Table 4. *Distances (Å) from least-squares planes*

	A	B	C		A	B	C
Cu	−0·041	0·000	−0·000	C(4)	0·021	0·025	−0·019
O(1)	−0·015	0·007	0·000	C(5)	−0·030	−0·038	−0·101
O(2)	0·006	0·028	0·000	C(6)	0·156	0·126	0·063
C(1)	−0·009	−0·017	−0·042	C(7)	1·578	1·541	1·473
C(2)	0·001	0·004	−0·020	C(8)	2·113	2·066	1·993
C(3)	0·026	0·019	−0·024				

Planes defined by Cu, C(1)···C(5), O(1) and O(2) (*A*), by the atoms for plane *A* plus their centric mates (*B*), and by Cu, O(1) and O(2) (*C*). Dihedral angles: 0·84 (*A* and *B*), 0·87 (*B* and *C*), 1·66 (*A* and *C*), 48·3 (*A* and *ac*), 46·7 (*B* and *ac*), and 47·5° (*C* and *ac*). Angles from a towards c of the lines of intersection of *A*, *B*, and *C* with *ac*: 34·19, 34·62, and 34·58°. E.s.d.'s of atom positions about 0·005 Å; of points on the plane not available, but considerably different for the different planes *and* for different points on a given plane, the greatest possibly being no more than 0·01 Å.

The allyl torsion angles are C(8)−C(7)−C(6)−C(3) = 126·7 (8) (vinyl *cis* to methylene H as expected; see *e.g.* Pauling, 1960), C(7)−C(6)−C(5)−C(4) = 91·9 (5), and C(7)−C(6)−C(3)−C(2) = −83·8 (5)°, the C−C bond of the allyl group twisting down about 90° from the ligand plane. At 1·241 (8) Å, C(7)=C(8) is excessively short, mainly, we feel, by foreshortening, *U*[C(8)] being very large, and much larger than *U*[C(7)]. There are only two short C(8) contacts with non-H atoms, at 3·65 (1) Å with a C(8) and at 3·74 (1) Å with a C(5), and none along **b**, on which *U*[C(8)] has its largest component. It is not obvious whether the C(8) contacts, along with C(7)···C(7) at 4·13 (1) Å, are short enough or so disposed as to support the original suggestion that a solid-state polymerization might be possible.

References

BARCLAY, G. A. & COOPER, A. (1965). *J. Chem. Soc.* pp. 3746–3751.

BLACKSTONE, M., VAN THUIJL, J. & ROMERS, C. (1966). *Recl Trav. Chim. Pays-Bas*, **85**, 557–566.

CARMICHAEL, J. W., STEINRAUF, L. K. & BELFORD, R. L. (1965). *J. Chem. Phys.* **43**, 3959–3966.

COTTON, F. A., RICE, C. E., & RICE, G. W. (1977). *Inorg. Chim. Acta*, **24**, 231–234.

HORNG CHIN YEH (1981). PhD Thesis, Univ. of Washington.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

PAULING, L. (1960). *The Nature of the Chemical Bond*, pp. 140–142. Ithaca: Cornell Univ. Press.

PING-KAY HON, PFLUGER, C. E. & BELFORD, R. L. (1966). *Inorg. Chem.* **5**, 516–521.

PIPER, T. S. & BELFORD, R. L. (1962). *Mol. Phys.* **5**, 169–181.

ROBERTSON, I. & TRUTER, M. R. (1967). *J. Chem. Soc.* pp. 309–313.

STARIKOVA, Z. A. & SHUGAM, E. A. (1969). *Zh. Strukt. Khim.* **10**, 290–293.

