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Two two-dimensional hydrogen-bonded coordination networks: bis(3-carboxybenzoato-*κO*)bis(4-methyl-1*H*-imidazole-*κN*^{3})copper(II) and bis(3-methylbenzoato-*κN*)bis(4-methyl-1*H*-imidazole-*κN*^{3})copper(II) monohydrate

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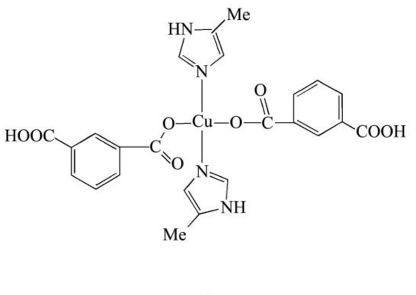
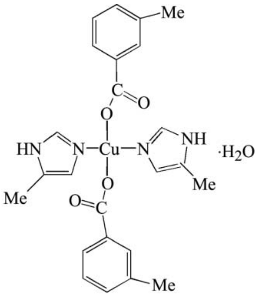
The title two-dimensional hydrogen-bonded coordination compounds, $[Cu(C_8H_5O_4)_2(C_4H_6N_2)_2]$, (I), and $[Cu(C_8H_7O_2)_2(C_4H_6N_2)_2]\cdot H_2O$, (II), have been synthesized and structurally characterized. The molecule of complex (I) lies across an inversion centre, and the Cu^{2+} ion is coordinated by two N atoms from two 4-methyl-1*H*-imidazole (4-MeIM) molecules and two O atoms from two 3-carboxybenzoate ($HBDC^-$) anions in a square-planar geometry. Adjacent molecules are linked through intermolecular N—H⋯O and O—H⋯O hydrogen bonds into a two-dimensional sheet with (4,4) topology. In the asymmetric part of the unit cell of (II) there are two symmetry-independent molecules, in which each Cu^{2+} ion is also coordinated by two N atoms from two 4-MeIM molecules and two O atoms from two 3-methylbenzoate ($3\text{-}MeBC^-$) anions in a square-planar coordination. Two neutral complex molecules are held together *via* N—H⋯O(carboxylate) hydrogen bonds to generate a dimeric pair, which is further linked *via* discrete water molecules into a two-dimensional network with the Schläfli symbol $(4^3)_2(4^6,6^6,8^3)$. In both compounds, as well as the strong intermolecular hydrogen bonds, π–π interactions also stabilize the crystal stacking.

Comment

Hydrogen bonds having good directionality and flexibility and suitable strength are very important and have been widely studied in physics, chemistry and biology (Beatty, 2003). Moreover, most reported work on crystal engineering has concentrated on organic supramolecular compounds (Rambaran *et al.*, 2009; Koshima *et al.*, 2005; Childs & Hardcastle, 2007; Aakeröy *et al.*, 2007). Crystal engineering with coordination bonds is a very popular research area because of the stable coordination bonds and versatile coordination modes of metal ions, especially transition metals. However, transition metal coordination compounds assembled by hydrogen-bonding interactions have been less well studied (Liu *et al.*, 2007; Beatty, 2001; Larsson & Öhrström, 2003; Aakeröy *et al.*, 1998, 2004). Therefore, our focus is on arranging transition metal cationic centres through hydrogen bonds, attempting to construct structures with interesting dimensions and topologies. We present here the two title two-dimensional hydrogen-bonded coordination networks, *viz.* (I) and (II).



(I)



(II)

The molecular structure of (I) is shown in Fig. 1. The Cu^{2+} ion is coordinated by two 4-methyl-1*H*-imidazole (4-MeIM) molecules and two 3-carboxybenzoate ($HBDC^-$) anions and is located on an inversion centre, giving an approximate square-planar arrangement [Cu1—O1 = 1.9442 (13) Å, Cu1—N1 = 1.9763 (18) Å and N1—Cu1—O1 = 89.95 (7)°]. Each 4-MeIM molecule and $HBDC^-$ anion binds to the metal centre through one N atom and one O atom, respectively. Obviously, the $HBDC^-$ anion coordinates as a monodentate ligand to the Cu^{2+} ion. The other carboxyl group does not lose its H atom, so each $[Cu(4\text{-}MeIM)_2(HBDC)_2]$ molecular unit simultaneously possesses two N—H donors and two O—H donors.

