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Structure and Absolute Configuration of a Quinic Acid–Copper(II) Complex

ITKA BKOUCHE-WAKSMAN

Laboratoire de Cristallographie, Institut de Chimie des Substances Naturelles, CNRS, Avenue de la Terrasse, 91198 Gif-sur-Yvette, France

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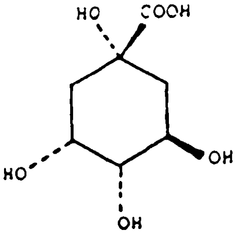
Abstract

In the title compound, *catena*-poly[(aquachlorocopper)-μ-(1,3,4,5-tetrahydroxycyclohexane-1-carboxylato-O,O^1:O^3,O^4) monohydrate], [CuCl($C_7H_{11}O_6$)(H_2O)].H_2O, the absolute configuration (1*R*,3*R*,4*R*,5*R*) has been verified. The 1,3,4,5-tetrahydroxycyclohexane-1-carboxylic acid (quin) ligand binds as a tetradentate ligand through the carboxylate, one axial and two adjacent *trans* equatorial hydroxy O atoms to two Cu atoms. Copper is in a distorted octahedral coordination; Cl and one water molecule complete the set of donor atoms. The structure consists of infinite chains running parallel to the *a* axis, held together *via* the solvated water molecule by two hydrogen bonds, one of which is very short.

Comment

The crystal structure determination of the title compound was undertaken as part of a study of quinic acid–metal complexes (Salazar-Garcia, Barba-Behrens, Bello-Ramirez, Contreras & Flores-Parra, 1993). The quinic acid (quin) molecule (I) has several functional groups available for cation binding and the structure determination was undertaken to discover its mode of binding.



(I)

Several studies of metal complexes have been made in solution (Katzin, 1973; Sakovich & Skoric, 1977; Brittain, Copeland, Ransom & Spaulding, 1983), but not in the solid state. To our knowledge, only two crystal structure determinations involving quinic acid have been published, the free quinic acid (Abell, Allen, Bugg, Doyle & Raithby, 1988) and the caffeine–potassium chlorogenate complex (Martin *et al.*, 1986, 1987).

The Cu atom has a distorted octahedral coordination consisting of the chlorine, one carboxylic and three hydroxy O atoms of two quinic moieties and one water molecule (Fig. 1). The best description of the octahedron is obtained by giving the bases Cl^- and $—COO^-$ equivalent roles in the coordination. These two ligands are, therefore, in axial positions, with the largest angle around copper being Cl—Cu—O7 = 173.7 (1)°. The four basal atoms, O1, O3^i, O4^i and O*W*, are less than 0.02 Å from their mean plane and the Cu is pulled out in the direction of Cl by 0.23 Å, in agreement with Cl being a more effective ligand than carboxylate. The five-atom mean planes [Cu, O1, C1, C7, O7] and [Cu, O3^i, C3^i, C4^i, O4^i] make a dihedral angle of 92°. The corresponding first ring has an envelope conformation with Cu out of the plane; the second ring is a half chair with very open torsion angles [O3—C3—C4—O4 = −56.5 (3), Cu—O3—C3—C4 = 41.3 (2), Cu—O4—C4—C3 = 43.5 (2)°].

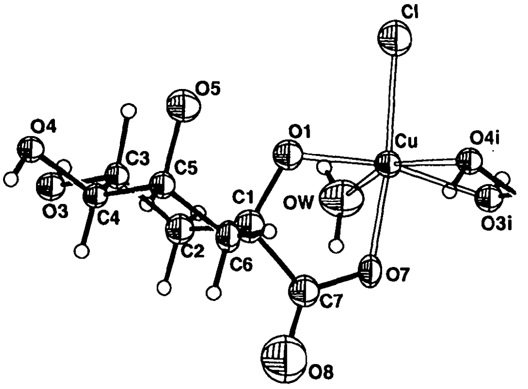


Fig. 1. Diagram of the coordination about copper and the atom labelling, showing the repeating unit. Thermal ellipsoids are shown at the 50% probability levels.

