catena-Poly[[bis(1*H*-benzimidaz-ole-κ*N*³)(salicylato-κ*O*)copper(II)]-μ-salicylato-*O*,*O*′:*O*″]

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The title compound, $[Cu(C_7H_5O_3)_2(C_7H_6N_2)_2]_n$, is a one-dimensional polymeric complex bridged by salicylate anions. The Cu^{II} atom is surrounded by three salicylate and two benzimidazole ligands, with a tetragonally elongated octahedral coordination geometry. The Cu—O bond distances in the axial directions are 2.6092 (16) and 2.6834 (17) Å. π–π stacking interactions exist between the benzimidazole rings of neighboring polymeric complex chains.

Comment

As π–π stacking between aromatic rings has been correlated with the electron transfer process in some biological systems (Deisenhofer & Michel, 1989), metal complexes incorporating aromatic ligands, such as phenanthroline, benzimidazole and bithiazole, have attracted our attention. A series of metal complexes with the benzimidazole (bzim) ligand have been prepared in our laboratory, and their structures have shown the existence of π–π stacking between the bzim rings (Chen *et al.*, 2003). As part of our ongoing investigations into π–π stacking, we report here the structure of the title compound, $[Cu(bzim)_2(sali)_2]_n$ (sali is salicylate), (I). A search of the Cambridge Structural Database (November 2003 update; Allen, 2002) indicated that no $[M(bzim)_2(sali)_2]_n$ compound has been reported previously.

(I)
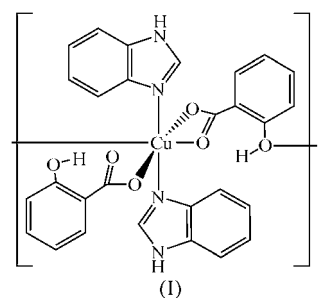
The structure of a fragment of (I) is illustrated in Fig. 1. The repeat unit of the polymeric complex contains one Cu^{II} atom, two salicylate anions and two bzim molecules. N atoms of the
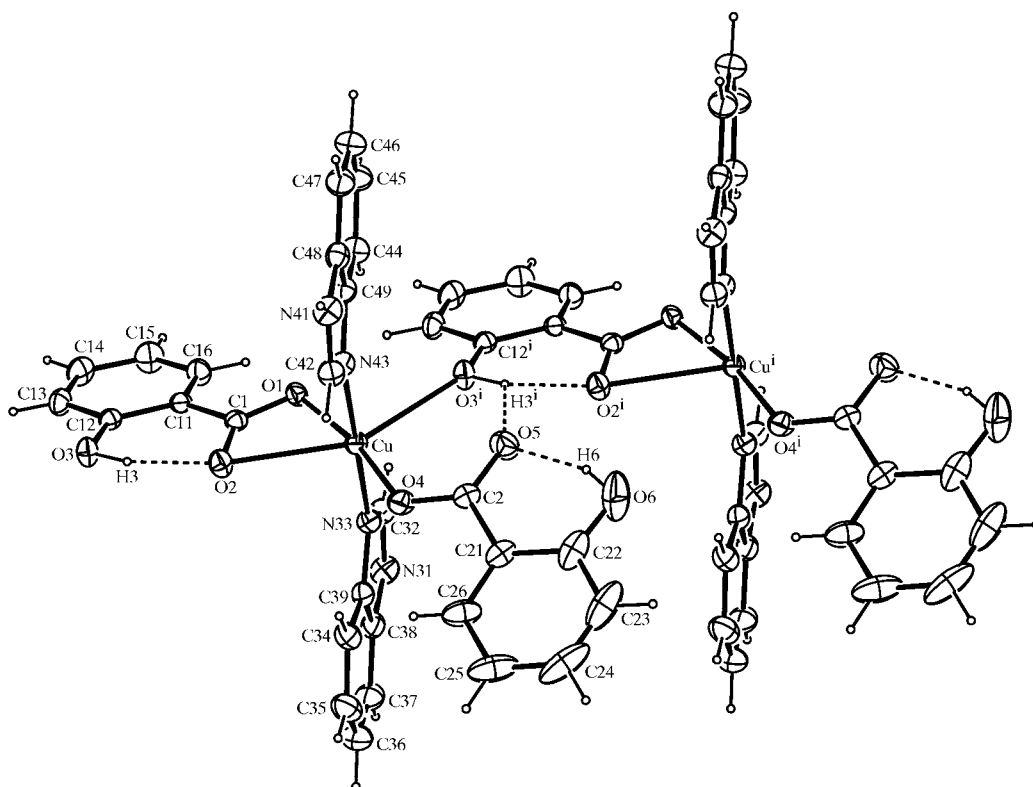
Figure 1
The structure of a fragment of (I), shown with 30% probability displacement ellipsoids. Dashed lines indicate the hydrogen bonding. [Symmetry code: (i) *x* − 1, *y*, *z*.]

