

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

| D—H...A | D—H | H...A | D...A | D—H...A |
|-------------------------------|----------|----------|-----------|---------|
| OW1—H1...O21 | 0.75 (4) | 2.37 (4) | 2.836 (5) | 122 (4) |
| OW1—H2...OW2 ⁱ | 0.82 (5) | 2.46 (6) | 3.007 (5) | 125 (5) |
| OW2—H3...O22 | 0.91 (4) | 1.88 (4) | 2.741 (5) | 156 (4) |
| OW2—H4...O41 ⁱⁱ | 0.81 (4) | 2.13 (4) | 2.895 (4) | 157 (5) |
| O31—H31...O21 | 0.82 | 1.846 | 2.570 (4) | 146.4 |
| O32—H32...O22 | 0.82 | 1.848 | 2.559 (5) | 144.2 |
| N21—H211...O42 ⁱⁱⁱ | 1.08 (5) | 1.78 (5) | 2.850 (5) | 171 (4) |
| N21—H212...O21 ^{iv} | 0.80 (3) | 2.42 (4) | 2.971 (4) | 127 (4) |
| N22—H221...O41 ^v | 0.94 (5) | 2.04 (4) | 2.974 (5) | 173 (4) |

Symmetry codes: (i) $x - 1, y, z$; (ii) $1 + x, y, z$; (iii) $x - 1, y, 1 + z$; (iv) $x, y, 1 + z$; (v) $1 + x, y, z - 1$.

Phenyl H atoms were made to ride on C atoms with $U(H) = 1.5U_{eq}(C)$. Hydroxy H atoms were also riding, but U_{iso} for these was refined freely as were coordinates and U_{iso} for amide and water H atoms. The absolute structure parameter indicates racemic twinning of the crystal.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1994). Cell refinement: *PARAM* in *XRAY76* (Stewart *et al.*, 1976). Data reduction: *NRCVAX* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEPII* (Johnson, 1971). Software used to prepare material for publication: *SHELX97*.

The financial support of the Ministry for Science and Technology, Republic of Slovenia, through grant No. J1-7313-103 is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1276). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 178–180

Pentaaqua(chelidonato-*O*⁴)copper(II) monohydrate

LJUBICA MANOJLOVIĆ-MUIR, KENNETH W. MUIR, ROBERT A. CAMPBELL, JOHN E. MCKENDRICK AND DAVID J. ROBINS

Chemistry Department, University of Glasgow, Glasgow G12 8QQ, Scotland. E-mail: ken@chem.gla.ac.uk

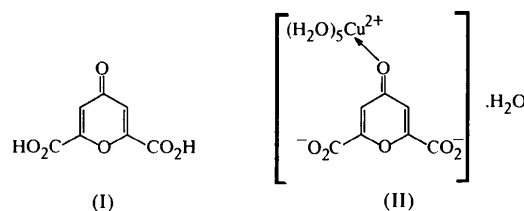
(Received 20 July 1998; accepted 16 September 1998)

Abstract

In crystals of pentaaqua(4-oxo-4*H*-pyran-2,6-dicarboxylato-*O*⁴)copper(II) hydrate, [Cu(C₇H₂O₆)(H₂O)₅].H₂O, the Cu^{II} cation is surrounded by an elongated O₆ octahedron. The chelidonate anion {chel, [C₅H₂O₂(COO)₂]²⁻} binds to the metal centre through the carbonyl rather than a carboxylate oxygen, and forms a long axial Cu—O bond [2.6746 (16) Å]. The axial Cu—O_{aq} bond is also relatively long [2.3763 (15) Å]. The molecular assembly in the crystal is stabilized by a complex three-dimensional network of intermolecular O—H...O bonds [O...O 2.597 (2)–2.851 (2) Å], the water molecules providing the donors, and the carboxylate and carbonyl groups of the chel ligand most of the acceptors, of the hydrogen bonding.

