Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1230). Services for accessing these data are described at the back of the journal.

References

Ahmed, I. Y. & Abuhijleh, A. L. (1982). *Inorg. Chim. Acta*, **61**, 241–246.
Bernarducci, E. E., Bharadwaj, P. K., Lalancette, R. A., Krogh-Jesperson, K., Potenza, J. A. & Schugar, M. J. (1983). *Inorg. Chem.* **22**, 3911–3920.
Bhirud, R. G. & Srivastava, T. S. (1990). *Inorg. Chim. Acta*, **173**, 121–125.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Hathaway, B. J. & Biling, D. E. (1970). *Coord. Chem. Rev.* **5**, 143–207.
Henriksson, H. A. (1977). *Acta Cryst.* B**33**, 1947–1950.
Hoang, N. N., Valach, F., Dunaj-Jurco, M. & Melnik, M. (1992). *Acta Cryst.* C**48**, 443–445.
Inoue, M., Kishita, M. & Kubo, M. (1964). *Inorg. Chem.* **3**, 239–242.
Melnik, M. (1981). *Coord. Chem. Rev.* **36**, 1–44.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Rissanen, K., Valkonen, J., Kokkonen, P. & Leskela, M. (1987). *Acta Chem. Scand. Ser. A*, **41**, 299–309.
Sheldrick, G. M. (1990*a*). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1990*b*). *SHELXTL/PC. Structure Determination Software Programs*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Sigel, H. (1980). *Inorg. Chem.* **19**, 1411–1413.
Tamura, H., Imai, H., Kuwahara, J. & Suguira, Y. (1987). *J. Am. Chem. Soc.* **109**, 6870–6871.
Uruska, I., Zielkiewicz, J. & Szpakowska, M. (1990). *J. Chem. Soc. Dalton Trans.* pp. 733–736.

Acta Cryst. (1999). C**55**, 1230–1234

catena-Poly[[bis(benzimidazole-N^3)copper(II)]-μ-suberato-$O,O':O'',O'''$] and *catena*-poly[[[bis(benzimidazole-N^3)copper(II)]-μ-sebacato-$O,O':O'',O'''$] dihydrate]

Lesław Sieroń† and Maria Bukowska-Strzyżewska

Institute of General & Ecological Chemistry, Technical University of Łódź, Żwirki 36, 90-924 Łódź, Poland. E-mail: mbs@ck-sg.p.lodz.pl

(*Received 10 March 1999; accepted 19 April 1999*)

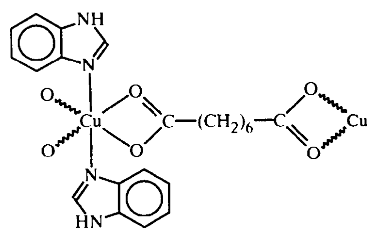
Abstract

Both title compounds, $[Cu(C_8H_{12}O_4)(C_7H_6N_2)_2]$, (I), and $[Cu(C_{10}H_{16}O_4)(C_7H_6N_2)_2]\cdot 2H_2O$, (II), display inversion symmetry. The Cu centres are bridged by the dicarboxylate ions in a bis-bidentate fashion, forming polymeric chains. In (I) and (II), these chains are differently associated *via* hydrogen bonds. The Cu···Cu intrachain distances are 10.974 (1) Å in (I) and 12.417 (5) Å in (II). In both structures, the base of the elongated octahedron of the Cu^{II} atoms is formed by two short Cu—O and Cu—N bonds [Cu—O 1.973 (1) and 1.974 (2) Å, and Cu—N 1.974 (1) and 1.977 (2) Å in (I) and (II), respectively]. The carboxylate groups form four-membered unsymmetrical chelate rings and complete the Cu^{II} coordination to sixfold by long Cu—O bonds of 2.645 (2) Å in (I) and 2.583 (2) Å in (II). The modes of coordination of the Cu^{II}–dicarboxylic acid ions and benzimidazole molecules are discussed in terms of the computed bond valences and the valences of the Cu and O atoms as the sums of bond valences.

