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Bis(μ-1*H*-benzimidazole-5,6-dicarboxylato)bis[tetraaquadicobalt(II)] pentahydrate

Yu-Lin Lo, Wen-Chieh Wang, Gon-Ann Lee and Yen-Hsiang Liu*

Department of Chemistry, Fu Jen Catholic University, Hsinchuang, Taipei 24205, Taiwan
Correspondence e-mail: chem2022@mails.fju.edu.tw

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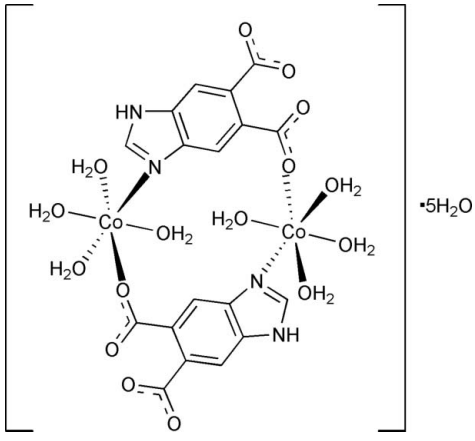
Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.004 Å; H-atom completeness 97%; disorder in solvent or counterion; R factor = 0.040; wR factor = 0.103; data-to-parameter ratio = 12.7.

The title compound, $[Co_2(C_9H_4N_2O_4)_2(H_2O)_8]\cdot 5H_2O$, contains two Co^{II} ions that are bridged by two 1*H*-benzimidazole-5,6-dicarboxylate ligands to form an M_2L_2 type complex (M = metal and L = ligand). There are two crystallographically distinct M_2L_2 units, each on an inversion centre, along with coordinated and uncoordinated water molecules, in the asymmetric unit. The Co^{II} ions are octahedral. Extensive hydrogen bonding exists between the complex and water molecules, and this helps to stabilize the crystal structure. One water molecule is disordered over two sites with occupancies 0.84:0.16.

Related literature

Metal–organic coordination polymers using 1*H*-benzimidazole-5-carboxylic acid as a bridging ligand were reported by Guo *et al.* (2006) and Liu *et al.* (2005).



Experimental

Crystal data

$[Co_2(C_9H_4N_2O_4)_2(H_2O)_8]\cdot 5H_2O$
M_r = 760.35
Monoclinic, $P2_1/c$
a = 13.4210 (2) Å
b = 9.1096 (2) Å
c = 23.8185 (4) Å
β = 99.5191 (6)°
V = 2871.95 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.25 mm^{-1}
T = 200 (2) K
0.30 × 0.18 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.776, T_{max} = 0.905
22168 measured reflections
5249 independent reflections
4216 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.103
S = 1.10
5249 reflections
412 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.72 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O94^{i}	0.86	1.96	2.779 (4)	159
N4—H4···O93	0.86	1.84	2.673 (4)	164
O81—H81*A*···O3^{ii}	0.86	1.84	2.683 (3)	166
O81—H81*B*···O85^{iii}	0.84	2.05	2.883 (3)	172
O82—H82*A*···O3	0.85	2.14	2.974 (3)	169
O82—H82*B*···O4^{ii}	0.85	1.84	2.691 (3)	176
O83—H83*A*···O95^{iv}	0.83	2.05	2.812 (4)	153
O83—H83*B*···O6^{ii}	0.85	1.96	2.721 (3)	147
O84—H84*A*···O2	0.85	1.8	2.616 (3)	162
O84—H84*B*···O4^{v}	0.85	1.88	2.708 (3)	165
O85—H85*A*···O92^{vi}	0.85	2.02	2.850 (4)	167
O85—H85*B*···O7^{vii}	0.85	1.82	2.649 (3)	168
O86—H86*A*···O8^{vii}	0.83	1.88	2.711 (3)	176
O86—H86*B*···O7	0.83	2.03	2.859 (3)	178
O87—H87*A*···O6	0.84	1.85	2.642 (3)	156
O87—H87*B*···O8^{viii}	0.85	1.86	2.689 (3)	166
O88—H88*A*···O91^{vii}	0.84	1.98	2.813 (3)	173
O88—H88*B*···O3^{vii}	0.85	1.9	2.732 (3)	165
O91—H91*A*···O95	0.85	1.99	2.836 (4)	180
O91—H91*B*···O84	0.86	1.98	2.837 (3)	174
O92—H92*A*···O91	0.86	2.05	2.813 (4)	148
O92—H92*B*···O87^{v}	0.85	2.34	3.089 (4)	148
O93—H93*A*···O2^{ix}	0.86	2.07	2.844 (3)	151
O93—H93*A*···O88^{x}	0.86	2.6	3.045 (4)	114
O93—H93*B*···O5^{x}	0.86	1.95	2.788 (3)	168
O94—H94*A*···O2^{ix}	0.84	2.1	2.889 (4)	158
O94—H94*A*···O93	0.84	2.62	3.180 (5)	126
O94—H94*B*···O6^{v}	0.84	2.04	2.873 (4)	174
O95—H95*A*···O1^{ii}	0.9	2.07	2.910 (4)	155

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

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor 1997); data reduction: *DENZO–SMN* (Otwinowski & Minor 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2050).