Comment

Dihydrodipicolinate synthase, a key enzyme in the biosynthesis of lysine *via* the diaminopimelate pathway (Borthwick *et al.*, 1995), can be inhibited by chelidonic acid [(I); 4-oxo-4*H*-pyran-2,6-dicarboxylic acid]. Our interest in interactions of this acid and its derivatives with water, which has led us to determine the crystal structure of the title compound, (II), stems from the mediating role of water in molecular recognition of enzymes and small-molecule inhibitors.



The molecular structure of $[\text{Cu}(\text{H}_2\text{O})_5(\text{chel})]\cdot\text{H}_2\text{O}$ is shown in Fig. 1. The chel anion displays bifunctional properties, combining the ability of the carbonyl O6 atom to form a bond to the metal centre with the ability of the carboxylate groups to act as hydrogen-bond acceptors. The Cu—O6 bond is long [2.6746 (16) Å], but it is comparable with weak axial $\text{Cu}^{\text{II}}\text{—O}$ bonds in other complexes with elongated octahedra (Lu *et al.*, 1995; Garcia-Lozano *et al.*, 1996; Kawata *et al.*, 1997). The axial Cu—O_{aqua} bond [2.3763 (15) Å] is longer than the equatorial ones [1.9206 (14)–1.9749 (13) Å]. These values are typical of Cu^{II} complexes (Alcock *et al.*, 1996; Orpen *et al.*, 1989).

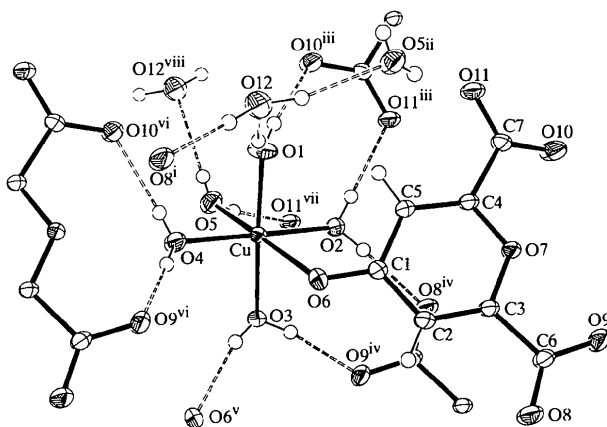


Fig. 1. The molecular structure of (II) and the atom numbering in the asymmetric unit, which comprises the $[\text{Cu}(\text{H}_2\text{O})_5(\text{chel})]$ complex and the O12 water molecule to which it is hydrogen bonded. Displacement ellipsoids are shown at the 50% probability level, except for H atoms, which are represented as spheres of arbitrary radii. Also shown are the 12 $\text{O—H}\cdots\text{O}$ hydrogen bonds in which the O atoms of the asymmetric unit act as donors. The symmetry codes are as given in Table 2.

The surface of the $[\text{Cu}(\text{H}_2\text{O})_5(\text{chel})]$ complex is composed of complementary hydrogen-bonding groups, and the complex is thus capable of self-recognition by means of multiple intermolecular $\text{O—H}\cdots\text{O}$ interactions (Table 2). All ten aqua ligand H atoms participate in hydrogen bonds, while the chel residue can and does accept a maximum of nine such bonds (two to each carboxylate O atom and one to O6 of the carbonyl group). Of the five aqua O atoms, only O5 acts as a hydrogen-bond acceptor; the donor is water oxygen O12, which participates in a total of four hydrogen bonds, two as acceptor and two as donor.

The basic motif in the crystal architecture is a centrosymmetric bimolecular aggregate, linked together by four $\text{O—H}\cdots\text{O}$ bonds [$\text{O2}\cdots\text{O8}^{\text{iv}}$, $\text{O3}\cdots\text{O9}^{\text{iv}}$, $\text{O2}^{\text{iv}}\cdots\text{O8}$ and $\text{O3}^{\text{iv}}\cdots\text{O9}$; symmetry code: (iv) $-1-x, 1-y, 1-z$] to form a dimeric loop containing two eight-membered $\text{Cu}(\text{OH})_2\text{OOC}$ rings, reminiscent of those in carboxylic acid dimers. Adjacent bimolecular aggregates are interlinked by a second $\text{Cu}(\text{OH})_2\text{OOC}$

ring involving O1 and O2, by the $\text{O3}\cdots\text{O6}^{\text{v}}$ bond [symmetry code: (v) $-x, -y, 1-z$], and by the donation from O4 to O9^{vi} and O10^{vi} [symmetry code: (vi) $1+x, y-1, z$]. The complex three-dimensional hydrogen-bonding network is completed by the bonds from O5 and O12.

