

Aqua[(±)-lactate-O,O'](1,10-phenanthroline-κ²N,N')copper(II) nitrateGerardo Medina,^{a†} Laura Gasque^a and Sylvain Bernès^{b*}^aDepartamento de Química Inorgánica, Facultad de Química UNAM, Ciudad Universitaria, México DF 04510, Mexico, and ^bCentro de Química, Instituto de Ciencias, Universidad Autónoma de Puebla, AP 1613, 72000 Puebla, Pue., Mexico

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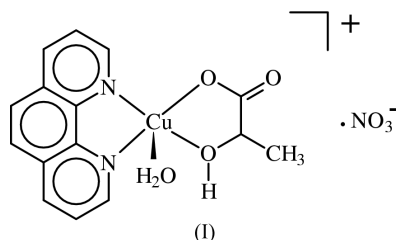
Key indicators

Single-crystal X-ray study
T = 300 K
Mean σ(C–C) = 0.004 Å
R factor = 0.037
wR factor = 0.099
Data-to-parameter ratio = 15.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the structure of the title compound, [Cu(C₃H₅O₃)(C₁₂H₈N₂)(H₂O)]NO₃, the Cu^{II} ion is five-coordinated through two N atoms of the 1,10-phenanthroline ligand, two O atoms of the lactate anion and a water molecule. The cations are well separated in the unit cell, the shortest metal–metal separation being 6.2127 (8) Å.

Comment

A large number of mixed copper chelates of the type [Cu(phen)(O–O)]ⁿ⁺ (*n* = 0 or 1, phen = different substituted 1,10-phenanthrolines and O–O = acetylacetonate, salicylaldehyde, oxalate or malonate) have been reported. We have studied their relative stability *via* solution equilibrium studies, as well as from far IR spectroscopy in the solid state (Gasque, Medina *et al.*, 1999). To validate the latter, isostructurality has first to be established by X-ray diffraction. In this context, most of the crystal structures for the compounds under study have been reported (Fabretti *et al.*, 1985; Kwik *et al.*, 1986; Solans *et al.*, 1987; Su *et al.*, 1995; Gasque, Moreno-Esparza *et al.*, 1999).



Our current interest in relation to this topic is focused on mixed complexes where the O–O ligand is an α -hydroxy acid anion, such as glycolate (Medina *et al.*, 2000) or lactate, of which an example, (I), is presented here.

The asymmetric unit of (I) (Fig. 1) contains one cation and one nitrate anion, both lying on general positions. The copper center is five-coordinated, in a common distorted square-pyramidal geometry, with a τ descriptor (Addison *et al.*, 1984) very close to 0, $\tau = 0.08$. The base of the pyramid is occupied by two O atoms of the racemic lactate ligand and two N atoms of the 1,10-phenanthroline ligand, with the expected coordination bond lengths (Table 1). The metal center is significantly displaced from this plane, the deviation from the calculated least-squares plane (N1, N12, O15 and O18), being 0.2206 (3) Å. This displacement is, for instance, 0.06 Å larger than that observed for the related complex including glycolate instead of lactate (Medina *et al.*, 2000). This difference results from the ability of the nitrate ion to interact with Cu^{II} in the glycolate-containing complex, giving a typical Jahn–Teller distorted octahedral coordination geometry, while in (I), an actual five-coordinated complex is obtained; the shortest

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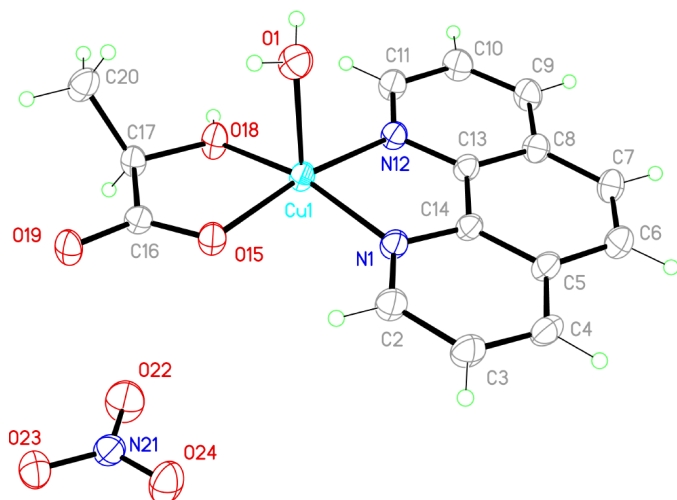


Figure 1
The structure of (I), with displacement ellipsoids drawn at the 40% probability level. H atoms are shown as small spheres of arbitrary radii.

