

- Lorenz, B., Schmidt, K., Hiller, W., Abram, U. & Hübener, R. (1993). *Inorg. Chim. Acta*, **208**, 195–199.
 Melnik, M. & van Lier, J. (1987). *Coord. Chem. Rev.* **77**, 275–324.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.

Acta Cryst. (1995). **C51**, 1985–1987

Heptacoordinate Cu^{II} in catena-Poly[aquabis(benzimidazole-*N*³)copper(II)- μ -adipato-*O,O'*:*O''*,*O'''*]

ANITA TOSIK, LESŁAW SIEROŃ AND
 MARIA BUKOWSKA-STRZYŻEWSKA

*Institute of General and Ecological Chemistry,
 Technical University, 90-924 Łódź, Poland*

(Received 3 February 1995; accepted 5 May 1995)

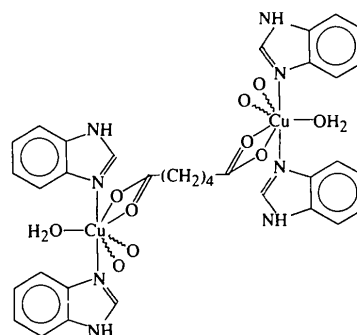
Abstract

The title compound, [Cu(C₆H₈O₄)(C₇H₆N₂)₂(H₂O)], has been synthesized and its crystal structure determined by single-crystal X-ray diffraction at room temperature. The seven-coordinate Cu^{II} complexes adopt a C₂ elongated tetragonal pyramidal geometry with double-capped base. The Cu atoms are located on the twofold axes and are connected by bridging tetradentate adipate ions to form polymeric chains. In the base of the coordination polyhedron, the two short Cu—N bonds are 2.007 (2) Å in length and the two short Cu—O bonds are 2.010 (2) Å. The length of the apical Cu—H₂O bond is 2.245 (4) Å; the lengths of the two long semicoordinate Cu—O bonds, which complete the seven coordination, are 2.930 (2) Å. The intermolecular hydrogen bonds and geometry of the carboxylate group are discussed.

Comment

This work forms part of a continuing study of Cu^{II} complexes with benzimidazole and dicarboxylic acids (Tosik & Bukowska-Strzyżewska, 1992). A fragment of the polymeric structure of the title compound, (I), is shown in Fig. 1. The structure represents the first example of a seven-coordinate alkylcarboxylate Cu^{II} complex (Orpen *et al.*, 1989).

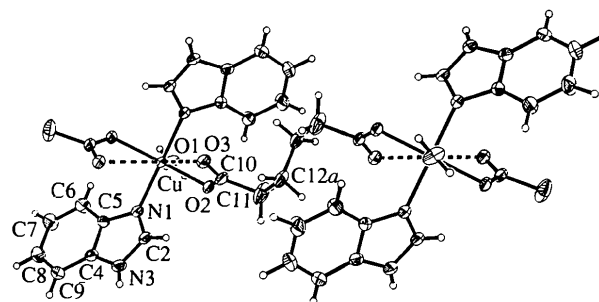
Each Cu atom and H₂O molecule are located on the twofold axis. The Cu atoms are connected by bridging tetradentate adipate ions to form polymeric chains. Two N atoms, one from each benzimidazole molecule, and two O atoms, one from each adipate ion, form short Cu—N and Cu—O bonds of lengths 2.007 (2) and 2.010 (2) Å, respectively. Along with this deformed square coordination, the Cu—H₂O bond of 2.245 (4) Å



(I)

forms an elongated pyramid. The observed short Cu—N and Cu—O bonds are distinctly longer than the average literature data for Cu^{II} of coordination number 5, and the long Cu—H₂O bond is somewhat shorter [according to Orpen *et al.* (1989), average short Cu—N = 1.966, average short Cu—O = 1.962, and average long Cu—H₂O = 2.331 Å]. Two long semicoordinate Cu—O bonds of 2.930 (2) Å complete the Cu coordination environment, forming an elongated tetragonal pyramid with a double-capped base. Thus, Cu^{II} heptacoordination is formed by the mutually perpendicular square coordination (four short bonds) and the triangular coordination (three long bonds). The carboxylate groups, in a similar manner to carboxylate groups in the only other known Cu^{II} adipate complex (Pajunen & Nasakkala, 1977), form four-membered almost planar chelate rings with two distinctly different C—O bonds and two distinctly different Cu—O bonds.

