Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\AA^2$)*

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

	x	y	z	U_{eq}
Ru	0.440237 (14)	0.121027 (14)	0.61647 (4)	0.03826 (14)
O1	0.49816 (13)	0.15941 (13)	0.4853 (4)	0.0553 (10)
O2	0.46300 (13)	0.07303 (12)	0.6680 (4)	0.0475 (9)
O3	0.48904 (12)	0.16375 (13)	0.7663 (4)	0.0492 (9)
O4	0.42223 (14)	0.17271 (13)	0.5682 (4)	0.0515 (9)
C1	0.5672 (2)	0.1783 (3)	0.3541 (8)	0.094 (3)
C2	0.5287 (2)	0.1454 (2)	0.4572 (6)	0.059 (2)
C3	0.5289 (2)	0.1049 (2)	0.5114 (7)	0.066 (2)
C4	0.4991 (2)	0.0732 (2)	0.6116 (6)	0.0534 (15)
C5	0.5087 (2)	0.0342 (2)	0.6653 (7)	0.077 (2)
C6	0.5284 (3)	0.2286 (2)	0.9222 (7)	0.085 (2)
C7	0.4936 (2)	0.2041 (2)	0.8052 (6)	0.0549 (15)
C8	0.4686 (2)	0.2260 (2)	0.7495 (7)	0.059 (2)
C9	0.4366 (2)	0.2110 (2)	0.6385 (6)	0.0527 (14)
C10	0.4155 (3)	0.2422 (2)	0.5959 (8)	0.085 (2)
C11	0.3923 (2)	0.0904 (2)	0.9246 (6)	0.061 (2)
C12	0.3817 (2)	0.0967 (2)	0.7774 (6)	0.0509 (14)
C13	0.3726 (2)	0.0625 (2)	0.6754 (6)	0.0489 (13)
C14	0.3708 (2)	0.0754 (2)	0.5341 (6)	0.0512 (14)
C15	0.4012 (2)	0.0718 (2)	0.4395 (6)	0.0566 (15)
C16	0.4085 (3)	0.0903 (3)	0.2932 (6)	0.083 (2)
O91†	0	0	0.2812 (5)	0.25 (1)
C92†	0	0	1.854 (8)	0.27 (5)
C93	0	0	0	0.26 (3)

† Site occupancy = 0.50.

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

Ru—O4	2.051 (3)	Ru—C12	2.242 (5)
Ru—O2	2.055 (3)	C9—C10	1.509 (8)
Ru—O3	2.057 (3)	C11—C12	1.491 (7)
Ru—O1	2.058 (4)	C12—C13	1.385 (7)
Ru—C14	2.104 (5)	C13—C14	1.429 (7)
Ru—C13	2.104 (5)	C14—C15	1.376 (7)
Ru—C15	2.226 (5)	C15—C16	1.498 (8)
O4—Ru—O2	176.06 (15)	O3—Ru—O1	83.02 (15)
O4—Ru—O3	92.83 (14)	C13—C12—C11	122.6 (5)
O2—Ru—O3	83.82 (14)	C12—C13—C14	118.0 (5)
O4—Ru—O1	85.0 (2)	C15—C14—C13	118.2 (5)
O2—Ru—O1	92.6 (2)	C14—C15—C16	124.3 (6)

Three peaks in the penultimate difference map not associated with the complex were found in a cylindrical void along the threefold axis having an approximate diameter of 5 Å, each peak with an electron density of 1.4 e $\AA^{-3}$. These peaks were assigned as a disordered co-crystallized ethanol molecule of solvation. The disordered solvent molecule was refined without H atoms. All non-H atoms were refined with anisotropic displacement parameters. The remaining H atoms were treated as idealized contributions constrained to the attached non-H atom using a riding model.

All software and sources of the scattering factors are contained in the *SHELXTL* (5.03) program library (Sheldrick, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1341). Services for accessing these data are described at the back of the journal.