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supplementary materials

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Bis(μ-1*H*-benzimidazole-5,6-dicarboxylato)bis[tetraaquadicobalt(II)] pentahydrate

Y.-L. Lo, W.-C. Wang, G.-A. Lee and Y.-H. Liu

Comment

N-Heterocyclic carboxylic acids are recognized as efficient N,*O*-donors exhibiting versatile coordination modes and hydrogen bonding interactions. Examples on the basis of 1*H*-benzimidazole-5-carboxylic acid have been reported, which give rise to various coordination polymers and supramolecular architectures (Guo *et al.*2006; Liu *et al.* 2005). Here we report the crystal structure of the title compound, $[Co_2(H_2O)_8(C_9H_4N_2O_4)_2]\cdot 5H_2O$, using a new family member of the N-heterocyclic carboxylic acids, 1*H*-benzimidazole-5,6-dicarboxylic acid (H_3BIDC).

The asymmetric unit consists of two 1*H*-benzimidazole-5,6-dicarboxylate (H_3BIDC) ligands, which are deprotonated to form $HBIDC^{2-}$ anions. Each of the Co^{II} cations has an octahedral coordination environment, and is surrounded by four coordinated water molecules, one nitrogen atom of the benzimidazole ring, and one oxygen atom of the monodentate carboxylate group. Two Co^{II} ions are bridged by two $HBIDC^{2-}$ ligands to form a M_2L_2 type complex (*M*: metal, *L*: ligand). There are two crystallographically distinct M_2L_2 units in the asymmetric unit (Fig. 1). A unit-cell packing diagram is shown in Fig. 2. The N-bound H atoms of the benzimidazole ring, the O atoms of the uncoordinated carboxylate group, and coordinated water molecules serve as hydrogen bonding donors and acceptors. Extensive hydrogen bonding interactions (Table 2) were observed among the title compound and solvent water molecules in the solid-state, and these help stabilize the crystal structure.

Experimental

Purple crystals form within 4 days of layering a 2.0 ml me thanol solution of $Co(NO_3)_2\cdot 6H_2O$ (0.1169 g, 0.40 mmol) through a 3.0 ml me thanol and 15 ml aqueous buffer layers onto a 10.0 ml aqueous solution containing 1*H*-benzimidazole-4,5-dicarboxylic acid (0.0415 g, 0.20 mmol) and KOH (4*M*, 0.4 ml).

Refinement

The C-bound H atoms were placed in calculated positions (C–H = 0.93 Å) and refined in the riding-model approximation with *U*iso(H) = 1.2 *U*eq(C). The N-bound H atoms were found in a difference Fourier map, but were placed in calculated positions (C–H = 0.86 Å) and refined in the riding-model approximation with *U*iso(H) = 1.2 *U*eq(N). The H atoms of the coordinated water molecules and solvent water molecules were located in a difference Fourier map, and refined using a riding model with *U*sio(H) = 1.5 *U*eq(O). The water molecule O94 is disordered over two positions; the occupancies of O94 and O94' refined to 0.84 and 0.16, respectively (O94' is only refined isotropically). Only one of the H atoms of solvent water molecule O95 could be found in a difference Fourier map because of its close proximity (*ca* 2.08 Å) to the disordered O94'.

Figures

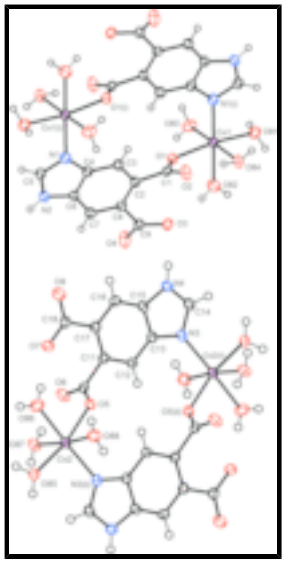

Fig. 1. The crystallographically distinct M_2L_2 units of the title compound with atom numbering scheme. Atomic displacement ellipsoids are drawn at the 50% probability level. (Symmetry code: (i) 1–*x*, 1–*y*, 2–*z*; (ii) 2–*x*, –*y*, 1–*z*)

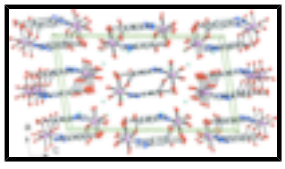

Fig. 2. A unit-cell packing diagram viewied down the *b*-axis. (*Key*: aqua sphere: solvent water molecules; pink sphere: Co; blue sphere: N; red sphere: O; gray sphere: C). H atoms are omitted for clarity.

