2155 réflexions mesurées
1988 réflexions indépendantes

1 réflexion de référence
fréquence: 120 min
variation d'intensité: 1,7%

Affinement

Affinement à partir des F^2
$R[F^2 > 2\sigma(F^2)] = 0{,}042$
$wR(F^2) = 0{,}090$
$S = 1{,}093$
1988 réflexions
173 paramètres
Tous les paramètres des atomes d'hydrogène affinés

$w = 1/[\sigma^2(F_o^2) + (0{,}0263P)^2 + 1{,}0719P]$
où $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0{,}001$
$\Delta\rho_{\max} = 0{,}334$ e Å^{-3}
$\Delta\rho_{\min} = -0{,}300$ e Å^{-3}
Pas de correction d'extinction
Facteurs de diffusion des *International Tables for Crystallography* (Tome C)

Tableau 1. *Paramètres géométriques (Å, °)*

Cu1—O1^i	1,954 (3)	N1—C3	1,474 (4)
Cu1—O1	1,954 (3)	N1—C5	1,486 (4)
Cu1—N1^i	2,059 (3)	N1—C1	1,489 (4)
Cu1—N1	2,059 (3)	C1—C2^i	1,513 (4)
Cu1—O2	2,328 (2)	C1—H1C1	0,97 (4)
Cu1—O2^i	2,328 (2)	C1—H2C1	0,93 (4)
O1—C2	1,258 (4)	C3—C4	1,512 (4)
O2—C4	1,206 (4)	C3—H1C3	0,90 (4)
O3—C4	1,301 (4)	C3—H2C3	0,95 (3)
O3—HO3	1,03 (4)	C5—C6	1,523 (4)
O4—C6	1,187 (4)	C5—H1C5	1,00 (3)
O5—C6	1,324 (4)	C5—H2C5	0,88 (3)
O5—HO5	0,77 (5)	OW1—H1*W*1	0,95 (7)
O6—C2	1,243 (4)	OW1—H2*W*1	0,79 (7)
O1^i—Cu1—O1	180,0	C3—N1—C1	112,2 (3)
O1^i—Cu1—N1^i	93,9 (1)	C5—N1—C1	110,5 (3)
O1—Cu1—N1^i	86,1 (1)	C3—N1—Cu1	107,4 (2)
O1^i—Cu1—N1	86,1 (1)	C5—N1—Cu1	108,4 (2)
O1—Cu1—N1	93,9 (1)	C1—N1—Cu1	105,9 (2)
N1^i—Cu1—N1	180,0	N1—C1—C2^i	113,5 (3)
O1^i—Cu1—O2	87,2 (1)	O6—C2—O1	124,6 (3)
O1—Cu1—O2	92,7 (1)	O6—C2—C1^i	116,3 (3)
N1^i—Cu1—O2	102,23 (9)	O1—C2—C1^i	119,1 (3)
N1—Cu1—O2	77,77 (9)	N1—C3—C4	112,2 (2)
O1^i—Cu1—O2^i	92,7 (1)	O2—C4—O3	124,5 (3)
O1—Cu1—O2^i	87,2 (1)	O2—C4—C3	123,3 (3)
N1^i—Cu1—O2^i	77,77 (9)	O3—C4—C3	112,2 (3)
N1—Cu1—O2^i	102,23 (9)	N1—C5—C6	113,8 (3)
O2—Cu1—O2^i	180,0	O4—C6—O5	124,9 (3)
C2—O1—Cu1	114,4 (2)	O4—C6—C5	126,9 (3)
C4—O2—Cu1	105,3 (2)	O5—C6—C5	108,2 (3)
C3—N1—C5	112,1 (2)		

Code de symétrie: (i) $-x, 1-y, -z$.

La largeur de balayage est $(1{,}00 + 0{,}70\tan\theta)°$. Les intensités ont été corrigées des facteurs de Lorentz–polarisation. La structure a été résolue par les méthodes directes (*SHELXS*86; Sheldrick, 1990) puis affinée par la méthode des moindres carrés (*SHELXL*93; Sheldrick, 1993).

Collection des données: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Affinement des paramètres de la maille: *CAD*-4 *EXPRESS*. Réduction des données: *MolEN* (Fair, 1990). Graphisme moléculaire: *ORTEP*II (Johnson, 1976). Logiciel utilisé pour préparer le matériel pour publication: *SHELXL*93.

Des documents complémentaires concernant cette structure peuvent être obtenus à partir des archives électroniques de l'UICr (Référence: MU1346). Les processus d'accès à ces archives est donné au dos de la couverture.

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

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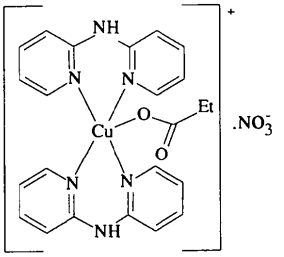
Abstract

The crystal structure of the title compound comprises $[Cu(C_3H_5O_2)(C_{10}H_9N_3)_2]^+$ cations and NO_3^- anions. The cation structure is intermediate between a distorted square-based pyramidal five-coordinate geometry with an additional long bond and an asymmetric *cis*-distorted octahedral geometry, both giving a (4+1+1*)-type coordination.