STEWART, J. M., MACHIN, P. A., AMMON, H. L., DICKINSON, C., HECK, H. & FLACK, H. (1976). The XRAY system−version of March, 1976. Tech.Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Structure of *catena*-μ-Aqua-bis(benzimidazole)diformatocopper(II), [Cu(C7H6N2)2(CHO2)2(H2O)]

BY M. BUKOWSKA-STRZYŻEWSKA AND A. TOSIK

Institute of General Chemistry, Technical University, 36 Żwirki, 90–924 Łódź, Poland

Abstract. $M_r = 407·9$, monoclinic, $C2/c$, $a = 12·94$ (4), $b = 12·70$ (4), $c = 10·40$ (2) Å, $\beta = 96·0$ (3)°, $V = 1699·8$ Å^3, $Z = 4$, $D_x = 1·590$, $D_m = 1·62$ (2) Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å. The structure determination was based upon 844 independent reflections. Full-matrix least-squares refinement yielded a conventional R factor of 0·065. A specific one-dimensional polymeric structure has been established. The formate ions and benzimidazole molecules are monodentate ligands, forming two Cu−O bonds of 1·997 (5) Å and two Cu−N bonds of 2·017 (6) Å. The square coordination is expanded to elongated octahedral coordination by the bridging H2O molecules with Cu−O(H2O) distances of 2·625 (2) Å and an angle Cu−O(H2O)−Cu^i of 164·2 (5)°.

Introduction. The interaction of imidazole and benzimidazole or their derivatives with transition-metal ions is believed to be important in determining the activity of many biologically important molecules (Sundberg & Martin, 1974). In proteins, the imidazole groups of histidine residues are known to be metal-binding sites (Freeman, 1967). The behaviour of imidazole groups as ligands has hitherto been charac-

terized less precisely than that of amino, carboxyl and peptide groups. Also, copper(II) formate complexes need structural characterization to explain their significant structural and magnetic differences as compared with copper(II) acetates and the higher alkanoates (Doedens, 1976).

The results of the preparation and structure investigation of a new aqua(benzimidazole)copper(II) formate are reported in this paper.

Experimental. Equimolar amounts of cupric formate and benzimidazole were dissolved in water, the solutions were mixed and a few drops of 84% formic acid added; evaporation of the filtered solution produced blue crystals; composition: calculated for $C_{16}H_{16}CuN_4O_5$: C 47·09, H 3·92, N 13·73%; found: C 47·10, H 4·00, N 12·81%. Cell dimensions determined from 15 high-angle $0kl$ and $h0l$ reflexions, Weissenberg photographs, Cu radiation, density measured by flotation in a benzene solution of CH_3I; intensity data of 844 reflections collected (crystal 0·04 × 0·03 × 3·00 mm, mounted along the z axis) by means of a multiple-film pack on a Weissenberg camera; $2\theta_{max} = 158\cdot6°$; range of hkl: $15 \leq h \leq -15$, $14 \leq k \leq 0$, $8 \leq l \leq 0$; 132 unobserved reflections; intensities estimated visually with a calibrated intensity scale; Lorentz and polarization corrections applied; structure solved by means of three-dimensional Patterson and Fourier syntheses, refined by full-matrix least-squares calculations with anisotropic temperature factors for the nonhydrogen atoms, H atoms included in calculated positions and not refined; final conventional $R = 0\cdot065$, goodness-of-fit $S = 1\cdot73$; $F(000) = 836$; average ratio of shift to error and maximum least-squares shift to error in the final refinement cycle were 0·3 and 1·3 respectively; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); all calculations performed on a Riad-32 computer using the XRAY system (Stewart, Kundell & Baldwin, 1970).

Discussion. Final atomic coordinates, and bond distances and angles are given in Tables 1* and 2. Fig. 1 shows the structure projected along x. The Cu atom at a symmetry centre is surrounded by two N atoms of two benzimidazole molecules and by two O atoms of two formate ions in a square plane with Cu—O(1) = 1·997 (5) and Cu—N(1) = 2·017 (6) Å. The equatorial Cu—N(1) distance is similar to corresponding lengths in the known structures of copper(II)–imidazole(im) complexes: [Cu(im)_4I_2], 1·98–2·04 Å (Akhtar, Goodgame, Goodgame, Ravner-Canham & Skapski, 1968); [Cu(im)_4-

$(CH_3OCH_2COO)_2]$, 1·91–2·05 Å (Prout, Allison & Rossotti, 1971); [Cu(im)_4SO_4], 2·00–2·02 Å (Fransson & Lundberg, 1972); [Cu(im)_4(ClO_4)_2], 1·997–2·007 Å (Ivarsson, 1973); [Cu(im)_6](NO_3)_2, 2·012–2·049 Å (McFadden, McPhail, Gros, Garner & Mabbs, 1975). The H_2O molecule in the special position $0y\frac{1}{4}$ forms a bridge between two square complexes and completes the coordination around Cu atoms to form an elongated octahedron with two very long Cu—O(H_2O) bonds of 2·625 (2) Å. The angle Cu—O(H_2O)—Cu^i is 164·2 (5)°. The tetragonality of