Bis(μ-1*H*-benzimidazole-5,6-dicarboxylato)bis[tetraaquadicobalt(II)] pentahydrate

Crystal data

$[Co_2(C_9H_4N_2O_4)_2(H_2O)_8]\cdot 5H_2O$	F_{000} = 1568
M_r = 760.35	D_x = 1.759 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 16539 reflections
a = 13.4210 (2) Å	θ = 2.0–25.4º
b = 9.1096 (2) Å	μ = 1.26 mm^{-1}
c = 23.8185 (4) Å	*T* = 200 (2) K
β = 99.5191 (6)º	Plate, purple
V = 2871.95 (9) Å^3	0.30 × 0.18 × 0.08 mm
Z = 4	

Data collection

Nonius KappaCCD diffractometer	5249 independent reflections
Radiation source: sealed tube	4216 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.032
T = 200(2) K	θ_{max} = 25.4º
φ and ω scans	θ_{min} = 2.1º

Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
T_{min} = 0.776, T_{max} = 0.905
22168 measured reflections

h = −16→16
k = −10→8
l = −28→28

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.103
S = 1.10
5249 reflections
412 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0316P)^2 + 5.0966P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.72 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}
Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0011 (2)

Special details

Experimental. Comment on transmission values: The program *SADABS* (Sheldrick, 2003) outputs the ratio of minimum to maximum apparent transmission (0.858265). We have set *T*(max) to the expected value, *i.e.* exp(-r_{min}× μ) and we calculate *T*(min) from the minimum to maximum apparent transmission given by *SADABS*.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Co1	0.41028 (3)	0.65075 (4)	0.836342 (16)	0.01866 (14)	
Co2	1.08333 (3)	−0.16005 (4)	0.658602 (16)	0.01864 (14)	
N1	0.6294 (2)	0.2084 (3)	1.10033 (10)	0.0222 (6)	
N2	0.64479 (19)	−0.0092 (3)	1.06047 (11)	0.0232 (6)	
H2	0.654	−0.1022	1.0578	0.028*	
N3	0.8847 (2)	0.3124 (3)	0.40404 (10)	0.0217 (6)	
N4	0.86074 (19)	0.5298 (3)	0.44314 (10)	0.0215 (6)	
H4	0.849	0.6222	0.4455	0.026*	
O1	0.47640 (15)	0.4841 (2)	0.88915 (8)	0.0202 (5)	
O2	0.62779 (17)	0.5805 (2)	0.92141 (10)	0.0295 (5)	
O3	0.59954 (16)	0.2945 (2)	0.83126 (9)	0.0235 (5)	
O4	0.5648 (2)	0.0581 (3)	0.83878 (9)	0.0385 (6)	
O5	1.01958 (15)	0.0059 (2)	0.60354 (8)	0.0200 (5)	
O6	0.85409 (16)	−0.0311 (2)	0.59619 (10)	0.0272 (5)	
O7	0.92964 (19)	0.2287 (3)	0.67434 (9)	0.0336 (6)	
O8	0.9010 (2)	0.4670 (2)	0.66411 (9)	0.0340 (6)	
O81	0.34490 (16)	0.7930 (2)	0.77188 (9)	0.0261 (5)	

