

The Crystal Structure of Aqua(*N*¹-isopropyl-2-methyl-1,2-propanediamine)[(*S*)-lactato]copper(II) (*S*)-Lactate

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The title compound crystallizes in the monoclinic space group $P2_1$ with two formula units in a cell of dimensions $a=10.046(1)$, $b=8.972(1)$, $c=10.676(1)$ Å and $\beta=92.63(1)^\circ$. The structure was solved by direct and Fourier techniques and refined by least-squares calculations to $R=0.035$ for 2203 independent reflections. The structure consists of monomeric $[\text{Cu}(\text{C}_3\text{H}_5\text{O}_3)(\text{C}_7\text{H}_{18}\text{N}_2)\text{H}_2\text{O}]^+$ cations and (*S*)-lactate ions which are connected to each other by hydrogen bonds in layers perpendicular to the a axis. The geometry around Cu(II) is distorted square pyramidal, the bidentate organic ligands forming the base [Cu–N 1.982(3) and 2.025(3), Cu–O 1.952(3) and 1.995(3) Å] and the water O atom occupying the apical position [Cu–O 2.284(3) Å].

Complex formation in aqueous solution between Cu(II) and substituted ethylenediamines has been investigated in our laboratory.^{1–3} Crystallographic analyses of some mono- and bis-(diamine)copper(II) L-lactate complexes have also been carried out. In bis(L-lactato)-(*N,N,N',N'*-tetramethylethylenediamine)copper(II) the coordination geometry of Cu(II) is distorted octahedral (4+2) with out-of-plane coordination of L-lactate ions forming 5-membered chelate rings.⁴ Bis(L-lactato)(*N,N,N',N'*-tetraethylethylenediamine)-copper(II) hemihydrate can also be considered to have distorted octahedral (4+1+1) geometry with out-of-plane coordination of the lactate ions, but here one of the lactate ions forms a 5-membered chelate ring and the other a highly unsymmetrical 4-membered ring.⁵ In bis(*N*¹-isopropyl-2-methyl-1,2-propanediamine) (L-lactato)copper(II) L-lactate

monohydrate the coordination geometry of Cu(II) is square pyramidal (4+1), the apical position being occupied by a carboxyl oxygen atom of the lactate ion.⁶

To examine further the behaviour of substituted ethylenediamines and L-lactate ion in the coordination geometry of Cu(II) we have now investigated aqua(*N*¹-isopropyl-2-methyl-1,2-propanediamine) [(*S*)-lactato]copper(II) (*S*)-lactate by X-ray structural measurements.

EXPERIMENTAL

Blue crystals were obtained by slow evaporation of ethanol solution containing copper(II) (*S*)-lactate monohydrate (prepared from L(+)-lactic acid, Fluka AG, and copper(II) carbonate, J. T. Baker, as described in Ref. 7) and *N*¹-isopropyl-2-methyl-1,2-propanediamine, Fluka AG, in molar ratio 1:1. A single crystal of dimensions 0.15×0.30×0.50 mm was selected for the X-ray investigation.

Unit cell dimensions were obtained from least-squares refinement of 25 well-centered reflections measured on a Nicolet P3 diffractometer using graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda=0.71069$ Å). Crystal data: $a=10.046(1)$, $b=8.972(1)$, $c=10.676(1)$ Å, $\beta=92.63(1)^\circ$, $V=961.2(2)$ Å³, $Z=2$, $M_r=389.94$, $D_c=1.35$ g cm⁻³, space group $P2_1$, $\mu(\text{MoK}\alpha)=12.1$ cm⁻¹.

Intensity data were collected ($5 < 2\theta < 58^\circ$) at room temperature using ω -scan technique and a scan rate varying from 2.0 to 29.3° min⁻¹ depending upon the peak intensity. Out of 2700 independent reflections measured, 2203 had $I > 3\sigma(I)$ and

were used in the structure determination. The data were corrected for Lorentz and polarization factors. The empirical absorption correction from ϕ -scan data proved to be insignificant as the fluctuation of the intensities of the used reflections was comparable to that of the check reflection ($\pm 3\%$).

STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved by a combination of direct and Fourier methods using programs MULTAN 78⁸ and XRAY 76.⁹ The function minimized in least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. Scattering factors for the nonhydrogen atoms were from Cromer and Mann¹⁰ and for H atoms from Stewart, Davidson and Simpson.¹¹ Anomalous dispersion corrections were included for Cu.¹²

Isotropic refinement of the model led to an R value of 0.074 ($R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$). Refinement with anisotropic temperature factors for nonhydrogen atoms and isotropic ones for geometrically positioned H atoms ($U_{iso} = 0.05 \text{ \AA}^2$ and $X-H = 1.0 \text{ \AA}$) except those bonded to O atoms, which were located from a difference Fourier map, gave the R value 0.035. The average shift/error and the maximum shift/error ratios in the last cycle were 0.001 and 0.007, respectively.

The atomic coordinates and equivalent isotropic thermal parameters

$$(B_{eq} = \frac{8}{3}\pi^2 \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \vec{a}_i \cdot \vec{a}_j)$$

with standard deviations in parentheses are given in Table 1. Lists of structure factors and anisotropic thermal parameters are obtainable from the authors.

Table 1. Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{\AA}^2)$
Cu	727(1)	5000	7133(1)	2.71(2)
N1	2418(3)	5415(3)	6232(3)	2.8(1)
N2	1176(3)	6833(4)	8099(3)	2.8(1)
Cl	3186(4)	6500(5)	7020(4)	3.2(2)
C2	2272(4)	7683(5)	7536(4)	3.2(2)
C3	1698(5)	8692(6)	6517(4)	4.1(2)
C4	3037(5)	8603(6)	8521(5)	4.6(2)
C5	3194(4)	4093(6)	5834(4)	3.7(2)
C6	3604(5)	3119(7)	6942(6)	5.1(3)
C7	4367(5)	4525(7)	5057(5)	5.5(3)
O11	375(3)	3068(3)	6346(3)	3.4(1)
O12	-1014(3)	1168(3)	6289(3)	3.9(1)
O13	-535(3)	4247(3)	8376(2)	2.7(1)
C11	-554(4)	2323(5)	6787(4)	2.8(2)
C12	-1158(4)	2882(5)	7984(4)	2.9(2)
C13	-2645(5)	3124(6)	7760(5)	4.6(2)
O21	568(3)	3932(5)	505(3)	4.2(2)
O22	2445(3)	4803(6)	-220(3)	6.5(2)
O23	1798(3)	3477(4)	2801(3)	4.1(1)
C21	1805(4)	4151(5)	565(4)	3.3(3)
C22	2598(4)	3606(5)	1745(4)	3.5(2)
C23	3160(5)	2094(6)	1483(5)	4.9(3)
O1	-959(3)	6001(4)	5896(3)	3.8(1)
H(O13)	-175	4333	9263	
H(O23)	1472	4667	2957	
H1(O1)	-1480	6667	6266	
H2(O1)	-665	6365	5210	

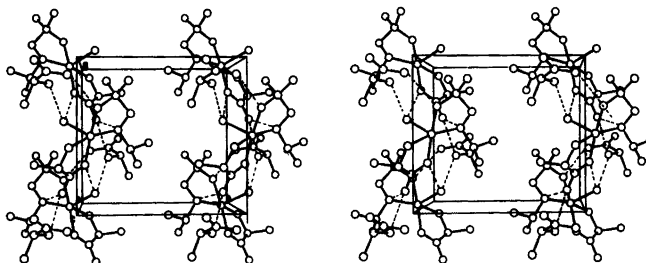


Fig. 1. Stereoview of the packing along the *c*-axis.

RESULTS AND DISCUSSION

The structure consists of aqua(*N*¹-isopropyl-2-methyl-1,2-propanediamine)[(*S*)-lactato]copper(II) cations and (*S*)-lactato ions held together by hydrogen bonds and electrostatic forces (Fig. 1). The complex cation with the atomic labelling is shown in Fig. 2. The atomic labelling of the lactate ion is similar to the chelated lactate group. The bond lengths and angles are listed in Table 2.