All copper–ligand distances agree with generally observed values. In the following discussion, all comparisons are made with crystallized quinic acid (Abell *et al.*, 1988). The coordination effect (on electron delocalization of the carboxylate) is seen by a shortening of the C7—O7 bond length [1.265 (4) Å] compared to the corresponding bond in quinic acid [1.306 (3) Å], while the C7—O8 bond length is not significantly modified.

The cyclohexane ring is in a chair conformation with hydroxy O3 and O4 atoms and the carboxylic C7 atom in equatorial positions, and the hydroxy O1 and O5 atoms in axial positions as in free quinic acid. The same distortion is observed in that the torsion angle on one side of the ring exceeds the mean value of 55.7 (3)° by 5.9° (C2—C3—C4—C5) and there is a compensation on the other side by a flattening effect (C5—C6—C1—C2). Bonding to Cu of the two adjacent *trans* equatorial hydroxy O3 and O4 atoms modifies some of the distances between non-bonded O atoms; O3···O4 shrinks to 2.723 (6) Å [2.873 (4) in acid] and O5···O4 increases to 2.842 (6) Å [2.795 (4) Å in acid], while O1···O5 [2.863 (6) Å] is left unchanged. Atoms O1 and O7 are in an eclipsed arrangement as in the free acid. Bonding of O1 and O7 to Cu closes the O1—C1—C7—O7 torsion angle [2.6 (3) instead of 8.3 (3)°] and lengthens the O1···O7 non-bonded distance [2.545 (6) instead of 2.503 (4) Å]. The difference with the other end of the quinic moiety, the O3—C3—C4—O4 torsion angle and the O3···O4 distance, is expected since the rigid geometry of the —COO group can fit the coordination requirements of Cu by rotation about the C1—C7 bond.

The bonding of a quinic moiety to one Cu by one carboxylic O atom and one axial hydroxy O atom (both located at its 'head'), and to another Cu by two equatorial hydroxy O atoms (located at its 'end'), generates infinite polymeric chains (Fig. 2). Consequently, the Cu atom is located almost in one cyclohexane ring mean plane [0.33 Å below] and at 2.09 Å from the following ring plane in the chain, giving the chain the shape of stairs, extending in the **a** direction.

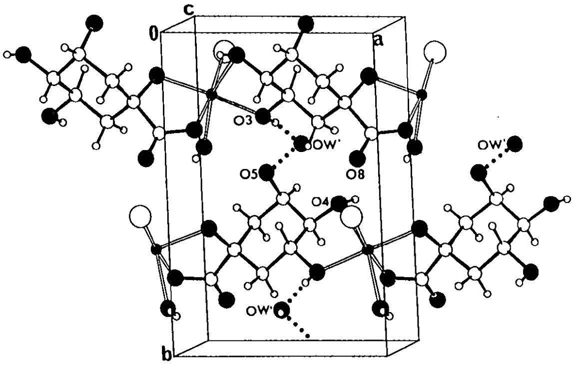


Fig. 2. Packing diagram of the title structure showing the hydrogen bonding. Cu and O atoms are shown as black circles, Cl and H atoms as white circles.

The chains are held together by two hydrogen bridges through the second water molecule present in the structure (Fig. 2). Corresponding O···O distances for O3($x-1, y, z$)···OW'···O5($2-x, \frac{1}{2}+y, 1-z$) are 2.582 (7) and 2.774 (7) Å, respectively, and show that the first hydrogen bond (where O3 is the donor atom; angle O3—HO3···OW' = 167°) is very strong. For the second hydrogen bond the H atom is not located. The shortest van der Waals interactions are O4···O8($3-x, -\frac{1}{2}+y, 2-z$) [3.021 (7) Å] between two chains and OW'···O4($2-x, \frac{1}{2}+y, 1-z$) [3.032 (7) Å] with the second water molecule.