bzim ligands and carboxyl O atoms (O1 and O4) of the two sali ligands form the equatorial coordination plane around the Cu atom, with bond distances in the range 1.9629 (16)– 2.0061 (15) Å (Table 1).

The distances between the Cu atom and the other two carboxyl O atoms (O2 and O5) are appreciably different, and both are much longer than those in the equatorial plane. The Cu—O2 distance is longer than the mean Cu—O distance in the equatorial plane [1.982 (2) Å] by 0.627 (3) Å, but the smaller Cu—O1—C1 angle [104.68 (14)°] suggests a bonding interaction between atoms Cu and O2 (as discussed below). On the other hand, the Cu···O5 distance [3.061 (2) Å] and the larger Cu—O4—C2 angle [120.94 (16)°] suggest no bonding interaction between atoms Cu and O5.

A comparison of the geometric parameters for the carboxyl groups in some Cu^{II} complexes is shown in Table 3. The Cu—O1—C1 angles in these complexes fall into two distinct ranges, *viz*. either larger than 120° or close to 105°. The bond angle of 120° indicates normal sp^2 hybridization for atom O1 and corresponds to the long Cu···O2 distance in the complexes, suggesting a monodentate coordinate mode for the carboxyl group. Conversely, the smaller Cu—O1—C1 angle of 105° implies the existence of a bonding interaction between the Cu atom and the other O atom (O2) of the carboxyl group, suggesting a chelate coordination mode. A similar situation has been found in carboxylate–Mn^{II} complexes, in which Mn—O—C angles of 120 and 95° correspond to the monodentate and chelate modes of the carboxyl group, respectively (Liu *et al.*, 2005). Thus, the M—O—C angle may be an additional criterion of the coordination mode for the carboxyl group in transition metal complexes. According to this criterion, the two sali ligands in (I) coordinate to the Cu atom in different modes.

The C1-containing sali group also plays the role of bridging ligand in (I); hydroxy atom O3 coordinates to the Cu atom of the neighboring repeat unit to form a polymeric complex chain along the crystallographic *a* axis (Figs. 1 and 2). The Cu—O3^{i} distance [symmetry code: (i) $x - 1, y, z$] is appreciably longer than the Cu—O2 distance (Table 1). The large Cu—O3^{i}—C12^{i} bond angle [143.93 (14)°], besides the Jahn–Teller effect, is a possible reason for the longer Cu—O3^{i} bond. Thus, each Cu^{II} atom is surrounded by three sali and two bzim ligands in a distorted octahedral coordination geometry.

The C2-containing sali group is not a bridging ligand. Carboxyl atom O5 is hydrogen bonded to hydroxy group O3^{i} of an adjacent sali ligand, resulting in there being a longer distance between atom O6 and the neighboring complex unit, the nearest distance between atom O6 and the non-H atoms of the neighboring complex unit being 3.684 (3) Å (O6···O4^{i}; Fig. 1).

