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(2,2′-Bipyridine-κ²N,N′)bis(2-bromo-4-carboxylbenzoato-κO)copper(II)

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Key indicators

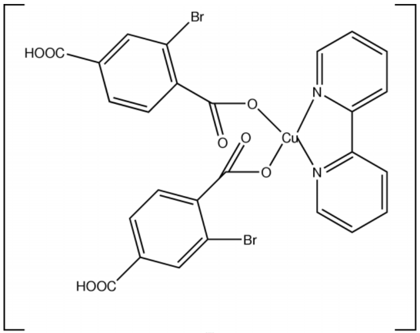
Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.008 Å
Disorder in main residue
R factor = 0.057
wR factor = 0.134
Data-to-parameter ratio = 15.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The reaction of copper(II) chloride with 2-bromo-1,4-benzenedicarboxylic acid (H_2bbdc) and 2,2′-bipyridine in aqueous solution under hydrothermal conditions gave the title compound, $[Cu(C_8H_4BrO_4)_2(C_{10}H_8N_2)]$. The Cu^{II} atom lies on a twofold axis and is coordinated by two singly deprotonated 2-bromo-1,4-benzenedicarboxylate groups and one 2,2′-bipyridine ligand in a square-planar geometry. Intermolecular O—H···O hydrogen bonds between carboxylate groups ensure a two-dimensional architecture with double sheets.

Comment

Recently, benzenedicarboxylates or benzenetricarboxylates have been extensively used to design and construct novel architectures because of potential applications in functional materials, such as magnetism, catalysis, chemical sensors *etc.* (Moulton & Zaworotko, 2001; Eddaoudi *et al.*, 2002). Partly deprotonated benzenetricarboxylates have been commonly used as ligands (Yaghi *et al.*, 1995; Huh *et al.*, 2002; Zhu *et al.*, 2003), while, in general, the phenyldicarboxylates are fully deprotonated. Slow deprotonation of carboxylates is very important for producing well formed crystals and can be achieved using weak N-donor bases, solvents or variable starting materials. Hydrothermal synthesis is also a good strategy for achieving this target. The present paper reports a rare example of partly deprotonated 2-bromo-1,4-benzenedicarboxylate (Hbbdc$^-$) in the title compound, (I).



(I)

Complex (I) is monomeric and has twofold symmetry (Fig. 1 and Table 1). Atom Cu1 is coordinated by two O atoms of two monodentate carboxylate groups and two N atoms of one 2,2′-bipyridine ligand. Each Hbbdc$^-$ ligand affords one deprotonated carboxylate and one carboxylic group, leading to a single negative charge on the ligand. The carboxylic group is confirmed by IR spectroscopy (strong absorption at 1716 cm^{-1}).

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Intermolecular hydrogen bonding between the uncoordinated atom O2 and the O4/H4 moiety of the carboxylic group provides the basis of a two-dimensional network, as shown in Fig. 2. Although the two-dimensional hydrogen-bonding network contains double sheets, there is no π–π stacking between the aromatic rings. The non-classical C—H$\cdots$O hydrogen-bonding interaction has attracted much attention in recent years. The C13$\cdots$O1^{i} and C11$\cdots$O3^{iii} distances are 3.028 (6) and 3.141 (8) Å (Table 2), which are comparable to widely accepted distances of C—H$\cdots$O hydrogen-bonding interactions (Steiner, 1997; Steiner & Desiraju, 1998). In summary, we have synthesized an uncommon species with singly deprotonated 2-bromo-1,4-benzenedicarboxylate under hydrothermal conditions. This successful example will be of great benefit for designing and controlling the architectures constructed from benzenedicarboxylates.

Experimental

Complex (I) was hydrothermally synthesized from a mixture of copper(II) chloride dihydrate (0.034 g, 0.2 mmol), 2-bromo-1,4-benzenedicarboxylic acid (0.050 g, 0.2 mmol), 2,2′-bipyridine (0.032 g, 0.2 mmol) and water (8 ml) in the molar ratio 1:1:1:2220. The starting mixture was put into a 25 ml Teflon-lined stainless steel autoclave and heated for 3 h at 413 K. The resulting solid phase, consisting of deep-blue blocks of (I), was filtered off and dried at room temperature.