An interesting feature of this structure is the three-dimensional hydrogen-bond system formed by O...O and O...N contacts (Table 3, Fig. 2). The neighbouring



[Cu(C₆H₈O₄)(C₇H₆N₂)₂(H₂O)]_∞ chains are connected by O1—H1···O2 and N3—H3···O3 hydrogen bonds with O···O and N···O distances of 2.917 (3) and 2.754 (3) Å, respectively. The H1···O2 and H3···O3 bonds of the same carboxylate group with lengths 2.10 (5) and 2.03 (4) Å, respectively, and O1—H1···O2 and N3—H3···O3 angles of 170 (5) and 164 (4)°, respectively, are very similar.

Experimental

CuCl₂O (1 mmol, 0.17 g) dissolved in water (50 ml) was mixed with benzimidazole (5 mmol, 0.59 g) dissolved in water (50 ml), and adipic acid (5 mmol, 0.73 g) dissolved in water (50 ml) was added. The blue solution was heated to boiling, filtered and allowed to evaporate slowly. After several days dark blue crystals were obtained. Elemental analysis for C₂₀H₂₂N₄O₅Cu: calculated C 51.94, N 12.10, H 4.76%; found C 51.95, N 11.99, H 4.75%. The density D_m was measured by flotation in a mixture of iodomethane and benzene.

Crystal data

[Cu(C ₆ H ₈ O ₄)(C ₇ H ₆ N ₂) ₂ (H ₂ O)]	Cu $K\alpha$ radiation
$M_r = 461.96$	$\lambda = 1.54184$ Å
Monoclinic	Cell parameters from 25 reflections
$C2/c$	$\theta = 15.0$ – 26.0°
$a = 14.397$ (1) Å	$\mu = 1.920$ mm ⁻¹
$b = 17.432$ (1) Å	$T = 293$ K
$c = 8.535$ (1) Å	Irregular
$\beta = 112.60$ (1)°	$0.30 \times 0.22 \times 0.15$ mm
$V = 1977.5$ (3) Å ³	Dark blue
$Z = 4$	
$D_x = 1.552$ Mg m ⁻³	
$D_m = 1.571$ Mg m ⁻³	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.013$
$\omega/2\theta$ scans	$\theta_{max} = 74.89^\circ$
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)	$h = -16 \rightarrow 18$
$T_{min} = 0.93$, $T_{max} = 0.99$	$k = 0 \rightarrow 21$
4495 measured reflections	$l = -10 \rightarrow 0$
2041 independent reflections	3 standard reflections
1916 observed reflections	frequency: 60 min
$[F > 4\sigma(F)]$	intensity decay: 1.8%

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.91$ e Å ⁻³
$R = 0.044$	$\Delta\rho_{min} = -0.70$ e Å ⁻³
$wR = 0.118$	Extinction correction:
$S = 1.037$	$F^* = F_c/[1.0 + (0.001\chi \times F_c^2\lambda^3/\sin 2\theta)]^{1/4}$
1916 reflections	Extinction coefficient:
169 parameters	$\chi = 0.0077$ (4)
$w = 1/[\sigma^2(F_o^2) + (0.0617P)^2 + 4.43P]$	Atomic scattering factors
where $P = [\max(F_o^2, 0) + 2F^2]/3$	from <i>SHELXL93</i>
$(\Delta/\sigma)_{max} = 0.0001$	(Sheldrick, 1993)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