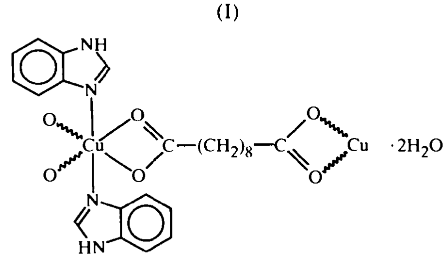
† A holder of the Foundation for Polish Science (FNP) grant.

Comment

This work forms part of a continuing study of Cu^{II} complexes with benzimidazole and dicarboxylic acids (Tosik & Bukowska-Strzyżewska, 1992; Tosik *et al.*, 1995*a*,*b*; Sieroń & Bukowska-Strzyżewska, 1998). A dicarboxylate ion is a polydentate ligand and owing to the variable ligation of the carboxylate group, it can form chelate, polynuclear or polymeric complexes. We are interested in the conformation of the aliphatic chains of dicarboxylic acids, the coordination mode of benzimidazole and carboxylate ligands, and the associated types of complexes formed.



(I)



(II)

Sections of the polymeric structures of (I) and (II) are shown in Figs. 1(*a*) and 1(*b*), respectively. In both structures, each Cu atom and dicarboxylate ion is associated with an inversion centre. The Cu atoms are connected by bridging tetradentate dicarboxylate ions to form polymeric chains. The more central C atoms of the $-(CH_2)_n-$ chains adopt fully staggered conformations, with C11—