Crystal data

$[Cu(C_8H_4BrO_4)_2(C_{10}H_8N_2)]$
$M_r = 707.77$
Monoclinic, $C2/c$
$a = 12.0675$ (12) Å
$b = 15.2713$ (16) Å
$c = 14.4430$ (15) Å
$\beta = 105.325$ (11)°
$V = 2567.0$ (5) Å^3
$Z = 4$

$D_x = 1.831$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2917 reflections
$\theta = 2.2$–27.4°
$\mu = 4.02$ mm^{-1}
$T = 296$ (2) K
Block, deep blue
$0.29 \times 0.21 \times 0.11$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.315$, $T_{\max} = 0.647$
10 701 measured reflections

2917 independent reflections
2127 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.057$
$\theta_{\max} = 27.4°$
$h = -15 \rightarrow 15$
$k = -19 \rightarrow 19$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.135$
$S = 1.12$
2917 reflections
186 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0435P)^2 + 15.099P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.67$ e Å^{-3}
$\Delta\rho_{\min} = -0.56$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.945 (3)	O2—C7	1.239 (7)
Cu1—N1	1.970 (4)	O3—C8	1.208 (7)
O1—C7	1.255 (6)	O4—C8	1.319 (7)
O1—Cu1—O1^{i}	90.0 (2)	O1^{i}—Cu1—N1	94.26 (16)
O1—Cu1—N1	175.07 (17)	N1—Cu1—N1^{i}	81.6 (2)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O4—H4$\cdots$O2^{ii}	0.81	1.78	2.578 (6)	168
C11—H11$\cdots$O3^{iii}	0.93	2.43	3.141 (8)	134
C12—H12$\cdots$O2^{iv}	0.93	2.60	3.368 (7)	140
C13—H13$\cdots$O1^{i}	0.92	2.51	3.028 (6)	116

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

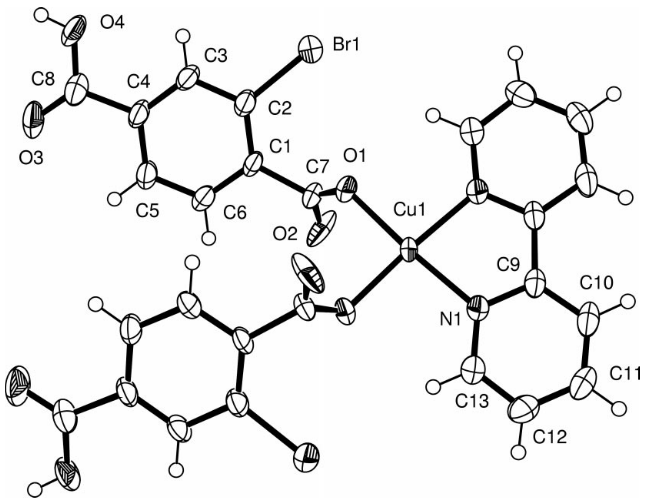

Figure 1
The molecular structure of (I), with displacement ellipsoids shown at the 50% probability level. There is positional disorder of the Br atoms. The occupation factor of atom Br1 is 90%. The minor component, atom Br2 bonded to atom C5, has been omitted for clarity.

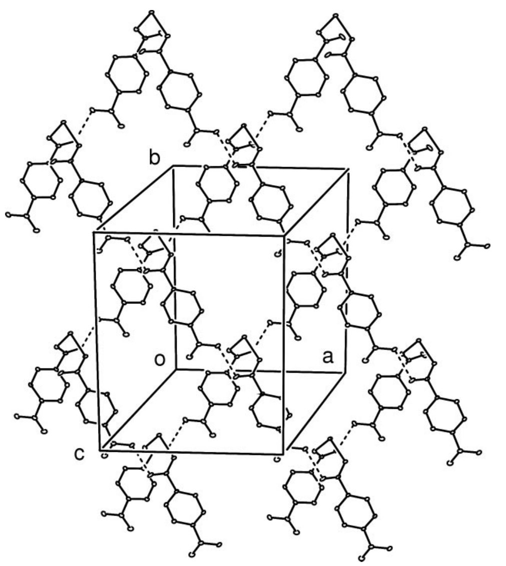

Figure 2
A view of the two-dimensional hydrogen-bonding network. The Br atoms and 2,2′-bipyridine molecules have been omitted for clarity.

Atom H4 of the carboxylic group was located in a difference Fourier map, and the other H atoms were positioned geometrically and treated as riding [C—H = 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C)]. The Br atoms are disordered over two sites, *viz*. Br1 (bonded to atom C2) and Br2 (bonded to atom C5). The site occupancy factors of Br1 and Br2 atoms were independently refined and converged to 0.896 (3) and 0.065 (3), respectively. In the final cycles of structure refinement they were fixed as 0.90 and 0.10, respectively.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/Molecular Structure Corporation, 2002); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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