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catena-Poly[[(di-2-pyridyl-*N*-amine)-(propionato-*O*,*O*′)copper(II)]-μ-nitrato-*O*:*O*′]

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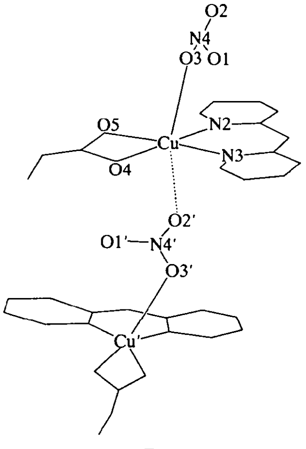
Abstract

The title compound, $[Cu(NO_3)(C_3H_5O_2)(C_{10}H_9N_3)]$, contains infinite chains of a six-coordinate $CuN_2O_2O'_2$ chromophore. The molecular chromophore has a distorted octahedral structure, with symmetrically bonding di-2-pyridylamine (dpyam) and bidentate propionate groups defining an equatorial O_2N_2 plane, and axial O

atoms of bridging 'semi-coordinate' nitrate groups completing the sixfold coordination.

Comment

The mode of bonding of the anions in $[Cu^{II}(dpyam)(OXO)(OYO)]$, where OXO and OYO are $[HCO_2]^-$, $[CH_3CO_2]^-$, $[NO_3]^-$, $[ClO_4]^-$ or $[NO_2]^-$, is ambiguous and only a few crystal structures in this series have been reported (Aduldecha & Hathaway, 1991; Ray *et al.*, 1982). As part of studies to examine the complexes in this series, the title complex, (I), was prepared and its structure determined.



(I)

The asymmetric unit of (I) consists of the $[Cu(NO_3)(C_3H_5O_2)(C_{10}H_9N_3)]$ complex. It involves a six-coordinate $CuN_2O_2O'_2$ chromophore, with distorted octahedral stereochemistry (Fig. 1). The octahedra are linked into infinite chains by the bridging bidentate nitrate groups (Addison *et al.*, 1971; Hathaway, 1988). Atoms N2, N3, O4 and O5 of the dpyam and propionate ligands bond almost symmetrically in the CuN_2O_2 plane. The two O atoms, O3 and O2^{i}, from the asymmetrically-bridging nitrate groups occupy axial positions above and below the CuN_2O_2 plane, with Cu—O distances of 2.411 (2) and 2.848 (2) Å, respectively [symmetry code: (i) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$]. These distances are consistent with 'semi-coordination' of the bridging nitrate groups (Procter *et al.*, 1968). The N—O distances involving the coordinated O atoms of the nitrate group are significantly longer compared with those involving the non-coordinated O atoms. Atoms N2, N3, O4 and O5 are essentially coplanar; the Cu atom lies 0.1380 (3) Å above this plane towards the O3 atom. The planar pyridine rings make a dihedral angle of 4.72 (9)° with each other.

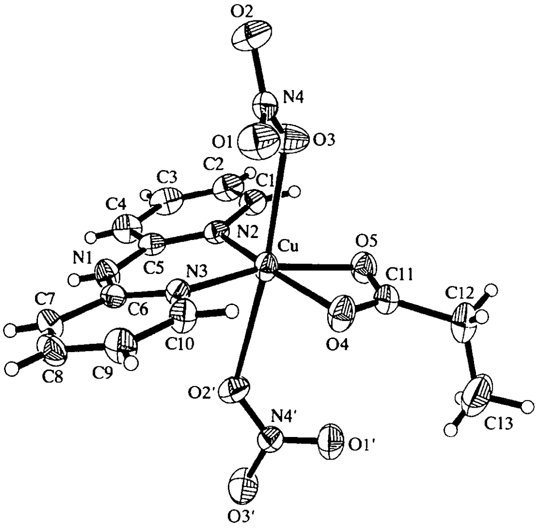


Fig. 1. The structure of title compound showing 30% probability displacement ellipsoids and the atom-numbering scheme.

The bond lengths and angles in (I) are comparable with those observed in the related complexes $[Cu(dpyam)(CH_3CO_2)(NO_3)]$ (Aduldecha & Hathaway, 1991) and $[Cu(dpyam)(CH_3CO_2)(ClO_4)]$ (Ray *et al.*, 1982).

Experimental

The title complex was prepared by adding a boiling solution containing 0.48 g (2.0 mmol) $Cu(NO_3)_2.3H_2O$ in 40 ml water to a warm solution of 0.35 g (2.0 mmol) dpyam in 60 ml ethanol, after which 0.33 g (4.0 mmol) CH_3CH_2COONa was added. After a week, blue–green crystals were formed.