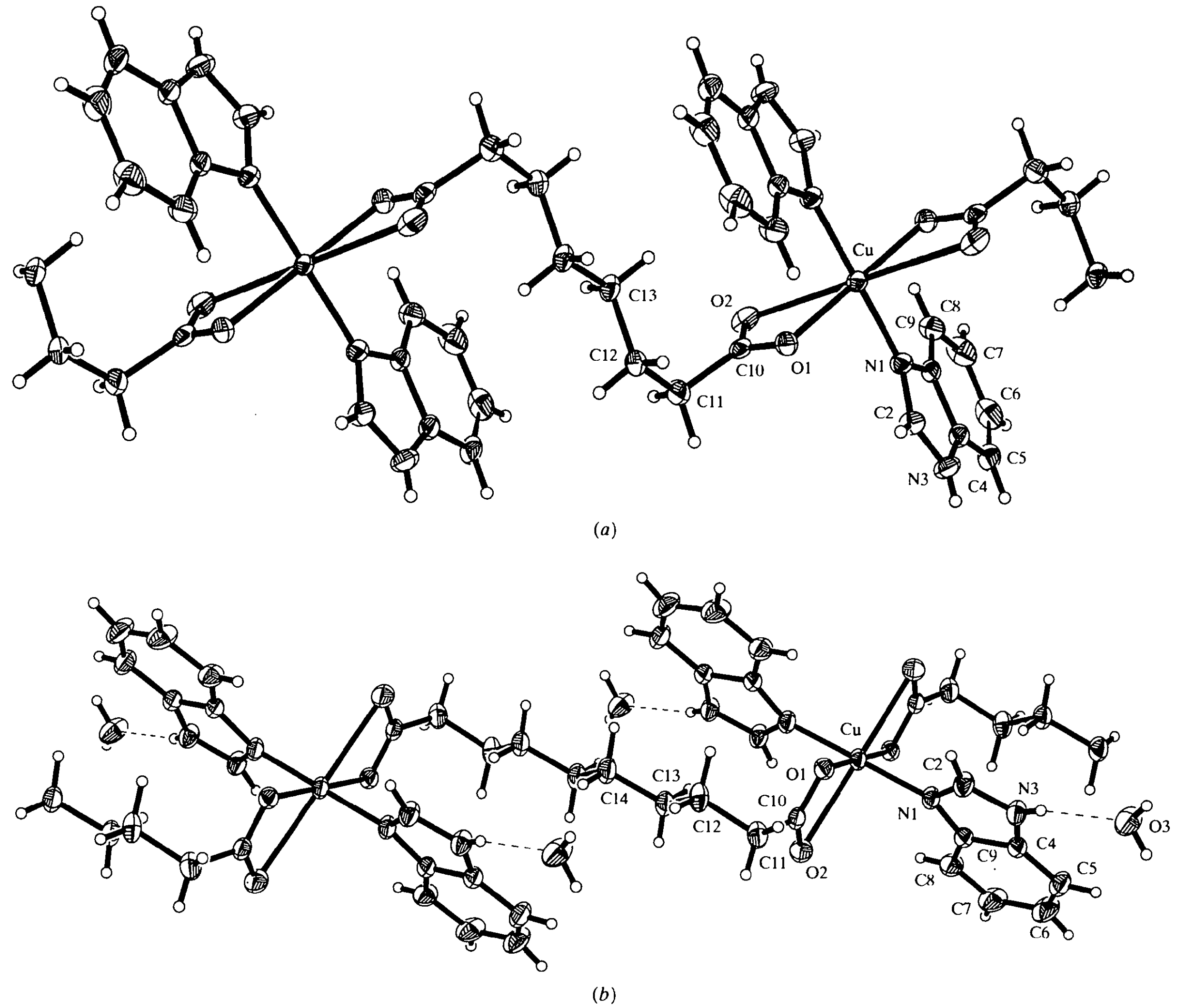


Fig. 1. Fragments of the polymeric structures of (*a*) (I) and (*b*) (II). Displacement ellipsoids are drawn at the 30% probability level.

C12—C13—C13^{i} = 177.1 (2)° in (I), and C11—C12—C13—C14 = 176.8 (3) and C12—C13—C14—C14^{ii} = 178.9 (3)° in (II), and the external C atoms adopt the *gauche* conformation, with C10—C11—C12—C13 = 59.8 (3)° in (I) and 57.2 (4)° in (II) [symmetry codes: (i) $-x-1$, $-y$, $-z+1$; (ii) $-x$, $-y-1$, $-z+1$]. The crystal packing shown in Figs. 2 and 3 illustrates the modes of chain association in (I) and (II), respectively. In (I), the $\{Cu(C_7H_6N_2)_2[OOC(CH_2)_6COO]\}_\infty$ chains are extended along [10$\bar{1}$] and two neighbouring chains are connected by N—H···O2 hydrogen bonds. In (II), the $\{Cu(C_7H_6N_2)_2[OOC(CH_2)_8COO]\}_\infty$ chains are extended along [01$\bar{1}$] and three neighbouring chains are connected by hydrogen bonds formed by interchain H_2O molecules. Each H_2O molecule forms three hydrogen bonds, one of the type N—H···O(H_2O) and two of the type O(H_2O)—H···O(carboxylate). The hydrogen-bond geometry is given in Tables 2 and 4.

According to Brown (1994), the bond length to bond valence correlation represents a measure of the strength of a bond that is independent of the atomic size. The application of this correlation allows us to compare the relative importance of Cu—N and Cu—O bonds of Cu polyhedra, and to check the valence-sum rule for Cu and O carboxylic atoms in the investigated crystals. The valence-sum rule states that the sum of the valences of the bonds formed by an atom is equal to the valence (formal oxidation state) of the atom. Violation of the valence-sum rule can indicate mistakes in the interpretation of the structure by omission of the weak hydrogen bonds, or can show that the bonds are strained as the result of crystallographic constraints that prevent the bonds from attaining their ideal lengths (Wagner & O'Keeffe, 1988).