H81A	0.3723	0.7869	0.7418	0.039*	
H81B	0.2843	0.7657	0.7627	0.039*	
O82	0.44968 (18)	0.5094 (3)	0.77371 (9)	0.0322 (6)	
H82A	0.4951	0.4471	0.7859	0.048*	
H82B	0.4481	0.5232	0.7381	0.048*	
O83	0.27314 (16)	0.5386 (3)	0.83000 (10)	0.0306 (5)	
H83A	0.2782	0.4493	0.8248	0.046*	
H83B	0.2304	0.5541	0.8522	0.046*	
O84	0.55289 (15)	0.7614 (2)	0.83995 (9)	0.0245 (5)	
H84A	0.584	0.7189	0.8694	0.037*	
H84B	0.5549	0.8532	0.8457	0.037*	
O85	1.14099 (16)	−0.2984 (2)	0.72871 (9)	0.0240 (5)	
H85A	1.1462	−0.3909	0.7256	0.036*	
H85B	1.1212	−0.2771	0.7596	0.036*	
O86	1.06101 (18)	−0.0035 (3)	0.72108 (9)	0.0336 (6)	
H86A	1.0698	−0.0114	0.7562	0.05*	
H86B	1.024	0.0648	0.707	0.05*	
O87	0.93868 (16)	−0.2432 (2)	0.66332 (9)	0.0265 (5)	
H87A	0.8983	−0.1937	0.6399	0.04*	
H87B	0.9264	−0.3336	0.6575	0.04*	
O88	1.22080 (16)	−0.0591 (2)	0.65935 (9)	0.0268 (5)	
H88A	1.2394	0.0176	0.6779	0.04*	
H88B	1.2743	−0.1056	0.6557	0.04*	
O91	0.7014 (2)	0.6817 (3)	0.77346 (12)	0.0492 (8)	
H91A	0.6887	0.7011	0.7381	0.074*	
H91B	0.6529	0.7054	0.7911	0.074*	
O92	0.8534 (2)	0.8892 (3)	0.76493 (11)	0.0534 (8)	
H92A	0.8201	0.8254	0.7812	0.08*	
H92B	0.894	0.8398	0.7485	0.08*	
O93	0.8302 (2)	0.8185 (3)	0.42952 (15)	0.0599 (9)	
H93A	0.7801	0.8784	0.4252	0.09*	
H93B	0.8778	0.8615	0.4162	0.09*	
O94	0.7031 (3)	0.7871 (3)	0.53038 (15)	0.0499 (14)	0.840 (8)
H94A	0.6928	0.8093	0.4958	0.075*	0.840 (8)
H94B	0.7502	0.8392	0.5476	0.075*	0.840 (8)
O94'	0.6714 (12)	0.8013 (18)	0.5717 (8)	0.038 (6)*	0.160 (8)
O95	0.6591 (3)	0.7469 (4)	0.65546 (15)	0.0719 (10)	
H95A	0.6035	0.8022	0.6458	0.108*	
C1	0.5651 (2)	0.4767 (3)	0.91659 (12)	0.0191 (7)	
C2	0.5928 (2)	0.3377 (3)	0.94980 (13)	0.0183 (6)	
C3	0.6041 (2)	0.3530 (3)	1.00843 (13)	0.0208 (7)	
H3	0.6019	0.445	1.0251	0.025*	
C4	0.6190 (2)	0.2267 (3)	1.04167 (12)	0.0197 (7)	
C5	0.6450 (2)	0.0662 (3)	1.10842 (13)	0.0239 (7)	
H5	0.6552	0.0227	1.1443	0.029*	
C6	0.6271 (2)	0.0893 (3)	1.01577 (13)	0.0189 (7)	
C7	0.6167 (2)	0.0728 (3)	0.95744 (13)	0.0214 (7)	
H7	0.6219	−0.019	0.9411	0.026*	
C8	0.5983 (2)	0.1984 (3)	0.92389 (12)	0.0184 (6)	

C9	0.5866 (2)	0.1816 (3)	0.85997 (13)	0.0213 (7)
C10	0.9289 (2)	0.0441 (3)	0.58849 (12)	0.0183 (7)
C11	0.9106 (2)	0.1849 (3)	0.55483 (12)	0.0177 (6)
C12	0.9058 (2)	0.1699 (3)	0.49677 (13)	0.0196 (7)
H12	0.9126	0.0781	0.4808	0.024*
C13	0.8906 (2)	0.2943 (3)	0.46267 (12)	0.0187 (6)
C14	0.8668 (2)	0.4547 (3)	0.39564 (13)	0.0237 (7)
H14	0.8591	0.4983	0.3599	0.028*
C15	0.8770 (2)	0.4308 (3)	0.48777 (13)	0.0185 (7)
C16	0.8824 (2)	0.4477 (3)	0.54609 (12)	0.0191 (7)
H16	0.8738	0.5393	0.5618	0.023*
C17	0.9008 (2)	0.3246 (3)	0.58027 (12)	0.0189 (7)
C18	0.9107 (2)	0.3408 (3)	0.64404 (13)	0.0210 (7)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0225 (2)	0.0194 (2)	0.0143 (2)	0.00200 (17)	0.00370 (17)	0.00148 (17)
Co2	0.0228 (2)	0.0182 (2)	0.0151 (2)	0.00204 (17)	0.00394 (17)	0.00131 (17)
N1	0.0294 (14)	0.0225 (14)	0.0147 (13)	0.0035 (12)	0.0033 (11)	0.0005 (11)
N2	0.0312 (15)	0.0180 (13)	0.0213 (14)	0.0038 (11)	0.0068 (12)	0.0026 (11)
N3	0.0293 (14)	0.0218 (14)	0.0146 (13)	0.0026 (11)	0.0053 (11)	0.0029 (11)
N4	0.0288 (14)	0.0173 (13)	0.0180 (14)	0.0029 (11)	0.0026 (11)	0.0020 (11)
O1	0.0218 (11)	0.0201 (11)	0.0182 (11)	0.0012 (9)	0.0018 (9)	0.0033 (9)
O2	0.0313 (13)	0.0216 (12)	0.0330 (13)	−0.0045 (10)	−0.0024 (10)	0.0076 (10)
O3	0.0314 (12)	0.0221 (12)	0.0180 (11)	−0.0017 (10)	0.0073 (9)	0.0001 (10)
O4	0.0743 (19)	0.0210 (13)	0.0193 (12)	−0.0099 (12)	0.0050 (12)	−0.0027 (10)
O5	0.0209 (11)	0.0211 (11)	0.0182 (11)	0.0030 (9)	0.0038 (9)	0.0043 (9)
O6	0.0232 (12)	0.0232 (12)	0.0347 (13)	−0.0012 (10)	0.0032 (10)	0.0095 (10)
O7	0.0611 (17)	0.0240 (13)	0.0177 (12)	0.0165 (12)	0.0123 (11)	0.0057 (10)
O8	0.0635 (17)	0.0201 (12)	0.0184 (12)	−0.0012 (12)	0.0068 (11)	−0.0024 (10)
O81	0.0270 (12)	0.0352 (13)	0.0162 (11)	0.0034 (10)	0.0035 (9)	0.0044 (10)
O82	0.0465 (15)	0.0324 (13)	0.0175 (12)	0.0148 (11)	0.0046 (10)	0.0012 (10)
O83	0.0257 (12)	0.0360 (14)	0.0313 (13)	−0.0021 (10)	0.0084 (10)	−0.0041 (11)
O84	0.0279 (12)	0.0194 (11)	0.0254 (12)	−0.0008 (9)	0.0016 (10)	0.0058 (9)
O85	0.0330 (12)	0.0231 (12)	0.0171 (11)	0.0056 (10)	0.0077 (10)	0.0023 (9)
O86	0.0490 (15)	0.0325 (13)	0.0183 (12)	0.0157 (12)	0.0021 (11)	−0.0024 (10)
O87	0.0286 (12)	0.0202 (12)	0.0302 (13)	−0.0010 (10)	0.0036 (10)	0.0063 (10)
O88	0.0227 (12)	0.0233 (12)	0.0345 (13)	0.0003 (9)	0.0052 (10)	−0.0006 (10)
O91	0.0509 (17)	0.0457 (17)	0.0576 (18)	0.0134 (14)	0.0278 (14)	0.0186 (14)
O92	0.070 (2)	0.0516 (18)	0.0443 (17)	−0.0194 (16)	0.0270 (15)	−0.0080 (14)
O93	0.0347 (15)	0.0281 (15)	0.120 (3)	0.0071 (12)	0.0217 (17)	0.0268 (16)
O94	0.067 (2)	0.0368 (19)	0.040 (2)	−0.0193 (17)	−0.0086 (18)	0.0133 (16)
O95	0.073 (2)	0.059 (2)	0.079 (2)	0.0141 (18)	−0.0002 (19)	−0.0172 (18)
C1	0.0250 (17)	0.0194 (16)	0.0139 (15)	0.0009 (13)	0.0065 (13)	0.0004 (12)
C2	0.0180 (15)	0.0166 (15)	0.0202 (16)	0.0007 (12)	0.0031 (13)	0.0031 (13)
C3	0.0260 (16)	0.0180 (16)	0.0185 (16)	0.0006 (13)	0.0038 (13)	−0.0011 (13)
C4	0.0225 (16)	0.0219 (16)	0.0147 (15)	0.0012 (13)	0.0030 (12)	0.0016 (13)