The coordination polyhedron around Cu(II) is a distorted square pyramid with the bidentate

organic ligands in the basal positions [Cu–N1 2.025(3), Cu–N2 1.982(3), Cu–O11 1.952(3), Cu–O13 1.995(3) Å]. The O atom of the water molecule occupies the apical position with the distance of 2.284(3) Å. The atoms of the basal plane are displaced from it by –0.104 to 0.106 Å, and the copper atom is displaced by 0.211 Å from the mean plane towards O1. A similar distortion has been found for other comparable square-pyramidal copper(II) compounds. For example, in bis(*N*¹-isopropyl-2-methyl-1,2-propanedi-

Table 2. Interatomic distances (Å) and angles (°) with standard deviations in parentheses.

Cu–N1	2.025(3)	N1–Cu–N2	85.3(1)	O11–Cu–O13	83.0(1)
Cu–N2	1.982(3)	N1–Cu–O11	95.6(1)	O1–Cu–N1	105.6(1)
Cu–O11	1.952(3)	N1–Cu–O13	162.0(1)	O1–Cu–N2	96.9(1)
Cu–O13	1.995(3)	N2–Cu–O11	173.4(1)	O1–Cu–O11	89.2(1)
Cu–O1	2.284(3)	N2–Cu–O13	94.1(1)	O1–Cu–O13	92.3(1)
N1–C1	1.480(5)	Cu–N1–C1	106.1(2)	C5–N1–C1	114.8(3)
C1–C2	1.523(6)	Cu–N2–C2	111.7(3)	C1–C2–C3	112.0(4)
C2–N2	1.488(6)	N1–C1–C2	110.9(3)	C1–C2–C4	109.6(4)
N1–C5	1.492(6)	C1–C2–N2	105.0(4)	C3–C2–C4	109.7(4)
C5–C6	1.512(8)	Cu–N1–C5	116.8(2)	C3–C2–N2	109.5(3)
C5–C7	1.523(7)	N1–C5–C6	111.4(4)	C4–C2–N2	111.1(4)
C2–C3	1.510(6)	N1–C5–C7	112.4(4)	C6–C5–C7	112.5(4)
C2–C4	1.518(7)				
C11–O11	1.257(5)	Cu–O11–C11	115.7(3)	C11–C12–C13	110.0(3)
C11–O12	1.244(5)	O11–C11–O12	123.4(4)	O13–C12–C13	109.8(4)
C11–C12	1.525(6)	O11–C11–C12	118.0(4)	Cu–O13–C12	112.3(2)
C12–O13	1.428(5)	O12–C11–C12	118.6(4)		
C12–C13	1.518(6)	C11–C12–O13	110.0(3)	O13...O11	2.614(4)
C21–O21	1.257(5)	O21–C21–O22	125.9(4)	O23–C22–C23	107.8(4)
C21–O22	1.227(6)	O21–C21–C22	117.7(4)		
C21–C22	1.539(6)	O22–C21–C22	116.3(4)		
C22–O23	1.418(5)	C21–C22–O23	112.7(3)	O23...O21	2.724(4)
C22–C23	1.500(7)	C21–C22–C23	108.6(4)		

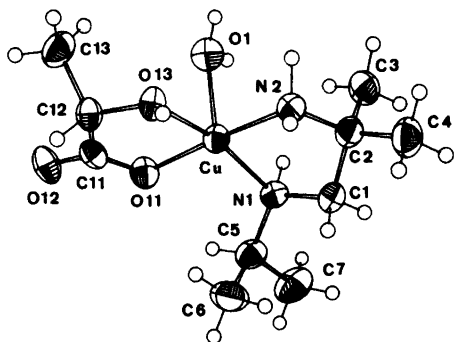


Fig. 2. View of the complex cation.

amine)- μ -(oxalato- $O, O': O''$)-oxalatodicopper(II) monohydrate,¹³ *catena*-(N^1 -isopropyl-2-methyl-1,2-propanediamine)- μ -(malato- $O, O': O''$)-copper(II) pentahydrate¹⁴ and aqua(N^1 -isopropyl-2-methyl-1,2-propanediamine)malonato-copper(II) monohydrate,¹⁵ the copper(II) atom is displaced 0.127–0.279 Å from the mean basal plane towards the apical oxygen atom (Table 3). The displacement is greatest in malonate complex although the Cu–O(apical) bond distance of 2.501(7) Å is significantly longer than in lactate, malate and oxalate complexes [Cu–O(apical) 2.226(5)–2.284(3) Å]. Evidently the orientation of the substituents of the diamine chelate ring is responsible for the displacement. The isopropyl group is situated above the basal plane towards the apical water molecule and the axial methyl group below the basal plane towards the sixth unoccupied coordination site. In lactate, malate