Table 1. *Positional parameters* $(\times 10^4)$ *and equivalent isotropic temperature factors* $(\times 10^4)$

$$\beta_{eq} = \tfrac{1}{3}(\beta_{11} + \beta_{22} + \beta_{33}).$$

	x	y	z	$\beta_{eq}(\text{Å}^2)$
Cu	0	0	0	39 (1)
O(1)	−777 (3)	1272 (4)	492 (4)	41 (5)
O(2)	−1455 (4)	1859 (5)	−1477 (5)	75 (5)
O(3)	0	−284 (9)	2500	70 (10)
C(1)	1462 (7)	1402 (7)	1542 (7)	63 (7)
C(2)	4020 (6)	1571 (7)	505 (7)	64 (8)
C(3)	4319 (6)	1099 (5)	−530 (6)	50 (6)
C(4)	3602 (6)	485 (7)	−1361 (7)	56 (8)
C(5)	2594 (7)	313 (6)	−1063 (7)	43 (8)
C(6)	2312 (5)	753 (6)	−20 (6)	45 (7)
C(7)	3003 (6)	1448 (6)	827 (6)	43 (7)
C(8)	−1286 (5)	1907 (5)	−239 (6)	40 (7)
N(1)	1318 (4)	813 (4)	509 (5)	32 (6)
N(2)	2433 (4)	1788 (5)	1750 (5)	47 (6)

Table 2. *Bond distances* (Å) *and angles* (°) *with their standard deviations*

(*a*) Coordination polyhedron

Cu—O(1)	1·997 (5)	O(1)—Cu—N(1)	87·3 (2)
Cu—O(3)	2·625 (2)	N(1)—Cu—O(3)	84·2 (2)
Cu—N(1)	2·017 (6)	O(1)—Cu—O(3)	78·8 (2)
		Cu—O(3)—Cu^i	164·2 (5)

(*b*) Formate group

C(8)—O(1)	1·248 (8)	O(1)—C(8)—O(2)	127·1 (7)
C(8)—O(2)	1·285 (8)		

(*c*) Benzimidazole molecule

N(1)—C(1)	1·306 (10)	C(1)—N(1)—C(6)	106·6 (6)
C(1)—N(2)	1·345 (10)	N(1)—C(1)—N(2)	113·1 (7)
N(2)—C(7)	1·342 (10)	C(1)—N(2)—C(7)	110·0 (6)
C(7)—C(3)	1·401 (11)	C(3)—C(2)—C(7)	120·3 (7)
C(2)—C(3)	1·325 (11)	C(2)—C(3)—C(4)	120·8 (7)
C(3)—C(4)	1·430 (10)	C(3)—C(4)—C(5)	121·0 (7)
C(4)—C(5)	1·390 (12)	C(4)—C(5)—C(6)	117·9 (7)
C(5)—C(6)	1·306 (10)	C(5)—C(6)—C(7)	123·1 (7)
C(6)—N(1)	1·453 (9)	N(1)—C(6)—C(7)	104·3 (9)
C(6)—C(7)	1·479 (10)	N(1)—C(6)—C(5)	132·2 (7)
		N(2)—C(7)—C(6)	106·0 (6)
		C(2)—C(7)—C(6)	116·7 (7)
		C(2)—C(7)—N(2)	137·4 (7)

(*d*) Short intermolecular contact

N(2)—O(2^ii)   2·805 (8)

Symmetry code:

(i) $-x, y, \tfrac{1}{2}-z$ (ii) $\tfrac{1}{2}+x, \tfrac{1}{2}-y, \tfrac{1}{2}+z$
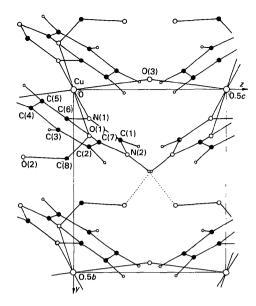
Fig. 1. A view of the unit-cell contents along the x axis.