Comment

The crystal structures of the $[Cu^{II}(chelate)_2(OXO)]^+$ cations, where chelate is di-2-bipyridyl or 1,10-*o*-phenanthroline and O*X*O is ONO^-, $CH_3CO_2^{2-}$ or HCO_2^- are well characterized (Hathaway, 1984) as fluxional copper(II) stereochemistries (Fitzgerald *et al.*, 1981; Simmonds *et al.*, 1987). In order to extend this series to more flexible chelate nitrogen ligands, complexes with the ligand di-2-pyridylamine (dpyam) have been examined. Only a few crystal structures of the dpyam complexes in this series have been reported (Aduldecha *et al.*, 1991).



(I)

The asymmetric unit comprises discrete $[Cu(C_3H_5O_2)(C_{10}H_9N_3)_2]^+$ cations and NO_3^- anions. The bond lengths and angles in the structure agree with those observed in bis(di-2-pyridylamine)(acetato)copper(II) nitrate (Aduldecha *et al.*, 1991). The Cu atom is basically five coordinate, but the second O atom of the propionate group occupies a sixth position at a distance of 2.669 (3) Å. Thus, the CuN_4O_2 chromophore involves a *cis*-distorted octahedral stereochemistry with an asymmetric coordination of the OXO^- anion. However, the structure can also be described as involving a square-pyramidal octahedral (4+1+1*)-type stereochemistry by taking atoms N1, N2, N4 and O1 as the basal plane, and O1—Cu—N2 as the basal angle (Aduldecha *et al.*, 1991). The Cu atom is displaced from the basal plane by 0.2657 (3) Å. The basal plane has a slightly trigonal distortion with a τ value of 0.22 (9) (Addison *et al.*, 1984). Hence, the structure can best be described as intermediate between an asymmetric *cis*-distorted octahedral geometry and a distorted square-based pyramidal five-coordinate geometry with an additional long bond at the sixth coordinating position.

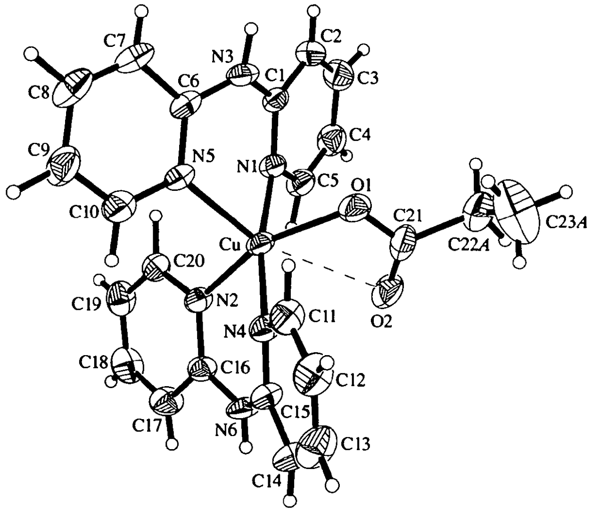


Fig. 1. The structure of the title compound showing 50% probability displacement ellipsoids.

The planar pyridine rings involve dihedral angles of 27.46 (9) and 23.8 (1)° for the ligands defined by the N1/N5 and N2/N4 atoms, respectively. The crystal structure is stabilized by C—H···O and N—H···O-type hydrogen bonds, the details of which are given in Table 2.

Experimental

The title complex was prepared by adding a boiling solution of $[Cu(NO_3)_2].3H_2O$ (0.48 g, 2.0 mmol) in 20 ml water to a warm solution of dpyam (0.68 g, 4.0 mmol) in 30 ml ethanol, after which CH_3CH_2COONa (0.38 g, 4.0 mmol) was added. After a few weeks, dark-green crystals formed.

Crystal data

$[Cu(C_3H_5O_2)(C_{10}H_9N_3)_2]NO_3$
$M_r = 541.02$
Monoclinic
$P2_1/c$
$a = 13.058 (3)$ Å
$b = 8.6770 (10)$ Å
$c = 21.842 (3)$ Å
$\beta = 92.790 (10)°$
$V = 2471.9 (7)$ Å^3
$Z = 4$
$D_x = 1.454$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 18 reflections
$\theta = 0.05–12.93°$
$\mu = 0.932$ mm^{-1}
$T = 293 (2)$ K
Slab
0.58 × 0.46 × 0.26 mm
Dark green

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
5640 measured reflections
4333 independent reflections
3261 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$