The bond lengths (d_{ij}), bond valences (ν_{ij}) and valences of the Cu and O atoms (V_{Cu} and V_O) of the four-membered –C10—O1—Cu—O2– chelate rings in (I) and (II), respectively, are given in Table 5. The bond valences were computed as $\nu_{ij} = \exp[(R_{ij} - d_{ij})/0.37]$ according to Brown (1992, 1997) and O'Keeffe & Brese (1991), where R_{ij} is the bond-valence parameter (in the formal sense R_{ij} is the single-bond length between i and j atoms). R_{Cu-O} was taken as 1.679 Å according to Brese & O'Keeffe (1991). R_{Cu-N} was determined by us to fit the bond lengths in 51 Cu^{II} complexes with $R < 8\%$, with different coordination numbers, taken from the Cambridge Structural Database (1998), where all donor atoms were aromatic N atoms. $R_{Cu-N} = 0.37\ln[2/\Sigma\exp(-d_{Cu-N}/0.37)]$ was computed for each complex and their average value of 1.713 Å was accepted as R_{Cu-N}. Our value of the Cu—N bond-valence parameter is different from R_{Cu-N} = 1.61 Å proposed by Brese & O'Keeffe (1991). R_{O-C} = 1.43 Å was taken as the single-bond length from structural data (Orpen *et al.*, 1989). Hydrogen-bond acceptor valences ($\nu_{O\cdots H}$) were obtained from the bond valence *versus* H···O(acceptor) distance given by Brown (1976). In both structures, the valences of the Cu and O1 atoms are consistent with the valence-sum rule ($V_i = \Sigma\nu_{ij}$), which gives V_{Cu} = 2.04 (5) and 2.05 (5) v.u. (v.u. = valence unit), and V_{O1} = 2.00 (5) and 1.97 (5) v.u. for (I) and (II), respectively. The valences of the O2 atoms [V_{O2} = 1.86 (5) and 1.90 (5) v.u. for (I) and (II), respectively] are less than the expected value of 2.00. This may indicate a tendency of the O2 atoms to form hydrogen bonds, but no additional non-classical C—H···O2 hydrogen bonds were observed. [According to Brese & O'Keeffe (1991), an error of 0.010 Å in R_{ij} and the bond length result in an error of 2.7% in the derived valence.]

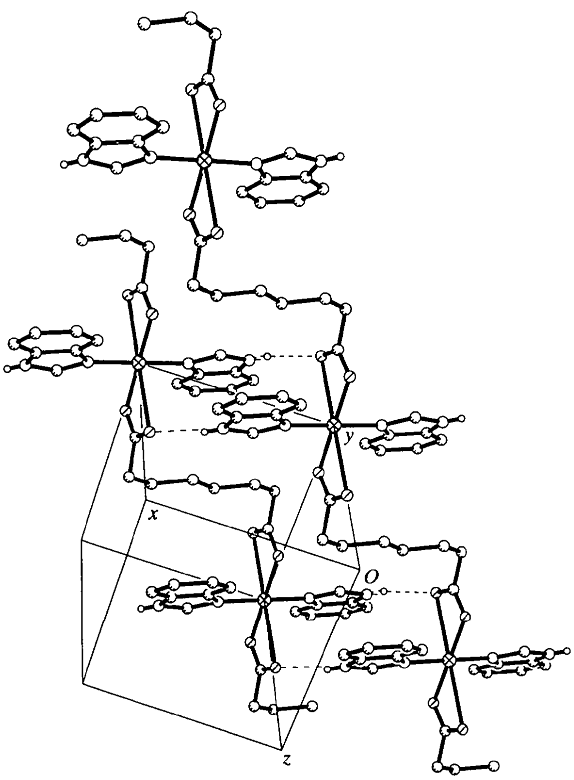


Fig. 2. The two-dimensional association of polymeric chains in (I). H atoms not involved in the hydrogen bonds have been omitted.