Crystal data

$[Cu(NO_3)(C_3H_5O_2)(C_{10}H_9N_3)]$
$M_r = 369.82$
Monoclinic
$P2_1/n$
$a = 12.615\ (2)$ Å
$b = 9.514\ (1)$ Å
$c = 13.721\ (1)$ Å
$\beta = 116.58\ (1)°$
$V = 1472.7\ (3)$ Å^3
$Z = 4$
$D_x = 1.668$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 39 reflections
$\theta = 5.37–12.45°$
$\mu = 1.515$ mm^{-1}
$T = 293\ (2)$ K
Rectangular slab
$0.60 \times 0.46 \times 0.40$ mm
Light blue

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical *via* ψ scans (Siemens, 1994)
$T_{min} = 0.434$, $T_{max} = 0.546$
4260 measured reflections
3358 independent reflections
2420 reflections with $I > 2\sigma(I)$

$R_{int} = 0.017$
$\theta_{max} = 27.50°$
$h = -1 \rightarrow 16$
$k = -1 \rightarrow 12$
$l = -17 \rightarrow 16$
3 standard reflections every 97 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.093$
$S = 0.985$
3358 reflections
245 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0521P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0083 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cu—N2	1.953 (2)	Cu—O3	2.411 (2)
Cu—N3	1.958 (2)	N4—O1	1.209 (3)
Cu—O4	1.994 (2)	N4—O3	1.248 (3)
Cu—O5	2.018 (2)	N4—O2	1.251 (2)
N2—Cu—N3	94.01 (7)	N2—Cu—O3	85.34 (7)
N2—Cu—O4	164.01 (7)	N3—Cu—O3	104.48 (8)
N3—Cu—O4	99.54 (7)	O4—Cu—O3	99.33 (8)
N2—Cu—O5	100.45 (7)	O5—Cu—O3	86.27 (8)
N3—Cu—O5	162.69 (7)	C11—Cu—O3	93.55 (8)
O4—Cu—O5	64.87 (7)	O3—Cu—O2^{i}	160.1 (2)

Symmetry code: (i) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

The H atoms in the dpyam ligand were located from a difference Fourier map and refined isotropically, whereas those in the propionate group were fixed geometrically and allowed to ride on the attached atoms.

Data collection, cell refinement and data reduction: *XSCANS* (Siemens, 1994). Structure solution and molecular graphics: *SHELXTL/PC* (Sheldrick, 1990). Structure refinement: *SHELXL*93 (Sheldrick, 1993). Geometrical calculations: *PARST* (Nardelli, 1983).

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Tris(*N*,*N*′-diethylthiourea-*S*)iodocopper(I) and Tris(*N*,*N*′-diethylthiourea-*S*)iodosilver(I)

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Abstract

The structures of the 1:3 mononuclear complexes of copper(I) and silver(I) iodide with diethylthiourea (detu), namely, $[CuI(C_5H_{12}N_2S)_3]$ and $[AgI(C_5H_{12}N_2S)_3]$, are isomorphous. The metal atoms are approximately tetrahedrally coordinated to three S atoms and to one I atom.

Comment

Copper and silver(I) halides or oxyanions form neutral or ionic complexes of various stoichiometries and structural types with thiourea (tu) or substituted thiourea ligands (Pakawatchai *et al.*, 1996). $[Cu(tu)_2Cl]$ and $[Ag(tu)_2Cl]$ are isomorphous and form chain structures containing a trigonally coordinated metal atom, whereas $[Cu(tu)_3Cl]$ has a tetrahedral chain structure (Spofford & Amma, 1968, 1970; Vizzini & Amma, 1966; Okaya & Knobler, 1964). $[Cu(dmtu)_3Cl]$ (dmtu is dimethylthiourea) contains tetrahedrally coordinated Cu^{I} (Girling & Amma, 1971). $[Ag(mtu)_3Cl]$ (mtu is methylthiourea) consists of distorted tetrahedral $[(mtu)_3AgCl]$ units (Lee & Amma, 1972). Copper(I) and silver(I) halides form many MXL_3 complexes, where L is a ligand containing group V donators such as PPh_3, *e.g.* $[XCu(PPh_3)_3]$ (X = F, Cl, Br, I) (Gill *et al.*, 1976; Gulliver *et al.*, 1981; Barron *et al.*, 1987) and $[XAg(PPh_3)_3]$ (X = Cl, Br, I) (Cassel, 1981; Engelhardt *et al.*, 1987; Camalli & Caruso, 1987; Hibbs *et al.*, 1996). For species where L

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