and oxalate complexes the axial methyl group points towards the apical oxygen atom and the isopropyl group away from it. In the malate complex, where the displacement is least, the out-of-plane chelation of the malate ion [Cu–O(carboxyl) 1.969(5), Cu–O(hydroxyl) 2.226(5) Å] and the bonding of the two oxygen atoms of the second carboxyl group of the malate ion from the neighbouring complex unit [Cu–O(basal) 2.011(5), Cu \cdots O(off-z-axis) 2.774(5) Å] diminish the displacement of Cu to 0.127 Å from the mean equatorial plane. The coordination sphere of Cu(II) could thus also be considered as very distorted octahedral (4+1+1).¹⁶

The bond lengths and angles within the bidentate diamine ligand compare well with those reported in other Cu(II) complexes.^{13–15, 17–19} The diamine chelate ring assumes an asymmetric gauche configuration (δ). The C1 and C2 atoms deviate 0.399 and –0.270 Å from the N1–Cu–N2 plane, respectively. The asymmetry is much less than in square-planar bis(N^1 -isopropyl-2-methyl-1,2-propanediamine)nickel(II) perchlorate²⁰ where intra- and intermolecular interactions are weaker.

Both the coordinated and uncoordinated carboxylate groups (C–COO) are planar. The α -hydroxyl oxygen atom O13 deviates 0.051 Å from the C–COO plane, and O23 deviates 0.559 Å. This unusually high value for the lactate group^{21–25} arises from the hydrogen bond interactions.

The complex cations and (*S*)-lactate ions are

Table 3. Selected relevant structural parameters (Å and °) for some [Cu(carboxylato)($C_7H_{18}N_2$)Y]-type complexes with CuN_2O_2O chromophore.

Carboxylate Y	Malate	Oxalate	Lactate H ₂ O	Malonate H ₂ O
Reference	14	13	This work	15
Cu–N1 (secondary)	2.053(6)	2.010(5)	2.038(5)	2.043(6)
Cu–N2 (primary)	1.990(6)	1.974(6)	1.997(5)	1.987(7)
Cu–O1 (trans to N1)	2.011(5)	1.950(4)	1.984(5)	1.952(6)
Cu–O2 (trans to N2)	1.969(5)	1.921(5)	1.963(4)	1.924(6)
Cu–O(apical)	2.226(5)		2.273(4)	2.501(7)
N1–Cu–O1	165.2(2)	179.2(2)	149.8(2)	155.7(3)
N2–Cu–O2	177.3(2)	174.7(2)	179.2(2)	170.2(3)
ΔZ^a	0.12–0.13	0.04–0.05	0.26–0.27	0.13–0.14
ΔCu^b	0.127	0.044	0.261	0.279

^a Deviations of the basal atoms from their mean plane. ^b Deviation of Cu(II) from the mean basal plane.

hydrogen bonded in layers perpendicular to the *a* axis (Fig. 1). The α -hydroxyl group of the lactate ion joins the complex cations related by the *b* translation into chains [O23...O12(-*x*, 1/2+*y*, 1-*z*)=2.732(5) and O23...O1(-*x*, *y*-1/2, 1-*z*)=2.773(5) Å]. Two such chains, related by screw axis and *c* translation as shown in Fig. 1, are associated by hydrogen bonds O1...O11(-*x*, 1/2+*y*, 1-*z*)=3.105(4) and N1...O12(-*x*, 1/2+*y*, 1-*z*)=3.056(4) Å. The carboxyl oxygen atoms of the lactate ion connect these "double chains" together in the direction of the *c* axis: O21...N2(-*x*, *y*-1/2, 1-*z*)=3.013(5), O21...O13(*x*, *y*, *z*-1)=2.499(4) and O22...N2(*x*, *y*, *z*-1)=2.860(6) Å. The O22 atom also occupies the sixth coordination site of Cu(II) at the equivalent position (*x*, *y*, *z*-1) but the distance of 3.247(3) Å is too long to be considered a bonding distance. All contacts between layers are greater than 3.6 Å.

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