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catena-Poly[[[aqua(2-methyl-4-oxo-4*H*-pyran-3-olato-$\kappa O^3,O^4$)copper(II)]-μ-chloro] monohydrate]

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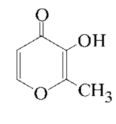
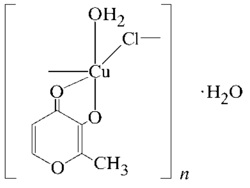
In the title complex, $\{[Cu(C_6H_5O_3)Cl(H_2O)]\cdot H_2O\}_n$, the Cu^{II} atom has a deformed square-pyramidal coordination geometry formed by two O atoms of the maltolate ligand, two bridging Cl atoms and the coordinated water O atom. The Cu atoms are bridged by Cl atoms to form a polymeric chain. The deprotonated hydroxyl and ketone O atoms of the maltolate ligand form a five-membered chelate ring with the Cu atom. Stacking interactions and hydrogen bonds exist in the crystal.

Comment

Maltol (3-hydroxy-2-methyl-4*H*-pyran-4-one), (I), is a naturally occurring non-toxic compound. It has the ability to be deprotonated readily (pK_a = 8.38; Hedlund & Öhman, 1988) and can act as an anionic chelating *O,O*′-bidentate ligand towards a number of biologically active metal ions. The metal complexes of (I) can be solubilized in water, and many biological studies have been reported employing this compound as a ligand. For instance, the Al^{III} complex has been studied in relation to apoptosis (Tsubouchi *et al.*, 2001) and Alzheimer's disease (Finnegan *et al.*, 1986), the Fe^{III} complex has been used in the treatment of iron deficiency anaemia (Harvey *et al.*, 1998), and the V^{IV} complex is a potent insulin mimic (Caravan *et al.*, 1995). The efficacy of the Cu^{II} and Sn^{II} complexes in oral-care formations (Creeth *et al.*, 2000) has also been reported. A number of crystal structures of maltolate–metal complexes have been reported, *viz*. Al^{III} (Finnegan *et al.*, 1986; Yu *et al.*, 2002), V^{IV} (Caravan *et al.*, 1995; Sun *et al.*, 1996, 1998), Fe^{III} (Ahmet *et al.*, 1988), Zn^{II} (Ahmed *et al.*, 2000), Mo^{IV} (Lord *et al.*, 1999), Ru^{IV} (Fryzuk *et al.*, 1997), Sn^{II} (Barret *et al.*, 2001) and Sn^{IV} (Denekamp *et al.*, 1992; Bhattacharya *et al.*, 1994). In this study, to obtain further evidence for the chelating mode of maltol with divalent metal ions, we have analyzed the crystal structure of the maltolate–Cu^{II} complex *catena*-poly[[[aqua(2-methyl-4-oxo-4*H*-pyran-3-olato-$\kappa O^3,O^4$)copper(II)]-μ-chloro] monohydrate], (II).



(I)



(II)

The crystal structure of (II) is shown in Fig. 1. The Cu atom is surrounded by five atoms in a square-pyramidal coordination geometry (Fig. 1), in which the basal plane is made up of two O atoms of the maltolate ligand, one Cl atom and one water O atom, with the Cl atom of the next complex occupying the apical position. The Cu atom is shifted by about 0.15 Å from the average basal plane toward the apical Cl atom. The deprotonated hydroxyl and ketone O atoms of the ligand form a five-membered chelate ring with the Cu atom. The ketone C1—O2 bond length [1.272 (2) Å] is longer than that of free maltol [1.244 (3)–1.254 (3) Å; Burgess *et al.*, 1996], and shorter than the enol bond length [C2—O3 = 1.339 (2) Å] (Table 1). This indicates a distinction between Lewis acid–base interactions for the two types of O atoms. The Cl atom coordinates from the apical position more weakly to the tetracoordinate basal plane around the Cu atom, forming a square-pyramidal geometry, then the complexes are related by the *a* glide forming the polymeric chain [Cl1—Cu1 = 2.2445 (6) Å, Cl1—Cu1^i = 2.7546 (9) Å, Cu1—Cl1—Cu1^i = 124.04 (3)° and Cl1—Cu1^i—Cl1^i = 101.38 (2)°; symmetry code: (i) $-\frac{1}{2}+x, \frac{1}{2}-y, z$] (Fig. 1). The two different Cu—Cl distances in the title

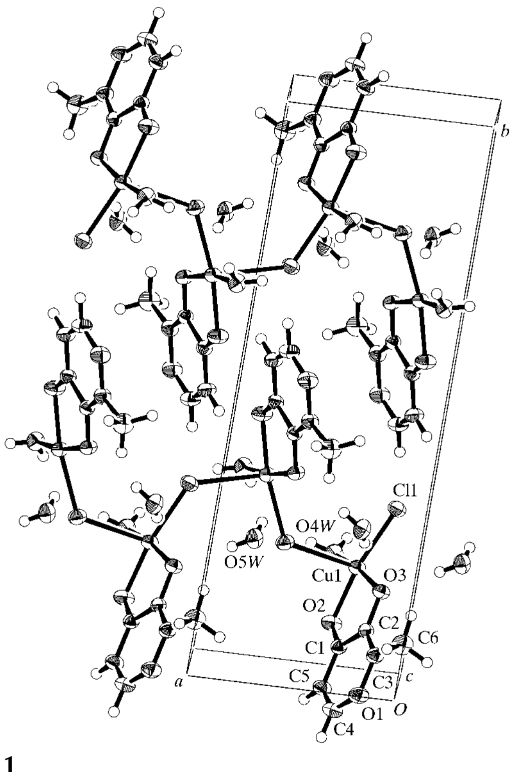


Figure 1
*ORTEP*II (Johnson, 1976) drawing of the title compound, showing the atomic numbering scheme. Ellipsoids for non-H atoms are shown at the 50% probability level.