The packing of the polymeric chains is illustrated in Fig. 2. Neighboring polymeric chains are linked to one another *via* hydrogen bonds between the bzim and carboxyl groups (Table 2). The nearly parallel arrangement of the bzim rings from neighboring polymeric chains is also shown in Fig. 2, a partial overlapping between the bzim rings being observed (Fig. 3). The dihedral angle between the planes of the bzim groups containing atoms N33 and N43^{ii} is 7.64 (5)°, as is the angle between the planes of the bzim groups containing atoms N33 and N43^{iii} [symmetry codes: (ii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$]. The distances of atoms N31 and C38 from the mean plane of the N43^{ii}-containing bzim group are 3.344 (2) and 3.436 (3) Å, respectively; the distances of atoms C36 and C38 from the mean plane of the N43^{iii}-containing bzim group are 3.467 (3) and 3.537 (3) Å, respectively. These distances are significantly shorter than that between uncoordinated parallel bzim rings in an Mn^{II}–bzim complex [3.600 (6) Å; Chen *et al.*, 2003] and clearly suggest the existence of π–π stacking of bzim rings between polymeric complex chains in (I).
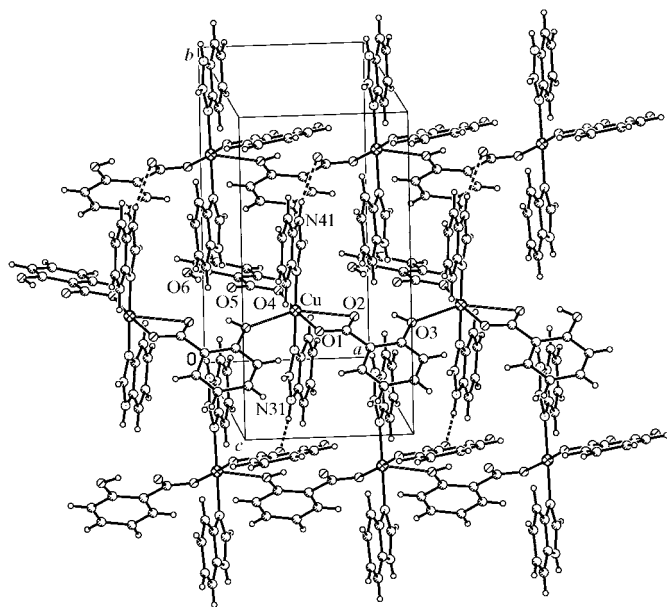
Figure 2
A crystal packing diagram, showing the nearly parallel arrangement of the bzim rings and the hydrogen bonding (dashed lines) between neighboring polymeric complex chains.
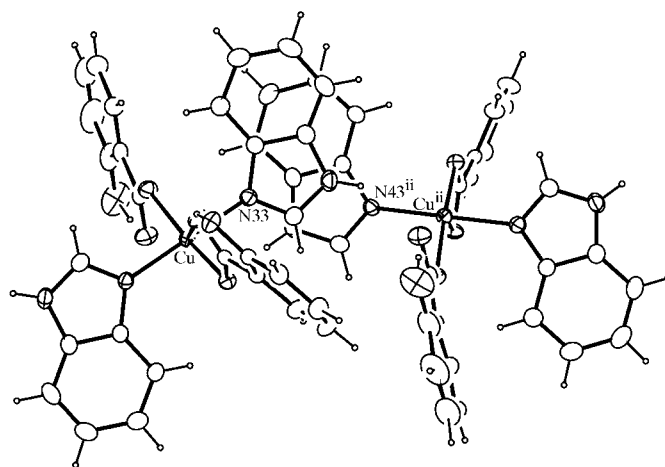
Figure 3
π–π stacking between the bzim rings of neighboring molecules. [Symmetry code: (ii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.]

Experimental

An ethanol solution (5 ml) of benzimidazole (0.24 g, 2 mmol) was mixed with an aqueous solution (8 ml) containing salicylic acid (0.28 g, 2 mmol), Na_2CO_3 (0.10 g, 1 mmol) and $CuCl_2 \cdot 2H_2O$ (0.17 g, 1 mmol). The mixture was refluxed for 4 h and filtered. Blue single crystals of (I) were obtained from the filtrate after 3 d.