This is the first structure determination of a quinic acid–metal complex. The binding of this ligand shows that it acts as a tetradentate ligand in the present copper(II) complex. In addition to the carboxylate O atom, one axial and two adjacent *trans* equatorial hydroxy O atoms bind to two metal atoms. This result differs from the conclusions of solution studies on Tb^{III} complexes (Brittain *et al.*, 1983) where quin was found to be terdentate.

Experimental

Crystal data

[CuCl($C_7H_{11}O_6$)(H_2O)].H_2O
M_r = 326.2
Monoclinic
$P2_1$
a = 7.774 (3) Å
b = 11.235 (4) Å
c = 6.463 (3) Å
β = 92.15 (1)°
V = 564.1 (1) Å^3
Z = 2
D_x = 1.92 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 8–15°
μ = 2.167 mm^{-1}
T = 298 K
Prism
0.45 × 0.40 × 0.30 mm
Green

Data collection

Philips PW1100 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
6419 measured reflections
5710 independent reflections
3979 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int}$ = 0.052
$\theta_{\rm max}$ = 38°
$h = -12 \rightarrow 12$
$k = -17 \rightarrow 17$
$l = 0 \rightarrow 11$
3 standard reflections
frequency: 180 min
intensity variation: none

Refinement

Refinement on F
R = 0.045
wR = 0.056
S = 1.29
3975 reflections
154 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.001F^2]$
$(\Delta/\sigma)_{\rm max} < 0.02$
$\Delta\rho_{\rm max}$ = 0.62 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.39 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Data collection: Philips diffractometer software. Data reduction: *PHIL* (Riche, 1981). Structure solution: *SHELXS86* (Sheldrick, 1986). Structure refinement: *SHELX76* (Sheldrick, 1976). Molecular graphics: *R3M* (Riche, 1983); *ORTEP* (Johnson, 1965).

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\rm eq} = \frac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cu	0.8234 (1)	0.7022 (1)	0.6989 (1)	0.021 (1)
Cl	0.7988 (2)	0.5877 (2)	0.4147 (2)	0.033 (1)
O1	1.0610 (4)	0.6425 (3)	0.7839 (5)	0.025 (2)

O3	1.5845 (3)	0.7708 (3)	0.6949 (4)	0.022 (2)
O4	1.6625 (4)	0.5724 (3)	0.9216 (5)	0.024 (2)
O5	1.3241 (5)	0.4764 (3)	0.9115 (5)	0.034 (2)
O7	0.8715 (4)	0.8013 (3)	0.9395 (5)	0.027 (2)
O8	1.0731 (5)	0.8805 (4)	1.1452 (7)	0.054 (4)
O*W*	0.8982 (6)	0.8758 (4)	0.5146 (6)	0.049 (4)
O*W*′	0.4567 (5)	0.8733 (4)	0.3662 (6)	0.042 (3)
C1	1.1539 (4)	0.7145 (5)	0.9363 (5)	0.023 (2)
C2	1.2984 (4)	0.7820 (4)	0.8290 (6)	0.023 (2)
C3	1.4467 (3)	0.7007 (5)	0.7764 (4)	0.018 (2)
C4	1.5150 (4)	0.6405 (3)	0.9720 (5)	0.019 (2)
C5	1.3752 (5)	0.5634 (3)	1.0646 (6)	0.022 (2)
C6	1.2223 (5)	0.6415 (4)	1.1178 (6)	0.027 (3)
C7	1.0242 (4)	0.8083 (4)	1.0133 (6)	0.027 (3)

Table 2. *Geometric parameters* (Å, °)