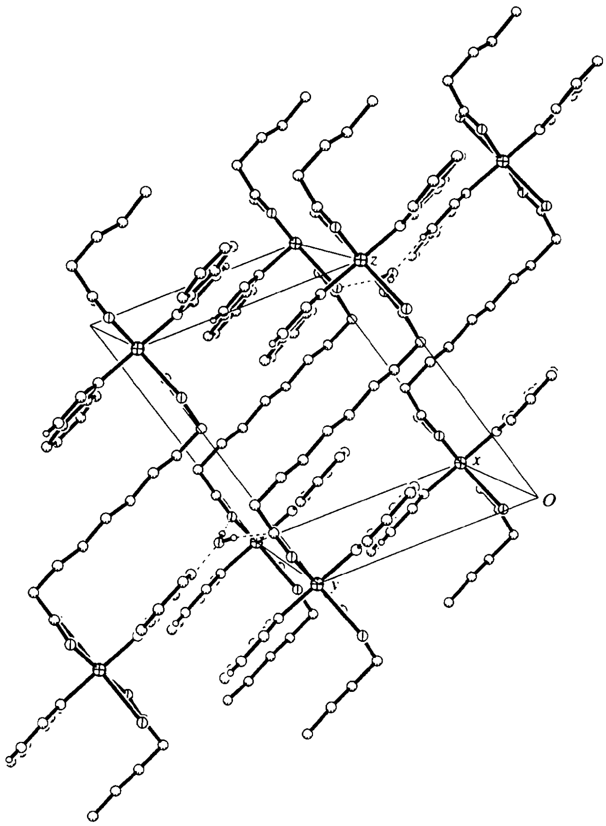


Fig. 3. The three-dimensional association of polymeric chains in (II). H atoms not involved in the hydrogen bonds have been omitted.

In the Cu^{II} polyedra, the Cu—N bonds are distinctly stronger than the shorter Cu—O bonds (average ν_{Cu-N} = 0.492 v.u. and average ν_{Cu-O1} = 0.451 v.u.). The longer axial Cu—O2 bonds are very weak with an average bond valence (ν_{Cu-O2}) of 0.080 v.u.

Experimental

Benzimidazole (0.5 mmol) and the appropriate dicarboxylic acid (1 mmol) dissolved in water (200 ml) were mixed. After heating to boiling point, an aqueous solution of $CuCl_2$ (0.1 mmol l^{-1}) was added dropwise until turbidity appeared. The solution was filtered and allowed to evaporate. Crystals suitable for X-ray diffraction formed after several days.

Compound (I)

Crystal data

$[Cu(C_8H_{12}O_4)(C_7H_6N_2)_2]$	Cu $K\alpha$ radiation
M_r = 471.99	λ = 1.54178 Å

Triclinic
$P\bar{1}$
$a = 7.338\ (1)$ Å
$b = 8.6269\ (5)$ Å
$c = 8.877\ (1)$ Å
$\alpha = 80.98\ (1)°$
$\beta = 84.62\ (1)°$
$\gamma = 72.65\ (1)°$
$V = 529.1\ (1)$ Å^3
$Z = 1$
$D_x = 1.481$ Mg m^{-3}
D_m not measured

Cell parameters from 97 reflections
$\theta = 5.4–32.2°$
$\mu = 1.771$ mm^{-1}
$T = 293\ (2)$ K
Prism
$0.20 \times 0.20 \times 0.15$ mm
Violet

Data collection

Kuma KM-4 diffractometer
$\omega–2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.718$, $T_{max} = 0.777$
2960 measured reflections
2179 independent reflections
2170 reflections with $I > 2\sigma(I)$
$R_{int} = 0.011$
$\theta_{max} = 80.56°$
$h = -9 \rightarrow 7$
$k = -10 \rightarrow 10$
$l = -9 \rightarrow 11$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.088$
$S = 1.083$
2179 reflections
191 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2 + 0.2534P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.361$ e Å^{-3}
$\Delta\rho_{min} = -0.592$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.042 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (I)*

Cu—O1	1.973 (1)	N1—C2	1.316 (2)
Cu—O2	2.645 (2)	N1—C9	1.395 (2)
Cu—N1	1.974 (1)	N3—C2	1.337 (3)
O1—C10	1.268 (2)	N3—C4	1.366 (3)
O2—C10	1.241 (2)		
O1—Cu—O2	54.61 (5)	N1—C2—N3	112.77 (19)
O1—Cu—N1	89.08 (6)	C2—N3—C4	107.66 (17)
O2—Cu—N1	89.05 (5)	N3—C4—C5	132.54 (19)
Cu—O1—C10	106.80 (11)	N3—C4—C9	105.95 (16)
Cu—O2—C10	76.02 (11)	N1—C9—C4	108.25 (16)
C2—N1—C9	105.36 (15)	O1—C10—O2	122.55 (17)
C2—N1—Cu	124.41 (13)	O1—C10—C11	116.51 (17)
C9—N1—Cu	130.12 (12)	O2—C10—C11	120.94 (19)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O2^i	0.70 (3)	2.04 (3)	2.730 (2)	169 (3)

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

Compound (II)