almost identical C(1)—N(1) and C(1)—N(2) bond lengths of 1·326 (5) and 1·349 (5) Å, respectively, and two longer C—N bond lengths of 1·378 (5) and 1·369 (5) Å. As can be seen from Table 2, the coordination of the N(1) atoms results in shortening of C(1)—N(1) to 1·306 (10) Å and elongation of N(1)—C(6) to 1·453 (9) Å. A similar effect can be noticed in other monodentate-coordinated benzimidazole molecules (Bukowska-Strzyżewska, Skoweranda & Tosik, 1982; Hamilton, Ferraro & Sinn, 1979) where shortened C(1)—N(1) bonds are 1·316 (7) and 1·326 (1) Å, respectively.

The polymeric chains of $[Cu(HCOO)_2$-(benzimidazole)$_2(H_2O)]_n$ are extended along the x axis and, as can be seen from Fig. 1, are joined by $O(2)\cdots H—N(2^i)$ with hydrogen bonds $O(2)\cdots N(2^i)$ 2·805 (8) Å.

the Cu^{II} complex [defined by Procter, Hathaway & Nicholls (1968) as the ratio of the mean equatorial to axial bond lengths] is 0·76 here. As found by Hathaway & Hodgson (1973) for many other six-coordinated Cu^{II} complexes involving N and O donor atoms the tetragonality of 0·76 corresponds to axial Cu—O bond lengths of 2·6—2·7 Å, in good agreement with this structure.

The C—O distances of the formate ion [C(8)—O(1) = 1·248 (8) and C(8)—O(2) = 1·285 (8) Å] indicate some delocalization of the π bond between the two C—O bonds, but the difference is in the opposite sense to that observed in monodentate bis-(propionato)(p-toluidine)copper(II) (Yawney, Moreland & Doedens, 1973).

The benzimidazole molecule is planar within experimental error, but is not coplanar with the Cu atoms. The Cu—N(imidazole) bond deviates by about 5° from the benzimidazole-ring plane. Significant differences between the dimensions of free (Martínez-Carrera, 1966) and monodentate-coordinated imidazole rings can be observed. The non-coordinated ring shows two

References

AKHTAR, F., GOODGAME, D. M. L., GOODGAME, M., RAVNER-CANHAM, G. W. & SKAPSKI, A. C. (1968). Chem. Commun. pp. 1389–1390.

BUKOWSKA-STRAZYŻEWSKA, M., SKOWERANDA, J. & TOSIK, A. (1982). Acta Cryst. B38, 2904–2906.

DOEDENS, R. J. (1976). Prog. Inorg. Chem. 21, 209–231.

FRANSSON, G. & LUNDBERG, B. K. S. (1972). Acta Chem. Scand. 26, 3969–3976.

FREEMAN, H. C. (1967). Adv. Protein. Chem. 22, 257–427.

HAMILTON, G. J., FERRARO, J. F. & SINN, E. (1979). J. Chem. Soc. Dalton Trans. pp. 515–519.

HATHAWAY, B. J. & HODGSON, P. G. (1973). J. Inorg. Nucl. Chem. 35, 4071–4081.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

IVARSSON, G. (1973). Acta Chem. Scand. 27, 3523–3530.

McFADDEN, D. L., McPHAIL, A. T., GROS, P. M., GARNER, C. D. & MABBS, F. E. (1975). J. Chem. Soc. Dalton Trans. pp. 263–268.

MARTÍNEZ-CARRERA, S. (1966). Acta Cryst. 20, 783–789.

PROCTER, J. M., HATHAWAY, B. J. & NICHOLLS, P. (1968). J. Chem. Soc. A, pp. 1678–1684.

PROUT, C. K., ALLISON, G. B. & ROSSOTTI, F. J. C. (1971). J. Chem. Soc. A, pp. 3331–3335.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

SUNDBERG, R. J. & MARTIN, R. B. (1974). Chem. Rev. 74, 471–517.

YAWNEY, D. B., MORELAND, J. A. & DOEDENS, R. J. (1973). J. Am. Chem. Soc. 95, 1164–1170.