Coordination to Cu through the carbonyl O6 atom thus places the chel anion in a favourable hydrogen-bonding environment. Coordination through the more basic carboxyl O atoms would seem to offer less opportunity for hydrogen-bond formation, and might require more disruption of the stable Cu^{II} hydration sphere. It is also worth noting that the longer Cu—OH₂ bond to O5 is associated with enhanced ability to accept a hydrogen bond compared with O1—O4.

Experimental

An aqueous suspension of equimolar amounts of chelidonic acid and copper sulfate was heated at 348 K for 30 min and then filtered. The crystals used in the analysis formed when the resulting solution was kept at room temperature for two weeks.

Crystal data

$[\text{Cu}(\text{C}_7\text{H}_2\text{O}_6)(\text{H}_2\text{O})_5]\cdot\text{H}_2\text{O}$

$M_r = 353.72$

Triclinic

$P\bar{1}$

$a = 7.3402 (13) \text{ \AA}$

$b = 8.7066 (13) \text{ \AA}$

$c = 11.179 (2) \text{ \AA}$

$\alpha = 70.591 (16)^\circ$

$\beta = 81.513 (18)^\circ$

$\gamma = 71.158 (17)^\circ$

$V = 637.07 (19) \text{ \AA}^3$

$Z = 2$

$D_x = 1.844 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 20.8\text{--}26.1^\circ$

$\mu = 1.777 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Plate

$0.45 \times 0.38 \times 0.15 \text{ mm}$

Blue

Data collection

Enraf–Nonius CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction:

ψ scan (Enraf–Nonius, 1994)

$T_{\text{min}} = 0.390$, $T_{\text{max}} = 0.766$

3894 measured reflections

3717 independent reflections

3462 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.006$

$\theta_{\text{max}} = 30^\circ$

$h = -10 \rightarrow 10$

$k = -11 \rightarrow 12$

$l = 0 \rightarrow 15$

3 standard reflections

frequency: 120 min

intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.088$

$S = 1.089$

3717 reflections

236 parameters

H atoms: see below

$\Delta\rho_{\text{max}} = 0.68 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.61 \text{ e \AA}^{-3}$

Extinction correction:

SHELXL97 (Sheldrick, 1997)

Extinction coefficient:

0.039 (3)

$$w = 1/[\sigma^2(F_o^2) + (0.0568P)^2 + 0.3136P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

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Table 1. Selected bond lengths (Å)

| | | | |
|-------|-------------|--------|-------------|
| Cu—O1 | 1.9206 (14) | O9—C6 | 1.252 (2) |
| Cu—O3 | 1.9351 (13) | O10—C7 | 1.253 (2) |
| Cu—O4 | 1.9585 (13) | O11—C7 | 1.2414 (19) |
| Cu—O2 | 1.9749 (13) | C1—C5 | 1.441 (2) |
| Cu—O5 | 2.3763 (15) | C1—C2 | 1.444 (2) |
| Cu—O6 | 2.6746 (16) | C2—C3 | 1.346 (2) |
| O6—C1 | 1.2471 (19) | C3—C6 | 1.517 (2) |
| O7—C3 | 1.3485 (17) | C4—C5 | 1.341 (2) |
| O7—C4 | 1.3524 (17) | C4—C7 | 1.512 (2) |
| O8—C6 | 1.240 (2) | | |