C5	0.0311 (18)	0.0237 (17)	0.0176 (16)	0.0044 (14)	0.0066 (14)	0.0051 (14)
C6	0.0221 (16)	0.0170 (16)	0.0178 (16)	0.0015 (12)	0.0039 (13)	0.0020 (13)
C7	0.0262 (17)	0.0184 (16)	0.0200 (16)	0.0001 (13)	0.0052 (13)	−0.0015 (13)
C8	0.0183 (15)	0.0204 (16)	0.0173 (15)	0.0000 (12)	0.0055 (12)	−0.0003 (13)
C9	0.0245 (16)	0.0210 (17)	0.0188 (16)	0.0004 (13)	0.0048 (13)	0.0012 (14)
C10	0.0264 (17)	0.0183 (16)	0.0110 (14)	0.0016 (13)	0.0052 (13)	−0.0022 (12)
C11	0.0155 (14)	0.0197 (16)	0.0184 (16)	0.0015 (12)	0.0042 (12)	0.0000 (13)
C12	0.0263 (16)	0.0158 (15)	0.0173 (15)	0.0023 (13)	0.0053 (13)	−0.0003 (12)
C13	0.0202 (15)	0.0200 (16)	0.0161 (15)	0.0016 (13)	0.0037 (12)	0.0011 (13)
C14	0.0323 (18)	0.0225 (17)	0.0163 (16)	0.0004 (14)	0.0042 (14)	0.0033 (14)
C15	0.0182 (15)	0.0186 (16)	0.0179 (16)	−0.0001 (12)	0.0010 (12)	0.0035 (13)
C16	0.0210 (15)	0.0168 (15)	0.0195 (16)	0.0009 (13)	0.0029 (13)	−0.0028 (13)
C17	0.0187 (15)	0.0215 (16)	0.0160 (15)	0.0006 (12)	0.0017 (12)	0.0003 (13)
C18	0.0220 (16)	0.0228 (18)	0.0191 (16)	−0.0011 (13)	0.0056 (13)	−0.0003 (14)

Geometric parameters (Å, °)