Crystal data

$[Cu(C_7H_5O_3)_2(C_7H_6N_2)_2]$	$D_x = 1.538$ Mg m^{-3}
$M_r = 574.04$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 13 793
$a = 7.3032$ (9) Å	reflections
$b = 14.0380$ (12) Å	$\theta = 2.0$–$24.0°$
$c = 24.1952$ (18) Å	$\mu = 0.93$ mm^{-1}
$\beta = 91.812$ (4)°	$T = 295$ (2) K
$V = 2479.3$ (4) Å^3	Platelet, blue
$Z = 4$	$0.32 \times 0.22 \times 0.08$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer	4320 independent reflections
ω scans	3426 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$R_{int} = 0.031$
	$\theta_{max} = 25.0°$
$T_{min} = 0.740$, $T_{max} = 0.925$	$h = -8 \rightarrow 8$
18 148 measured reflections	$k = -16 \rightarrow 16$
	$l = -28 \rightarrow 28$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0382P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.036$	$+ 1.4329P]$
$wR(F^2) = 0.084$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
4320 reflections	$\Delta\rho_{max} = 0.28$ e Å^{-3}
352 parameters	$\Delta\rho_{min} = -0.31$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cu—O1	2.0061 (15)	Cu—O4	1.9629 (16)
Cu—O2	2.6092 (16)	Cu—N33	1.996 (2)
Cu—O3^i	2.6834 (17)	Cu—N43	1.985 (2)
O2—Cu—O3^i	140.50 (5)	O3^i—Cu—N41	98.53 (5)
O3^i—Cu—O1	85.15 (6)	C1—O1—Cu	104.68 (14)
O3^i—Cu—O4	104.15 (6)	C2—O4—Cu	120.94 (16)
O3^i—Cu—N31	81.06 (5)	Cu^{iv}—O3—C12	143.93 (14)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H3$\cdots$O2	0.91	1.77	2.596 (2)	149
O3—H3$\cdots$O5^{iv}	0.91	2.27	2.856 (3)	122
O6—H6$\cdots$O5	0.91	1.71	2.558 (3)	153
N31—H31$\cdots$O5^{ii}	0.86	2.07	2.840 (3)	149
N41—H41$\cdots$O2^{v}	0.86	2.18	3.026 (3)	167
C34—H34$\cdots$O4	0.93	2.50	3.064 (3)	119

Symmetry codes: (ii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $1 + x, y, z$; (v) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

H atoms on aromatic rings were placed in calculated positions, with C—H = 0.93 Å and N—H = 0.86 Å, and were included in the final cycles of refinement in a riding model, with U_{iso}(H) values of $1.2U_{eq}$(carrier atom). H atoms of hydroxy groups were located in difference Fourier maps and refined as riding in their as-found positions, with fixed isotropic displacement parameters of 0.05 Å^2.

Table 3
Geometric parameters (Å, °) for selected carboxylate groups in Cu^{II} complexes.

Carboxylate	Cu—O1—C1	Cu—O1	Cu$\cdots$O2
Salicylate[1,a]	127.4 (2)	1.981 (2)	3.233 (2)
Hydroxybenzoate[1,b]	126.4 (1)	1.956 (2)	3.199 (2)
Nitrobenzoate[1,c]	127.0 (2)	1.959 (2)	3.279 (2)
Chlorofluorobenzoate[1,d]	126.9 (4)	2.019 (3)	3.141 (3)
Benzenetetracarboxylate[1,e]	121.5 (2)	1.994 (2)	3.110 (2)
Terephthalate[2,f]	106.0 (5)	2.006 (8)	2.657 (8)
Phthalate[2,g]	104.9 (2)	1.981 (2)	2.632 (2)
Aminomethylbenzoate[2,h]	104.8 (2)	1.954 (3)	2.572 (3)
Methylbenzoate[2,i]	104.54 (13)	1.9435 (14)	2.5923 (19)
Salicylate[2,j]	104.68 (14)	2.0061 (15)	2.6092 (16)

Notes: (1) chelate coordination mode; (2) monodentate coordination mode. References: (*a*) Hoang *et al.* (1992); (*b*) Hökelek *et al.* (1998); (*c*) Hökelek *et al.* (1997); (*d*) Hoang *et al.* (1995); (*e*) Chen *et al.* (1996); (*f*) Cano *et al.* (1997); (*g*) Bakalbassis & Terzis (1994); (*h*) Boudreau & Haendler (1986); (*i*) Xu & Xu (2004); (*j*) this work.

The large anisotropy in the displacement parameters of atoms O6 and C24 may imply that the non-bridged sali ligand is disordered.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC & Rigaku, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *XP* (Siemens, 1994); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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