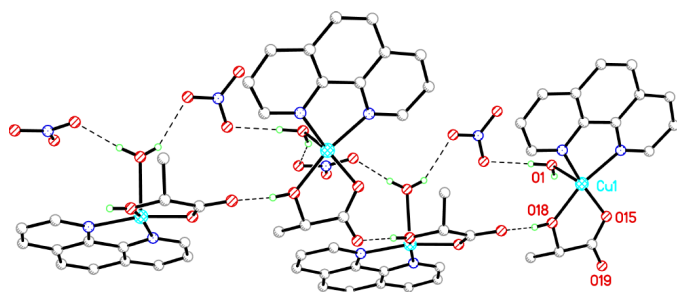


Figure 2
The one-dimensional chains running along [101], formed by hydrogen bonds in (I). Four asymmetric units are displayed and, for the sake of clarity, H atoms not involved in this network have been omitted.

separation between the anion and the metallic center is $\text{Cu1} \cdots \text{O22}$ of 5.000 (3) Å. Finally, the apical coordination site in (I) is occupied by a water molecule, with a long bond length of 2.2283 (19) Å.

The functionality of the cation, together with the presence of nitrate as anion, greatly favors hydrogen bonding in the crystalline state (Table 2). Thus, the hydroxy group O18–H18 of the lactate ligand forms a remarkably strong hydrogen bond with the carboxylate atom O19 of a symmetry-related cation. Other significant O–H \cdots O hydrogen bonds involve the coordinated water molecule. The resulting network is a one-dimensional supramolecular aggregate with [101] as base vector (Fig. 2), the steric hindrance of the 1,10-phenanthroline ligand avoiding inter-chain contacts. These features result in large metal–metal separations in the cell, the shortest Cu \cdots Cu distance being Cu \cdots Cuⁱ of 6.2127 (8) Å [symmetry code: (i) 1 – x, –y, 2 – z].

Experimental

The title compound was obtained by mixing 1 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (0.233 g) with 1 mmol of 1,10-phenanthroline (0.180 g) in 20 ml of MeOH and adding 1 mmol of lithium lactate (0.096 g), previously dissolved in the minimal amount of water. This solution was left standing and air-stable crystals were collected the following day.

Crystal data

$[\text{Cu}(\text{C}_3\text{H}_5\text{O}_3)(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})]\text{NO}_3$
 $M_r = 412.84$
 Monoclinic, $P2_1/n$
 $a = 8.5646$ (13) Å
 $b = 19.985$ (3) Å
 $c = 9.7854$ (13) Å
 $\beta = 104.960$ (11)°
 $V = 1618.2$ (4) Å³
 $Z = 4$

$D_x = 1.695$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 68 reflections
 $\theta = 4.8$ – 12.5°
 $\mu = 1.40$ mm⁻¹
 $T = 300$ (1) K
 Prism, blue
 0.62 × 0.26 × 0.22 mm