U_{iso} for C12b; $U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$ for all others.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Cu	0	0.39551 (3)	1/4	0.0356 (3)
O1	0	0.5243 (2)	1/4	0.0615 (10)
O2	0.0404 (2)	0.38119 (13)	0.0511 (2)	0.0466 (5)
O3	0.0950 (2)	0.26533 (13)	0.1527 (3)	0.0492 (5)
N1	-0.1444 (2)	0.38959 (13)	0.0889 (3)	0.0387 (5)
N3	-0.2732 (2)	0.3286 (2)	-0.1033 (3)	0.0426 (6)
C2	-0.1741 (2)	0.3415 (2)	-0.0404 (3)	0.0414 (6)
C4	-0.3127 (2)	0.3695 (2)	-0.0061 (3)	0.0380 (6)
C5	-0.2322 (2)	0.4088 (2)	0.1128 (3)	0.0375 (6)
C6	-0.2485 (3)	0.4576 (2)	0.2289 (5)	0.0530 (8)
C7	-0.3454 (3)	0.4631 (2)	0.2226 (5)	0.0626 (10)
C8	-0.4248 (3)	0.4218 (2)	0.1049 (5)	0.0573 (8)
C9	-0.4108 (2)	0.3745 (2)	-0.0120 (4)	0.0462 (7)
C10	0.0869 (2)	0.3185 (2)	0.0537 (3)	0.0531 (8)
C11	0.1303 (3)	0.3118 (3)	-0.0822 (5)	0.0886 (6)
C12a†	0.1981 (2)	0.2406 (2)	-0.0646 (4)	0.0566 (15)
C12b‡	0.2450 (5)	0.2938 (3)	0.0041 (16)	0.043 (5)

† Occupancy = 0.81.

‡ Occupancy = 0.19.

Table 2. Selected geometric parameters (Å, °)

Cu—N1	2.007 (2)	C4—C9	1.397 (4)
Cu—O1	2.245 (4)	C5—C6	1.392 (4)
Cu—O2	2.010 (2)	C6—C7	1.378 (5)
Cu—O3	2.930 (2)	C7—C8	1.398 (5)
O2—C10	1.277 (4)	C8—C9	1.367 (5)
O3—C10	1.230 (4)	C10—C11	1.518 (4)
N1—C2	1.319 (4)	C11—C12a	1.551 (4)
N1—C5	1.397 (3)	C11—C12b	1.559 (7)
N3—C2	1.336 (4)	C12a—C12a'	1.512 (6)
N3—C4	1.372 (4)	C12b—C12b'	1.537 (8)
C4—C5	1.393 (4)		
N1—Cu—N1 ⁱⁱ	174.10 (14)	O2—C10—O3	124.5 (2)
N1—Cu—O1	92.95 (7)	O2—C10—C11	114.8 (3)
N1—Cu—O2	88.54 (9)	O3—C10—C11	120.6 (3)
N1—Cu—O2 ⁱⁱ	90.73 (9)	C10—C11—C12a	114.6 (3)
N1—Cu—O3	103.9 (1)	C10—C11—C12b	109.1 (5)
O1—Cu—O2	97.13 (7)	C11—C12a—C12a'	107.8 (4)
O1—Cu—O3	140.8 (1)	C11—C12b—C12b'	106.3 (7)
O2—Cu—O2 ⁱⁱ	165.73 (14)		

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

Table 3. Hydrogen-bonding geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N3—H3···O3 ⁱ	0.75 (4)	2.03 (4)	2.754 (3)	164 (4)
O1—H1···O2 ⁱⁱ	0.82 (5)	2.10 (5)	2.917 (3)	170 (5)

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

The structure was solved by conventional Patterson and Fourier methods and was refined by full-matrix least-squares calculations. The large displacement factors of two central C atoms of the adipate ion indicated disordered localization of the aliphatic chain. Two different positions (*a* and *b*) of C12 were established with occupancy factors of 0.81 and 0.19, respectively. C12b was refined isotropically. All other non-H atoms were refined anisotropically. The H atoms of the H₂O group and of the benzimidazole ligand were located from a difference synthesis and refined isotropically. Only H atoms of the aliphatic chain were included in calculated positions with C—H = 0.97 Å and refined isotropically using a riding model, with the fixed isotropic displacement factors taken as $1.2U_{eq}$ of the bonded C atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4 Software*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1990). Software used to prepare material for publication: *XPUBL* in *SHELXTL/PC*.