Crystal data

$[Cu(C_{10}H_{16}O_4)(C_7H_6N_2)_2]\cdot 2H_2O$
$M_r = 536.08$
Triclinic
$P\bar{1}$
$a = 6.850\ (4)$ Å
$b = 9.071\ (3)$ Å
$c = 11.208\ (4)$ Å
$\alpha = 74.68\ (3)°$
$\beta = 74.46\ (3)°$
$\gamma = 71.13\ (3)°$
$V = 622.7\ (5)$ Å^3
$Z = 1$
$D_x = 1.429$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 56 reflections
$\theta = 4.2–29.1°$
$\mu = 1.632$ mm^{-1}
$T = 293\ (2)$ K
Prism
$0.20 \times 0.15 \times 0.10$ mm
Violet

Data collection

Kuma KM-4 diffractometer
$\omega–2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.736$, $T_{max} = 0.854$
2605 measured reflections
2448 independent reflections
2244 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$
$\theta_{max} = 75.12°$
$h = -7 \rightarrow 8$
$k = -11 \rightarrow 7$
$l = -14 \rightarrow 13$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.115$
$S = 1.084$
2448 reflections
225 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2 + 0.4765P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.353$ e Å^{-3}
$\Delta\rho_{min} = -0.694$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.0050 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (II)*

Cu—O1	1.974 (2)	N1—C2	1.307 (3)
Cu—O2	2.583 (2)	N1—C9	1.386 (3)
Cu—N1	1.977 (2)	N3—C2	1.334 (3)
O1—C10	1.274 (3)	N3—C4	1.367 (3)
O2—C10	1.237 (3)		
O1—Cu—O2	55.53 (7)	C2—N3—C4	107.3 (2)
O1—Cu—N1	90.49 (8)	N3—C4—C5	131.8 (3)
O2—Cu—N1	88.22 (8)	N3—C4—C9	105.8 (2)
Cu—O1—C10	105.12 (15)	N1—C9—C4	108.6 (2)
Cu—O2—C10	77.65 (16)	O1—C10—O2	121.4 (2)
C2—N1—C9	105.4 (2)	O1—C10—C11	116.6 (2)
N1—C2—N3	113.0 (2)	O2—C10—C11	122.0 (3)

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O3	0.72 (3)	2.08 (3)	2.765 (3)	160 (3)
O3—H9···O1^i	0.68 (4)	2.10 (4)	2.773 (3)	169 (4)
O3—H10···O2^{ii}	0.83 (4)	2.02 (4)	2.842 (3)	172 (4)

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

Table 5. *Valence sums around the Cu and O atoms in the Cu—O1—C10—O2 chelate rings in (I) and (II)*

d_{ij} is the observed bond length between i and j atoms, v_{ij} is the computed bond valence (in valence units) and $V_i = \sum v_{ij}$.

	(I)			(II)		
i—*j* bond	d_{ij} (Å)	v_{ij} (v.u.)	V_i (v.u.)	d_{ij} (Å)	v_{ij} (v.u.)	V_i (v.u.)
Cu—O1	1.973 (1)	0.452†	2.04 (5)	1.974 (2)	0.451†	2.05 (5)

Cu—O2	2.645 (2)	0.073†		2.583 (2)	0.087†	
Cu—N1	1.974 (1)	0.494†		1.977 (2)	0.490	
O1—C10	1.268 (2)	1.549	2.00 (5)	1.274 (3)	1.524	1.97 (5)
O1—Cu	1.973 (1)	0.452		1.974 (2)	0.451	
O2—C10	1.241 (2)	1.667	1.86 (5)	1.237 (3)	1.685	1.90 (5)
O2—Cu	2.645 (2)	0.073		2.583 (2)	0.087	
O2···H10	2.04 (3)	0.122		2.02 (4)	0.128	

† Occurs twice around the *i* atom.

The title structures were solved by the conventional Patterson method and were refined by full-matrix least-squares calculations. All non-H atoms were refined anisotropically. All H atoms were located from a difference synthesis and refined isotropically.

For both compounds, data collection: *KM*-4 *Software* (Kuma Diffraction, 1992); cell refinement: *KM*-4 *Software*; data reduction: *DATARED* in *KM*-4 *Software*; program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1997*b*); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL*97.