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

| D—H...A | D—H | H...A | D...A | D—H...A |
|------------------------------|------------|------------|-------------|---------|
| O12—H12A...O8 ⁱ | 0.925 (16) | 1.853 (16) | 2.776 (2) | 175 (3) |
| O12—H12B...O5 ⁱⁱ | 0.970 (16) | 1.963 (18) | 2.851 (2) | 151 (2) |
| O1—H1A...O10 ⁱⁱⁱ | 0.76 (3) | 1.85 (3) | 2.597 (2) | 173 (3) |
| O1—H1B...O12 | 0.76 (4) | 1.94 (4) | 2.693 (2) | 171 (4) |
| O2—H2A...O8 ^{iv} | 0.81 (4) | 1.93 (4) | 2.7343 (19) | 176 (4) |
| O2—H2B...O11 ⁱⁱⁱ | 0.77 (3) | 1.94 (3) | 2.7137 (18) | 179 (3) |
| O3—H3A...O6 ^v | 0.75 (3) | 1.95 (3) | 2.6812 (19) | 166 (3) |
| O3—H3B...O9 ^v | 0.80 (4) | 1.82 (4) | 2.6105 (18) | 169 (4) |
| O4—H4A...O9 ^{vi} | 0.82 (4) | 1.87 (4) | 2.691 (2) | 174 (3) |
| O4—H4B...O10 ^{vi} | 0.72 (3) | 1.99 (3) | 2.7122 (19) | 178 (3) |
| O5—H5A...O11 ^{vii} | 0.84 (3) | 1.95 (3) | 2.7835 (19) | 171 (3) |
| O5—H5B...O12 ^{viii} | 0.62 (5) | 2.20 (5) | 2.813 (2) | 168 (6) |

Symmetry codes: (i) $-1-x, -y, 1-z$; (ii) $x-1, y, z$; (iii) $-1-x, 1-y, -z$; (iv) $-1-x, 1-y, 1-z$; (v) $-x, -y, 1-z$; (vi) $1+x, y-1, z$; (vii) $1+x, y, z$; (viii) $-x, -y, -z$.

In the final calculations, restraints were applied to the parameters of the two O12 water molecule H atoms (O—H 0.97 Å and H—O—H 109.5°), but other H atoms were refined freely.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *GX* (Mallinson & Muir, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEP-3* (Farrugia, 1997). Software used to prepare material for publication: *CIFWRITE* (Muir & Pauson, 1996).

We wish to thank the EPSRC for an equipment grant.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1282). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 180–182

catena-Poly[[[bis(1,3-diaminopropane-*N,N'*)nickel(II)]- μ -(4,4'-bipyridine-*N:N'*)]diperchlorate]

YE-XIANG TONG, MING-LIANG TONG, XIAO-LAN YU AND XIAO-MING CHEN

School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou 510275, People's Republic of China. E-mail: cedc03@zsu.edu.cn

(Received 15 April 1998; accepted 2 September 1998)

Abstract

In the structure of the title polymer, $\{[\text{Ni}(\text{C}_3\text{H}_8\text{N}_2)_2(\text{C}_{10}\text{H}_8\text{N}_2)](\text{ClO}_4)_2\}_n$, the metal atom is in a slightly distorted octahedral NiN₆ geometry surrounded by four N atoms of two 1,3-diaminopropane ligands in equatorial positions [2.131 (2) and 2.145 (2) Å] and two N atoms from 4,4'-bipyridine ligands in axial sites [2.165 (3) and 2.205 (3) Å]. The 4,4'-bipyridine ligands bridge neighbouring Ni^{II} atoms to form polymeric chains in the lattice.

Comment

Coordination polymers using 4,4'-bipyridine as bridging ligands have been of special interest in recent years. These compounds may exhibit interesting topological structures (Gable *et al.*, 1990; MacGillovray *et al.*, 1994), and clathrates of the cavity structures have possible applications in catalysis and separation (Fujita *et al.*, 1994). Dinuclear and polynuclear metal complexes with 4,4'-bipyridine bridges are also of magnetic interest (Julve *et al.*, 1987; Slangan *et al.*, 1993; Xu & Su, 1990). We have recently prepared some interesting one- and two-dimensional coordination polymers using 4,4'-bipyridine as bridging ligands (Chen *et al.*, 1996; Tong, Cai *et al.*, 1998; Tong, Chen *et al.*, 1998; Tong, Ye *et al.*, 1998). We describe herein the crystal structure of another one-dimensional coordination polymer using