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compound are similar to those in the 5-formyluracil thiosemicarbazone–Cu^{II} complex [apical Cu—Cl = 2.665 (3) Å and basal Cu—Cl = 2.260 (3) Å], and the longer apical Cu—Cl bond is due to a Jahn–Teller effect (Ferrari *et al.*, 1998). The polymeric chain and an analogous coordination sphere were observed in the crystal structure of *catena*-poly[bis(2-aminopyrimidine)aquacopper(II)-μ-sulfato dihydrate] (Lumme *et al.*, 1996).

In the crystal structure of (II), there are O—H···O hydrogen-bond interactions between the solvate water molecules and the deprotonated O atoms of the maltolate ligands, and between the solvate water molecules and the copper-coordinated water molecules (Table 2). Also, stacking interactions exist between neighboring pyran rings [O1···C1^{ii} = 3.493 (3) Å, C2···C4^{ii} = 3.506 (3) Å and C3···C5^{ii} = 3.515 (4) Å; symmetry code: (ii) $-x$, $-y$, $1 - z$].

The title compound is composed of maltolate and metal in a 1:1 ratio. This is the first observation of a 1:1 metal complex of maltol, although 2:1 and 3:1 maltolate–metal complexes, with Zn^{II} (2:1), Sn^{II} (2:1), Fe^{III} (3:1) and Al^{III} (3:1), have been reported. In all the metal complexes of maltol reported, the bidentate maltolate ligand forms a five-membered chelate ring.

Table 1
Selected geometric parameters (Å, °).

Cl1—Cu1	2.2445 (6)	Cu1—O4*W*	1.965 (1)
Cl1—Cu1^{i}	2.7546 (9)	O2—C1	1.272 (2)
Cu1—O2	1.957 (1)	O3—C2	1.339 (2)
Cu1—O3	1.947 (1)		
Cl1—Cu1—O2	169.82 (6)	O2—Cu1—O4*W*	86.49 (6)
Cl1—Cu1—O3	93.45 (4)	O3—Cu1—Cl1^{ii}	91.98 (5)
Cl1—Cu1—O4*W*	94.13 (5)	O3—Cu1—O4*W*	169.75 (6)
Cu1—Cl1—Cu1^{i}	124.04 (3)	Cu1—O2—C1	110.9 (1)
Cl1^{ii}—Cu1—Cl1	101.38 (2)	Cu1—O3—C2	109.4 (1)
O2—Cu1—Cl1^{ii}	88.72 (6)	O2—C1—C2	118.0 (2)
O2—Cu1—O3	84.84 (5)	O3—C2—C1	116.5 (2)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4*W*—H4*WA*···O5*W*^{i}	0.79 (2)	1.94 (2)	2.711 (2)	168 (3)
O4*W*—H4*WB*···O5*W*	0.80 (2)	1.94 (2)	2.706 (2)	162 (2)
O5*W*—H5*WA*···O3^{iii}	0.77 (2)	2.16 (2)	2.910 (2)	164 (3)
O5*W*—H5*WB*···O3^{ii}	0.79 (2)	1.98 (2)	2.768 (2)	172 (3)

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

Experimental

Maltol and $CuCl_2 \cdot 2H_2O$ were dissolved in a 50% ethanol–water mixture in a 4:1 molar ratio. Green plate-shaped crystals of (II) were obtained by slow evaporation at room temperature.

Crystal data

$[Cu(C_6H_5O_3)Cl(H_2O)] \cdot H_2O$
$M_r = 260.13$
Monoclinic, $P2_1/a$
$a = 7.163$ (2) Å
$b = 18.604$ (2) Å
$c = 7.357$ (2) Å
$\beta = 113.38$ (2)°
$V = 899.9$ (4) Å^3
$Z = 4$
$D_x = 1.920$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 22 reflections
$\theta = 14.6$–15.0°
$\mu = 2.71$ mm^{-1}
$T = 296.2$ K
Plate, green
0.40 × 0.20 × 0.10 mm

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.527$, $T_{max} = 0.763$
2302 measured reflections
2069 independent reflections
1778 reflections with $I > 2\sigma(I)$
$R_{int} = 0.009$
$\theta_{max} = 27.5$°
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 24$
$l = -9 \rightarrow 8$
3 standard reflections every 150 reflections
intensity decay: 0.5%

Refinement

Refinement on F^2
$R(F) = 0.021$
$wR(F^2) = 0.058$
$S = 1.07$
2069 reflections
132 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0270P)^2 + 0.3833P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0047 (8)

The H atoms of the ligand molecule were allowed for as riding atoms. Those of the water molecules were located from difference Fourier maps and their coordinates refined with fixed isotropic displacement parameters.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku, 2000); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1078). Services for accessing these data are described at the back of the journal.

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