Cu—Cl	2.245 (1)	C5—C6	1.527 (5)
Cu—O3^{i}	2.010 (2)	C6—C1	1.511 (5)
Cu—O7	1.937 (3)	C1—C7	1.554 (5)
Cu—O1	2.021 (2)	O1—C1	1.447 (4)
Cu—O4^{i}	2.429 (3)	O3—C3	1.445 (4)
Cu—O*W*	2.370 (4)	O4—C4	1.427 (4)
C1—C2	1.542 (5)	O5—C5	1.436 (4)
C2—C3	1.519 (5)	O8—C7	1.226 (6)
C3—C4	1.512 (4)	O7—C7	1.265 (4)
C4—C5	1.530 (4)		
Cl—Cu—O7	173.7 (1)	O4^{i}—Cu—O*W*	159.1 (1)
O1—Cu—O3^{i}	164.8 (1)		
C1—C2—C3—C4	−56.7 (3)	O3—C3—C2—C1	−174.5 (4)
C2—C3—C4—C5	61.9 (3)	O3—C3—C4—O4	−56.5 (3)
C3—C4—C5—C6	−60.4 (3)	O3—C3—C4—C5	−179.3 (3)
C4—C5—C6—C1	54.3 (3)	O5—C5—C6—C1	−63.7 (3)
C5—C6—C1—C2	−49.7 (3)	O5—C5—C4—O4	−60.9 (3)
C6—C1—C2—C3	50.9 (3)	O5—C5—C4—C3	59.5 (3)
O1—C1—C6—C5	73.0 (3)	O1—C1—C2—C3	−73.7 (3)

Symmetry code: (i) $x - 1, y, z$.

As the product is air sensitive, the crystal was coated with vaseline oil and sealed in a Lindemann capillary. 12 H atoms out of the 15 present in the compound (HO1, HO5, H2*W* missing) were located from a Fourier map, introduced in fixed positions and attributed isotropic thermal factors equal to those of the bound atoms. The absolute configuration of the original product (1*R*,3*R*,4*R*,5*R*) has been checked by refinement (*R* was equal to 0.045 instead of 0.063 for the opposite enantiomer) and by comparison of 88 selected Bijvoet pairs $\pm h \pm k + l$ corresponding to $\Delta F_c > 1.5$ e using the anomalous dispersion of the Cu and Cl atoms.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond angles, least-squares-planes data and selected Bijvoet pairs have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71411 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1060]

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cis-[IrCl(CO)(PPh_3)(μ-P_4S_3)]$_2$.2$CH_3C_6H_5$

ESTELLE KUWABARA AND ROBERT BAU

Department of Chemistry, University of Southern California, Los Angeles, California 90089-0744, USA

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Abstract

The structure of *cis*-bis(μ-2,6,7-trithia-1,3,4,5-tetraphosphabicyclo[2.2.1]heptanato)-1κP^3,1:2$\kappa^2 P^5$;-2κP^3,1:2$\kappa^2 P^5$-bis[carbonylchloro(triphenylphosphine)-iridium] toluene solvate, *cis*-[IrCl(CO)(PPh_3)(μ-P_4S_3)]$_2$.-2$CH_3C_6H_5$, has been determined by single-crystal X-ray diffraction. Each P_4S_3 ligand is bidentate, binding to the two Ir centers through oxidative addition and the cleavage of a basal P—P bond.

Comment

Tetraphosphorus trisulfide, P_4S_3, has exhibited interesting coordination chemistry with a variety of transition-metal complexes and is the subject of two review articles (di Vaira, Stoppioni & Peruzzini, 1990; di Vaira & Stoppioni, 1992). The complex *trans*-[IrCl(CO)(PPh_3)(μ-P_4S_3)]$_2$, which exhibited a single carbonyl stretching band at 2055 cm^{-1} in its Nujol-mull infrared spectrum, was the reported product from the equimolar reaction between Vaska's complex, [IrCl(CO)(PPh_3)$_2$], and P_4S_3 in benzene at 333 K; its X-ray crystal structure was determined (Ghilardi, Midollini & Orlandini, 1983).

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