$\theta_{max} = 25.01°$
$h = -1 \rightarrow 14$
$k = -1 \rightarrow 10$
$l = -25 \rightarrow 25$
3 standard reflections every 97 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.105$
$S = 0.984$
4333 reflections
430 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0685P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.497$ e Å^{-3}
$\Delta\rho_{min} = -0.346$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cu—N4	1.989 (2)	Cu—N2	2.020 (2)
Cu—N1	2.005 (2)	Cu—N5	2.148 (2)
Cu—O1	2.020 (2)	Cu—O2	2.669 (3)
N4—Cu—N1	170.59 (10)	O1—Cu—N2	157.14 (9)
N4—Cu—O1	88.05 (10)	N4—Cu—N5	100.76 (10)
N1—Cu—O1	84.33 (9)	N1—Cu—N5	86.47 (9)
N4—Cu—N2	89.06 (9)	O1—Cu—N5	104.00 (9)
N1—Cu—N2	95.82 (9)	N2—Cu—N5	98.82 (9)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C20—H20···O3	1.02 (4)	2.46 (4)	3.457 (6)	165 (3)
C2—H2···O5^{i}	0.90 (3)	2.52 (3)	3.291 (5)	144 (2)
N3—H1N3···O5^{i}	0.88 (3)	1.99 (3)	2.859 (5)	168 (3)
C3—H3···O4^{ii}	0.95 (4)	2.47 (4)	3.377 (9)	160 (3)
C13—H13···O5^{iii}	0.85 (5)	2.55 (4)	3.352 (6)	157 (4)
C14—H14···O2^{iv}	0.92 (4)	2.58 (4)	3.334 (4)	140 (3)
N6—H1N6···O2^{iv}	0.78 (3)	1.98 (3)	2.763 (4)	176 (3)

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

The title structure was solved by direct methods and refined by full-matrix least-squares techniques. Atoms C22 and C23 of the propionate group showed very high disorder with unreliable C—C bond lengths. Hence, it was decided to consider the propionate group as two entities with different orientations for the bonds C21—C22 and C22—C23. The occupancies of C22 and C23 were initially refined and then fixed at 0.45 for C22*A*/C23*A* and 0.55 for C22*B*/C23*B*. The O atoms of the disordered nitrate group were divided into two sets with occupancies of 0.78 and 0.22. All the disordered atoms were refined anisotropically with C—C, N—O and O—O distances involving the disordered atoms restrained. The H atoms of C22*A*, C22*B*, C23*A* and C23*B* were fixed geometrically and allowed to ride on the atoms to which they are attached. All other H atoms were located from a difference Fourier map and refined isotropically.

Data collection, cell refinement and data reduction: *XSCANS* (Siemens, 1994); structure solution and molecular graphics: *SHELXTL/PC* (Sheldrick, 1990); structure refinement: *SHELXL93* (Sheldrick, 1993); geometrical calculations: *PARST* (Nardelli, 1983, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1199). Services for accessing these data are described at the back of the journal.

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μ-(2-Thioxo-1,3-dithiole-4,5-dithiolato)-bis{[tris(p-methoxyphenyl)phosphine]-gold(I)}

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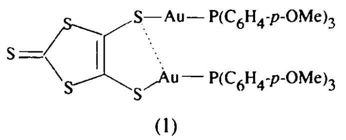
Abstract

The molecule $[Au_2(\mu\text{-}C_3S_5)\{P(p\text{-}C_6H_4OCH_3)_3\}_2]$ consists of two AuPR_3 fragments bridged by one dmit group. Although the Au—S [2.327 (2) and 2.331 (2) Å] and Au—P [2.264 (2) and 2.265 (2) Å] bond lengths are similar to those observed in related dithiolate complexes, the intramolecular Au···S [3.013 (2) Å] and Au···Au [3.2217 (8) Å] contacts are longer.

Comment

Dinuclear gold(I) complexes have been studied extensively during recent years (Melnik & Parish, 1986; Usón & Laguna, 1986; Mingos, 1984; Jones, 1981) because they provide a good basis for the study of weak metal–metal interactions (Schmidbaur *et al.*, 1989; Schmidbaur, 1990). Such interactions are often observed in polynuclear gold(I) derivatives and arise from relativistic effects (Pyykkö, 1988).

Interest in metal thiolate chemistry has increased because of the widespread applications of some of these compounds, *e.g.* for modelling protein sites, as anti-arthritic drugs, and in catalytic processes (Blower & Dilworth, 1987; Holm *et al.*, 1990; Wright *et al.*, 1990; Dance, 1986; Kuchn & Isied, 1980). In particular, several examples of complexes containing bridging dithiolate ligands coordinated to gold(I)–PR_3 units have been reported (Dávila *et al.*, 1993, 1994; Nakamoto *et al.*, 1993; Gimeno *et al.*, 1994; Cerrada *et al.*, 1996). We report here a dinuclear gold(I) derivative, (1), containing 2-thioxo-1,3-dithiole-4,5-dithiolate (dmit) as the bidentate ligand, which is an example of a so-called 'open-ring' complex (Dávila *et al.*, 1994).



(1)