°
 β = 106.398 (14)°
 γ = 99.953 (14)°
V = 1254.0 (4) Å³
Z = 2
D_x = 1.410 Mg m^{−3}
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 41 reflections
 θ = 5.29–12.58°
 μ = 1.013 mm^{−1}
T = 293 (2) K
 Parallelepiped
 0.50 × 0.48 × 0.18 mm
 Blue

Data collection

Siemens P4 diffractometer
 $\theta/2\theta$ scans
 Absorption correction:
 empirical ψ scans
 (Siemens, 1994)
T_{min} = 0.649, *T_{max}* = 0.852
 6747 measured reflections
 5694 independent reflections
 4040 reflections with
I > 2σ(*I*)

R_{int} = 0.040
 θ_{\max} = 27.50°
h = −1 → 11
k = −13 → 13
l = −18 → 17
 3 standard reflections
 every 97 reflections
 intensity decay: <3%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.050
wR(*F*²) = 0.148
S = 0.994
 5694 reflections
 378 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.092P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

(Δ/σ)_{max} < 0.001
 $\Delta\rho_{\max} = 0.55 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.60 \text{ e } \text{Å}^{-3}$
 Extinction correction: none
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cu—O1	1.992 (2)	Cu—N2	2.023 (2)
Cu—O2	2.640 (4)	Cu—N4	2.032 (2)
Cu—N1	1.993 (2)	Cu—N5	2.186 (3)
O1—Cu—N1	88.33 (10)	N2—Cu—N5	100.44 (11)
O1—Cu—N2	158.81 (12)	N4—Cu—N5	86.28 (10)
N1—Cu—N2	89.12 (10)	O1—Cu—O2	54.11 (12)
O1—Cu—N4	85.37 (10)	N1—Cu—O2	84.20 (11)
N1—Cu—N4	172.12 (11)	N2—Cu—O2	104.70 (12)
N2—Cu—N4	95.05 (10)	N4—Cu—O2	88.27 (11)
O1—Cu—N5	100.73 (11)	N5—Cu—O2	154.64 (11)
N1—Cu—N5	99.57 (10)		

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N6—H1N6···Cl	0.73 (3)	2.46 (3)	3.187 (3)	174 (3)
N3—H1N3···Cl ⁱ	0.63 (4)	2.54 (4)	3.165 (3)	173 (4)
C14—H14···Cl	0.88 (4)	2.82 (4)	3.591 (4)	148 (3)
C10—H10···N4	1.03 (4)	2.56 (4)	3.115 (4)	113 (3)
C12—H12···O1W ⁱⁱ	0.92 (5)	2.51 (5)	3.282 (6)	142 (4)

Symmetry codes: (i) *x* − 1, *y* − 1, *z*; (ii) −*x*, −*y*, −1 − *z*.

The title structure was solved by direct methods and refined by full-matrix least-squares techniques. Atom C23 of the

propionate group showed disorder. The occupancies of the disordered positions C23A and C23B were initially refined and then fixed at 0.66 (2) for C23A and 0.34 (2) for C23B. These atoms were isotropically refined with C22—C23A and C22—C23B distances restrained to be equal with an effective standard deviation of 0.02 Å. The H atoms of C22 and C23 (C23A and C23B) were geometrically fixed and allowed to ride on their parent atoms. The remaining H atoms were located from a difference Fourier map and refined isotropically. H atoms belonging to the water molecule could not be located.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXTL/PC (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL/PC. Software used to prepare material for publication: SHELXL93 and PARST95 (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1221). Services for accessing these data are described at the back of the journal.

References

- Addison, A. W., Nageswara Rao, T., Reedijk, J., van Run, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1340–1356.
- Aduldech, S., Keniry, M. E., Akhter, P., Tyagi, S. & Hathaway, B. J. (1991). *Acta Cryst.* **C47**, 1378–1383.
- Fitzgerald, W. & Hathaway, B. J. (1981). *J. Chem. Soc. Dalton Trans.* pp. 567–574.
- Fitzgerald, W. & Hathaway, B. J. (1985). *J. Chem. Soc. Dalton Trans.* pp. 141–149.
- Fitzgerald, W., Murphy, B., Tyagi, S., Walsh, A., Walsh, B. & Hathaway, B. J. (1981). *J. Chem. Soc. Dalton Trans.* pp. 2271–2279.
- Hathaway, B. J. (1973). *Struct. Bonding (Berlin)*, **14**, 49–69.
- Hathaway, B. J. (1984). *Struct. Bonding (Berlin)*, **57**, 55–118.
- Hathaway, B. J., Ray, N., Kennedy, D., O'Brien, N. & Hurphy, B. (1980). *Acta Cryst.* **B36**, 1371–1377.
- Hill, S. J., Hubberstey, P. & Li, W. S. (1997). *Polyhedron*, **16**, 2447–2453.
- Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
- Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1994). *XSCANS User's Manual*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Simmons, C. J., Clearfield, A., Fitzgerald, W., Tyagi, S. & Hathaway, B. J. (1983a). *J. Chem. Soc. Chem. Commun.* pp. 189–191.
- Simmons, C. J., Clearfield, A., Fitzgerald, W., Tyagi, S. & Hathaway, B. J. (1983b). *Inorg. Chem.* **22**, 2463–2466.
- Simmons, C. J., Hathaway, B. J., Amornjarusiri, K., Santar-Siero, B. D. & Clearfield, A. (1987). *J. Am. Chem. Soc.* **109**, 1947–1958.
- Youngme, S., Chandavong, K., Pakawatchai, C., Zhou, Z. Y. & Fun, H.-K. (1998). *Acta Cryst.* **C54**, 199–201.

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[1,4-Bis(diphenylphosphino)butane-*P,P'*]- (*N,N'*-diethyldithiocarbamato-*S,S'*)- nickel(II) Perchlorate

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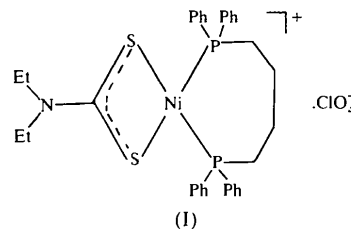
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Abstract

The title compound, [Ni(C₅H₁₀NS₂)(C₂₈H₂₈P₂)]ClO₄, is planar. The pairs of Ni—S [2.2089 (8) and 2.2075 (8) Å] and Ni—P [2.1945 (7) and 2.1932 (8) Å] bond lengths are respectively equal, and the P—Ni—P angle [95.12 (3)°] is large as a consequence of the flexible butyl chain between the two P atoms. The butyl chain lies on one side of the planar NiS₂P₂ chromophore and two of the phenyl rings are arranged laterally above the plane.

Comment

Since Ni^{II} is a borderline acceptor, its dithiocarbamate complexes show a preferential interaction towards phosphine ligands leading to the formation of NiS₂PCl and NiS₂P₂ chromophores (Venkatachalam *et al.*, 1997). Steric and electronic influences of alkyl substituents on the structures of various nickel dithiocarbamates have been investigated (McCleverty & Morrison, 1976; Lachenal, 1975; Burns *et al.*, 1980). The partial double-bond nature of the thioureide bond in the dithiocarbamate ligands has been correlated with the corresponding IR stretching frequencies (Maxfield, 1970).



The title compound, (I), contains discrete mononuclear [Ni(dedtc)(dppb)]⁺ cations [where dedtc is the S₂CN(C₂H₅)₂⁻ anion and dppb is (C₆H₅)₂PCH₂CH₂-

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