This work was supported by the Polish Committee of Scientific Research (project 2-0575-91-01).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1045). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* pp. S1–S84.
- Pajunen, A. & Nasakkala, E. (1977). *Finn. Chem. Lett.* p. 104.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
- Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
- Tosik, A. & Bukowska-Strzyżewska, M. (1992). *J. Crystallogr. Spectrosc. Res.* **22**, 225–229.

Acta Cryst. (1995). **C51**, 1987–1989

catena-Poly[aqua(benzimidazole-*N*³)-copper(II)- μ -malonato-*O,O''*:*O'*]

ANITA TOSIK, LESŁAW SIEROŃ AND
MARIA BUKOWSKA-STRZYŻEWSKA

*Institute of General and Ecological Chemistry,
Technical University, 90-924 Łódź, Poland*

(Received 3 February 1995; accepted 3 April 1995)

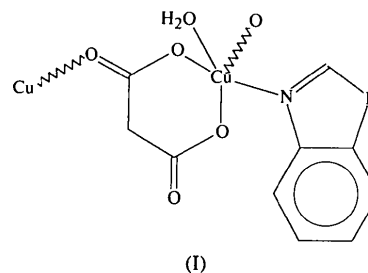
Abstract

The title compound forms a polymeric chain, $[\text{Cu}(\text{C}_3\text{H}_2\text{O}_4)(\text{C}_7\text{H}_6\text{N}_2)(\text{H}_2\text{O})]_\infty$. A malonate ion adopts a bridging position between two Cu atoms, coordinating *via* three of its O atoms. Two form a six-membered chelate ring, the third coordinates to the neighbouring Cu atom.

The square-pyramidal Cu^{II} coordination comprises one N and three O atoms as the base, and an H_2O molecule in the apical position. The equalization of C—O bonds of both carboxylate groups and a differentiation of Cu—O bond lengths is observed.

Comment

This work forms part of a wider study of the preparation, properties and structure of Cu^{II} complexes with dicarboxylic acids and benzimidazole (Tosik & Bukowska-Strzyżewska, 1992; Tosik, Sieroń & Bukowska-Strzyżewska, 1995). The structure of the title complex, (I), is polymeric with $[\text{Cu}(\text{C}_3\text{H}_2\text{O}_4)(\text{C}_7\text{H}_6\text{N}_2)\text{H}_2\text{O}]_\infty$ chains along the *x* axis. Fig. 1 shows the independent fragment of the chain.



The malonate ion adopts a bridging position between two Cu atoms, forming with one, a six-membered chelate ring through two short Cu—O bonds [Cu—O2 = 1.954 (3) and Cu—O3 = 1.970 (3) Å], and with a second Cu atom, a short Cu—O1 bond of 1.990 (3) Å.

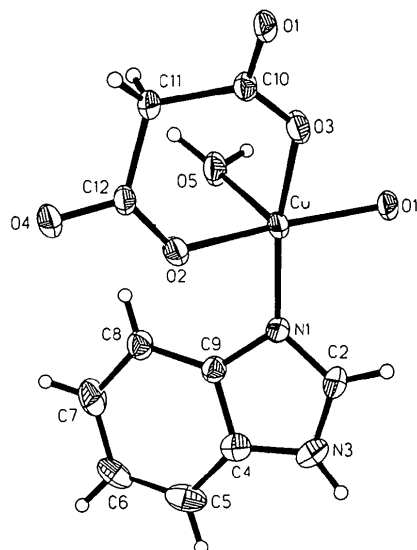


Fig. 1. An independent fragment of the $[\text{Cu}(\text{C}_3\text{H}_2\text{O}_4)(\text{C}_7\text{H}_6\text{N}_2)\text{H}_2\text{O}]_\infty$ chain. Displacement ellipsoids are plotted at the 30% probability level.