Co1—O1	2.075 (2)	O85—H85A	0.8492
Co1—O81	2.088 (2)	O85—H85B	0.8453
Co1—O83	2.089 (2)	O86—H86A	0.8289
Co1—O82	2.103 (2)	O86—H86B	0.8315
Co1—N1^{i}	2.114 (3)	O87—H87A	0.8418
Co1—O84	2.152 (2)	O87—H87B	0.8463
Co2—O88	2.059 (2)	O88—H88A	0.8427
Co2—O5	2.090 (2)	O88—H88B	0.8502
Co2—O87	2.104 (2)	O91—H91A	0.85
Co2—O86	2.118 (2)	O91—H91B	0.8579
Co2—N3^{ii}	2.133 (3)	O92—H92A	0.8623
Co2—O85	2.133 (2)	O92—H92B	0.8503
N1—C5	1.322 (4)	O93—H93A	0.859
N1—C4	1.391 (4)	O93—H93B	0.8553
N1—Co1^{i}	2.114 (3)	O94—O94'	1.142 (18)
N2—C5	1.332 (4)	O94—H94A	0.8377
N2—C6	1.383 (4)	O94—H94B	0.8405
N2—H2	0.86	O95—H95A	0.8987
N3—C14	1.328 (4)	C1—C2	1.507 (4)
N3—C13	1.395 (4)	C2—C3	1.386 (4)
N3—Co2^{ii}	2.133 (3)	C2—C8	1.419 (4)
N4—C14	1.336 (4)	C3—C4	1.392 (4)
N4—C15	1.383 (4)	C3—H3	0.93
N4—H4	0.86	C4—C6	1.408 (4)
O1—C1	1.261 (4)	C5—H5	0.93
O2—C1	1.258 (4)	C6—C7	1.381 (4)
O3—C9	1.262 (4)	C7—C8	1.394 (4)
O4—C9	1.248 (4)	C7—H7	0.93
O5—C10	1.259 (4)	C8—C9	1.512 (4)
O6—C10	1.254 (4)	C10—C11	1.511 (4)
O7—C18	1.252 (4)	C11—C12	1.380 (4)

O8—C18	1.260 (4)	C11—C17	1.425 (4)
O81—H81A	0.8597	C12—C13	1.390 (4)
O81—H81B	0.8436	C12—H12	0.93
O82—H82A	0.8483	C13—C15	1.405 (4)
O82—H82B	0.8541	C14—H14	0.93
O83—H83A	0.8276	C15—C16	1.387 (4)
O83—H83B	0.8533	C16—C17	1.384 (4)
O84—H84A	0.8491	C16—H16	0.93
O84—H84B	0.8475	C17—C18	1.510 (4)
O1—Co1—O81	170.17 (9)	Co2—O87—H87B	119.9
O1—Co1—O83	88.25 (9)	H87A—O87—H87B	109.1
O81—Co1—O83	89.55 (9)	Co2—O88—H88A	124.2
O1—Co1—O82	81.36 (8)	Co2—O88—H88B	123.1
O81—Co1—O82	89.00 (9)	H88A—O88—H88B	106.6
O83—Co1—O82	88.35 (9)	H91A—O91—H91B	113
O1—Co1—N1^{i}	98.29 (9)	H92A—O92—H92B	105.6
O81—Co1—N1^{i}	91.34 (9)	H93A—O93—H93B	106.4
O83—Co1—N1^{i}	91.46 (10)	H94A—O94—H94B	109.4
O82—Co1—N1^{i}	179.61 (10)	O2—C1—O1	124.5 (3)
O1—Co1—O84	91.72 (8)	O2—C1—C2	118.7 (3)
O81—Co1—O84	90.09 (8)	O1—C1—C2	116.5 (3)
O83—Co1—O84	177.69 (9)	C3—C2—C8	121.5 (3)
O82—Co1—O84	89.36 (9)	C3—C2—C1	114.9 (3)
N1^{i}—Co1—O84	90.83 (9)	C8—C2—C1	123.4 (3)
O88—Co2—O5	87.45 (8)	C2—C3—C4	118.1 (3)
O88—Co2—O87	173.57 (9)	C2—C3—H3	120.9
O5—Co2—O87	90.48 (8)	C4—C3—H3	120.9
O88—Co2—O86	85.63 (9)	N1—C4—C3	130.6 (3)
O5—Co2—O86	82.13 (8)	N1—C4—C6	109.4 (3)
O87—Co2—O86	88.05 (9)	C3—C4—C6	120.0 (3)
O88—Co2—N3^{ii}	90.76 (9)	N1—C5—N2	113.7 (3)
O5—Co2—N3^{ii}	98.09 (9)	N1—C5—H5	123.1
O87—Co2—N3^{ii}	95.57 (9)	N2—C5—H5	123.1
O86—Co2—N3^{ii}	176.37 (10)	C7—C6—N2	132.8 (3)
O88—Co2—O85	92.79 (8)	C7—C6—C4	122.4 (3)
O5—Co2—O85	167.66 (8)	N2—C6—C4	104.8 (3)
O87—Co2—O85	87.93 (8)	C6—C7—C8	117.8 (3)
O86—Co2—O85	85.59 (9)	C6—C7—H7	121.1
N3^{ii}—Co2—O85	94.25 (9)	C8—C7—H7	121.1
C5—N1—C4	104.5 (3)	C7—C8—C2	120.1 (3)
C5—N1—Co1^{i}	122.9 (2)	C7—C8—C9	118.3 (3)
C4—N1—Co1^{i}	130.5 (2)	C2—C8—C9	121.6 (3)
C5—N2—C6	107.6 (3)	O4—C9—O3	124.0 (3)
C5—N2—H2	126.2	O4—C9—C8	118.5 (3)
C6—N2—H2	126.2	O3—C9—C8	117.6 (3)
C14—N3—C13	104.2 (3)	O6—C10—O5	124.5 (3)