This work was supported by the Polish State Committee for Scientific Research (KBN) (grant 3 T09A 142 15).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1349). Services for accessing these data are described at the back of the journal.

References

Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.
Brown, I. D. (1976). *Acta Cryst.* A**32**, 24–31.
Brown, I. D. (1992). *Acta Cryst.* B**48**, 553–572.
Brown, I. D. (1994). *Bond-Length–Bond-Valence Relationships in Inorganic Solids*, in *Structure Correlation*, Part III, edited by H.-B. Burgi & J. D. Dunitz, pp. 405–429. Weinheim/New York: VCH Publishers.
Brown, I. D. (1997). *Acta Cryst.* B**53**, 381–393.
Cambridge Structural Database (1998). Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.
Kuma Diffraction (1992). *KM*-4 *Software*. Kuma Diffraction, Wrocław, Poland.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
O'Keeffe, M. & Brese, N. E. (1991). *J. Am. Chem. Soc.* **113**, 3226–3229.
Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* pp. S1–83.
Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997*a*). *SHELXL*97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXS*97. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sieroń, L. & Bukowska-Strzyżewska, M. (1998). *Acta Cryst.* C**54**, 1431–1435.
Tosik, A. & Bukowska-Strzyżewska, M. (1992). *J. Crystallogr. Spectrosc. Res.* **22**, 225–229.
Tosik, A., Sieroń, L. & Bukowska-Strzyżewska, M. (1995*a*). *Acta Cryst.* C**51**, 1985–1987.
Tosik, A., Sieroń, L. & Bukowska-Strzyżewska, M. (1995*b*). *Acta Cryst.* C**51**, 1987–1989.
Wagner, T. R. & O'Keeffe, M. (1988). *J. Solid State Chem.* **73**, 211–216.

Acta Cryst. (1999). C**55**, 1234–1236

Hydroxotriphenyltin 2,6-bis(1*H*-benzimidazol-2-yl)pyridine hydrate

Kong Mun Lo,[a] V. G. Kumar Das[a] and Seik Weng Ng[b]

[a]*Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia, and* [b]*Institute of Postgraduate Studies and Research, University of Malaya, 50603 Kuala Lumpur, Malaysia. E-mail: h1nswen@umcsd.um.edu.my*

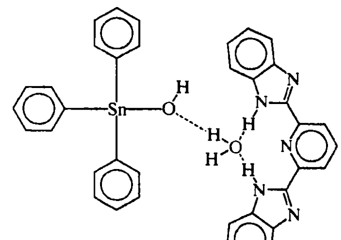
(*Received 11 February 1999; accepted 15 March 1999*)

Abstract

In hydroxotriphenyltin 2,6-bis(1*H*-benzimidazol-2-yl)pyridine hydrate (1/1/1), $[Sn(C_6H_5)_3(OH)]\cdot C_{19}H_{13}N_5\cdot H_2O$, the water molecule is hydrogen bonded to the hydroxo O atom, the two imino N atoms of the benzimidazolyls flanking the pyridine unit and one of the two amino N atoms of an adjacent *N*-heterocycle [O···O = 2.680 (5) Å; O···N = 2.831 (5), 2.930 (6) and 2.767 (6) Å]. The hydrogen-bonding architecture gives rise to a two-dimensional network structure in which alternate *N*-heterocycles are stacked perpendicular to each other when the structure is viewed along the *z* axis. The organotin moiety shows tetrahedral coordination at tin.

Comment

Hydroxotriphenyltin, a reagent used in the synthesis of a plethora of triphenyltin complexes, exists as hydroxo-bridged linear chains whose Sn atoms show *trans*-trigonal-bipyramidal coordination [Sn—O = 2.197 (5) and Sn←O = 2.255 (5) Å; Glidewell & Liles, 1978]. This compound is not known to afford adducts (Harrison, 1995), so that the title compound, (I), represents an unusual example of a hydroxotriphenyltin complex.



(I)

A view of the asymmetric unit of (I) is shown in Fig. 1. The two N—H groups of the 2,6-bis(benzimidazol-2-yl)pyridine molecule form N—H···O hydrogen bonds to the water molecule (details in Table 2); the water molecule is, in turn, hydrogen