Data collection

Bruker P4 diffractometer
 ω scans
 Absorption correction: Gaussian (XSCANS; Siemens, 1996)
 $T_{\text{min}} = 0.599$, $T_{\text{max}} = 0.782$
 4687 measured reflections
 3706 independent reflections
 3156 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -1 \rightarrow 11$
 $k = -25 \rightarrow 1$
 $l = -12 \rightarrow 12$
 3 standard reflections every 97 reflections
 intensity decay: 1.5%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.099$
 $S = 1.04$
 3706 reflections
 235 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0487P)^2 + 0.9828P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.47$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.54$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1–O15	1.9256 (16)	C8–C9	1.407 (4)
Cu1–O18	1.9516 (17)	C9–C10	1.369 (4)
Cu1–N1	1.9970 (19)	C10–C11	1.395 (4)
Cu1–N12	2.0096 (19)	C11–N12	1.331 (3)
Cu1–O1	2.2283 (19)	N12–C13	1.360 (3)
N1–C2	1.328 (3)	C13–C14	1.429 (3)
N1–C14	1.357 (3)	O15–C16	1.267 (3)
C2–C3	1.402 (4)	C16–O19	1.238 (3)
C3–C4	1.367 (4)	C16–C17	1.528 (3)
C4–C5	1.409 (4)	C17–O18	1.435 (3)
C5–C14	1.404 (3)	C17–C20	1.502 (4)
C5–C6	1.437 (4)	N21–O24	1.231 (3)
C6–C7	1.360 (4)	N21–O22	1.239 (3)
C7–C8	1.435 (4)	N21–O23	1.243 (3)
C8–C13	1.403 (3)		
O15–Cu1–O18	82.49 (7)	C10–C9–C8	118.7 (2)
O15–Cu1–N1	93.24 (7)	C9–C10–C11	120.6 (2)
O18–Cu1–N1	164.40 (9)	N12–C11–C10	122.0 (2)
O15–Cu1–N12	169.12 (8)	C11–N12–C13	118.0 (2)
O18–Cu1–N12	99.07 (7)	C11–N12–Cu1	130.06 (17)
N1–Cu1–N12	82.40 (8)	C13–N12–Cu1	111.93 (14)
O15–Cu1–O1	95.03 (8)	N12–C13–C8	123.4 (2)
O18–Cu1–O1	94.78 (8)	N12–C13–C14	116.73 (19)
N1–Cu1–O1	100.55 (8)	C8–C13–C14	119.9 (2)
N12–Cu1–O1	95.57 (8)	N1–C14–C5	123.3 (2)
C2–N1–C14	118.2 (2)	N1–C14–C13	116.18 (19)
C2–N1–Cu1	129.05 (17)	C5–C14–C13	120.6 (2)
C14–N1–Cu1	112.74 (15)	C16–O15–Cu1	116.12 (14)
N1–C2–C3	122.2 (2)	O19–C16–O15	125.1 (2)
C4–C3–C2	119.9 (2)	O19–C16–C17	116.8 (2)
C3–C4–C5	119.3 (2)	O15–C16–C17	118.15 (19)
C14–C5–C4	117.1 (2)	O18–C17–C20	110.5 (2)
C14–C5–C6	118.8 (2)	O18–C17–C16	106.91 (17)
C4–C5–C6	124.1 (2)	C20–C17–C16	112.1 (2)
C7–C6–C5	120.3 (2)	C17–O18–Cu1	115.01 (12)
C6–C7–C8	121.8 (2)	O24–N21–O22	120.7 (3)
C13–C8–C7	117.3 (2)	O24–N21–O23	120.5 (2)
C13–C8–C9	118.6 (2)	O22–N21–O23	118.8 (3)
C9–C8–C7	124.2 (2)		

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O18—H18 \cdots O19 ⁱⁱ	0.87	1.70	2.562 (2)	172
O1—H1B \cdots O23 ⁱⁱⁱ	0.88	1.94	2.819 (3)	174
O1—H1A \cdots O22 ^{iv}	0.77	2.17	2.871 (3)	151

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

H atoms for water molecule (H1A and H1B) and hydroxyl group (H18) were found in difference maps. The remaining H atoms, bonded to sp^2 - and sp^3 -hybridized C atoms, were placed at idealized positions. In the final cycles, all H atoms were constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{parent})$, where $x = 1.5$ for Csp^3-H and $O-H$, and $x = 1.2$ for Csp^2-H groups. Constrained distances: methine $C-H = 0.98 \text{ \AA}$, methyl $C-H = 0.96 \text{ \AA}$ and aryl $C-H = 0.93 \text{ \AA}$.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

SHELXTL-Plus; software used to prepare material for publication: *SHELXL97*.

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