C14—N3—Co2^{ii}	125.6 (2)	O6—C10—C11	118.5 (3)
C13—N3—Co2^{ii}	129.7 (2)	O5—C10—C11	116.8 (3)
C14—N4—C15	107.1 (3)	C12—C11—C17	121.5 (3)
C14—N4—H4	126.5	C12—C11—C10	115.1 (3)
C15—N4—H4	126.5	C17—C11—C10	123.4 (3)
C1—O1—Co1	128.73 (19)	C11—C12—C13	118.9 (3)
C10—O5—Co2	130.89 (19)	C11—C12—H12	120.5
Co1—O81—H81A	112.8	C13—C12—H12	120.5
Co1—O81—H81B	106.1	C12—C13—N3	131.3 (3)
H81A—O81—H81B	106.9	C12—C13—C15	119.3 (3)
Co1—O82—H82A	114.7	N3—C13—C15	109.4 (3)
Co1—O82—H82B	130.3	N3—C14—N4	114.0 (3)
H82A—O82—H82B	109.7	N3—C14—H14	123
Co1—O83—H83A	113.5	N4—C14—H14	123
Co1—O83—H83B	123.3	N4—C15—C16	132.3 (3)
H83A—O83—H83B	109.6	N4—C15—C13	105.4 (3)
Co1—O84—H84A	97.6	C16—C15—C13	122.4 (3)
Co1—O84—H84B	118.2	C17—C16—C15	118.3 (3)
H84A—O84—H84B	108.6	C17—C16—H16	120.8
Co2—O85—H85A	122.9	C15—C16—H16	120.8
Co2—O85—H85B	114.9	C16—C17—C11	119.6 (3)
H85A—O85—H85B	110.2	C16—C17—C18	119.3 (3)
Co2—O86—H86A	129.6	C11—C17—C18	121.1 (3)
Co2—O86—H86B	111.4	O7—C18—O8	123.3 (3)
H86A—O86—H86B	116.6	O7—C18—C17	118.4 (3)
Co2—O87—H87A	105.7	O8—C18—C17	118.3 (3)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+2; (ii) −*x*+2, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O94^{iii}	0.86	1.96	2.779 (4)	159
N4—H4···O93	0.86	1.84	2.673 (4)	164
O81—H81A···O3^{iv}	0.86	1.84	2.683 (3)	166
O81—H81B···O85^{v}	0.84	2.05	2.883 (3)	172
O82—H82A···O3	0.85	2.14	2.974 (3)	169
O82—H82B···O4^{iv}	0.85	1.84	2.691 (3)	176
O83—H83A···O95^{vi}	0.83	2.05	2.812 (4)	153
O83—H83B···O6^{iv}	0.85	1.96	2.721 (3)	147
O84—H84A···O2	0.85	1.8	2.616 (3)	162
O84—H84B···O4^{vii}	0.85	1.88	2.708 (3)	165
O85—H85A···O92^{viii}	0.85	2.02	2.850 (4)	167
O85—H85B···O7^{ix}	0.85	1.82	2.649 (3)	168
O86—H86A···O8^{ix}	0.83	1.88	2.711 (3)	176
O86—H86B···O7	0.83	2.03	2.859 (3)	178
O87—H87A···O6	0.84	1.85	2.642 (3)	156

O87—H87B···O8^{x}	0.85	1.86	2.689 (3)	166
O88—H88A···O91^{ix}	0.84	1.98	2.813 (3)	173
O88—H88B···O3^{ix}	0.85	1.9	2.732 (3)	165
O91—H91A···O95	0.85	1.99	2.836 (4)	180
O91—H91B···O84	0.86	1.98	2.837 (3)	174
O92—H92A···O91	0.86	2.05	2.813 (4)	148
O92—H92B···O87^{vii}	0.85	2.34	3.089 (4)	148
O93—H93A···O2^{xi}	0.86	2.07	2.844 (3)	151
O93—H93A···O88^{xii}	0.86	2.6	3.045 (4)	114
O93—H93B···O5^{xii}	0.86	1.95	2.788 (3)	168
O94—H94A···O2^{xi}	0.84	2.1	2.889 (4)	158
O94—H94A···O93	0.84	2.62	3.180 (5)	126
O94—H94B···O6^{vii}	0.84	2.04	2.873 (4)	174
O95—H95A···O1^{iv}	0.9	2.07	2.910 (4)	155

Symmetry codes: (iii) x, $-y+1/2$, $z+1/2$; (iv) $-x+1$, $y+1/2$, $-z+3/2$; (v) $x-1$, $y+1$, z; (vi) $-x+1$, $y-1/2$, $-z+3/2$; (vii) x, $y+1$, z; (viii) $-x+2$, $y-3/2$, $-z+3/2$; (ix) $-x+2$, $y-1/2$, $-z+3/2$; (x) x, $y-1$, z; (xi) x, $-y+3/2$, $z-1/2$; (xii) $-x+2$, $-y+1$, $-z+1$.

Fig. 1

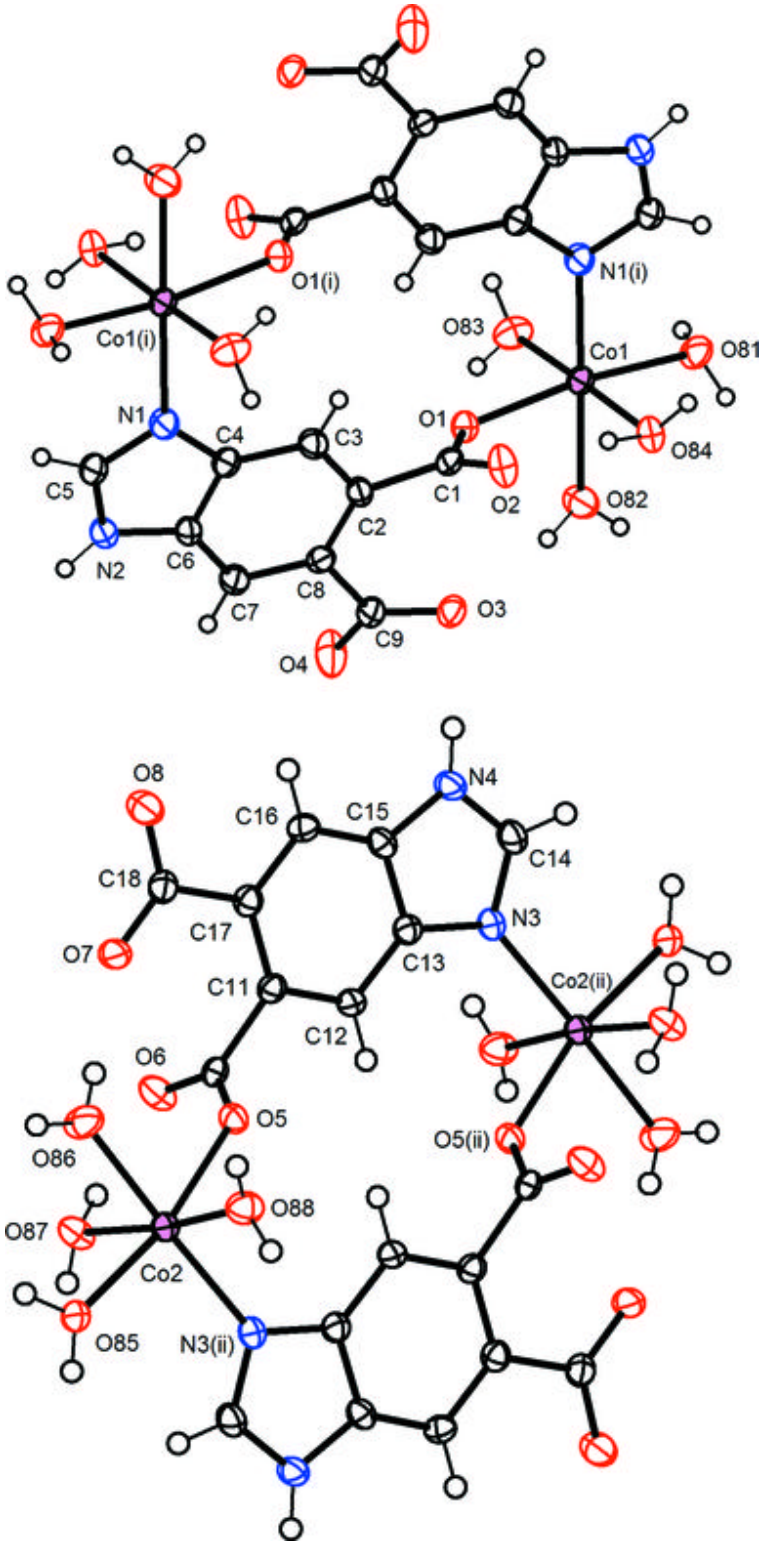
O1(i)
N1(i)
Co1(i)
O83
Co1
O81
N1
C4
C3
O1
O84
C5
C1
O2
O82
C2
N2
C6
C8
O3
C7
C9
O4
O8
N4
C16
C15
C14
C18
C17
N3
O7
C13
C11
Co2(ii)
C12
O6
O5
O86
O5(ii)
O88
O87
Co2
O85
N3(ii)

Fig. 2