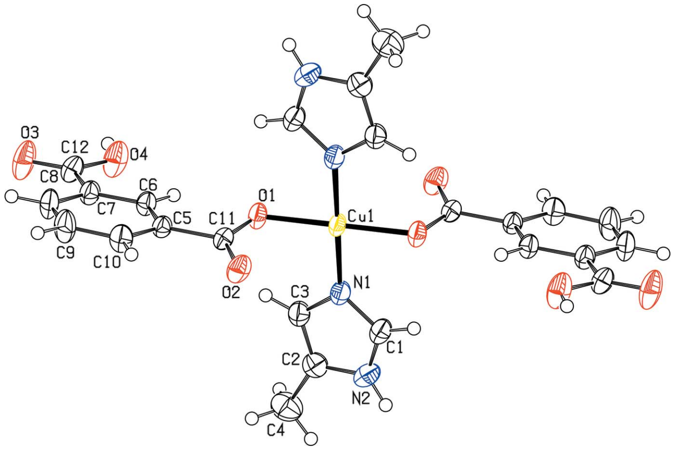


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Unlabelled atoms are related to labelled atoms by the symmetry transformation ($-x + 1$, $-y + 2$, $-z + 1$).

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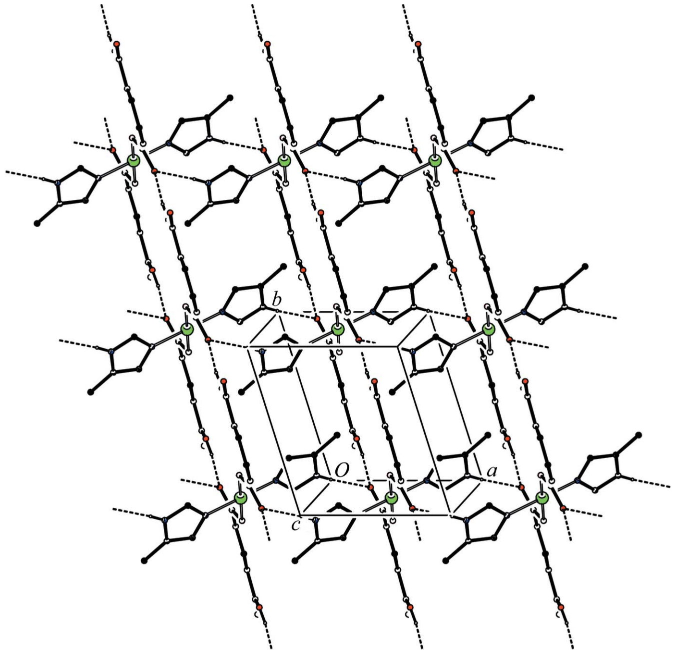

Figure 2
Part of the crystal structure of (I), showing the formation of the two-dimensional structure in the (001) plane. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity.

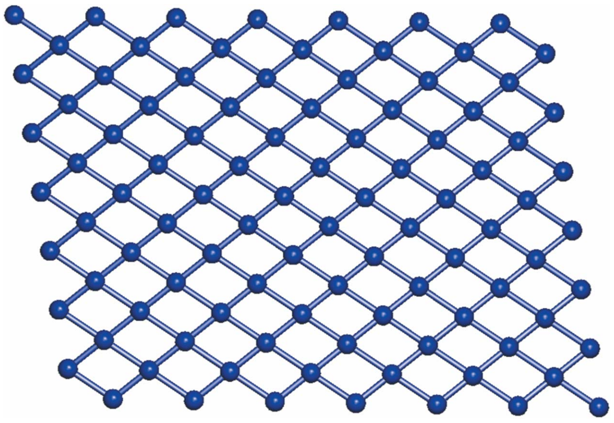

Figure 3
The (4,4) net of (I).

Adjacent structure units in (I) are firstly linked by two pairs of $\mathrm{N2{-}H2}A\cdots\mathrm{O2}^{\mathrm{i}}$ hydrogen bonds [symmetry code: (i) $-x$, $-y+2$, $-z+1$] into a chain along the [100] direction. Similarly, adjacent structure units are held together through two sets of $\mathrm{O4{-}H4}\cdots\mathrm{O2}$ hydrogen bonds, forming a one-dimensional chain substructure along the [010] direction. This combination of [100] and [010] chains results in a two-dimensional sheet parallel to the (001) plane (Fig. 2 and Table 1), and thus each $[\mathrm{Cu(4\text{-}MeIM)_2(HBDC)_2}]$ unit interacts with four neighbouring units through hydrogen-bonding contacts. Therefore, each $[\mathrm{Cu(4\text{-}MeIM)_2(HBDC)_2}]$ unit can be considered as a four-connected node, generating a (4,4) net (Öhrström & Larsson, 2005) with dimensions of 7.319 × 8.585 Å (Fig. 3). The connectivity for each node is four, corresponding to four four-membered circuits. Connections between adjacent units are further reinforced by π–π interactions, with $Cg3\cdots Cg3^{\mathrm{i}}$ = 3.4192 (14) Å and $Cg4\cdots Cg4^{\mathrm{ii}}$ = 3.7526 (15) Å (Table 4). These two rings are strictly parallel.

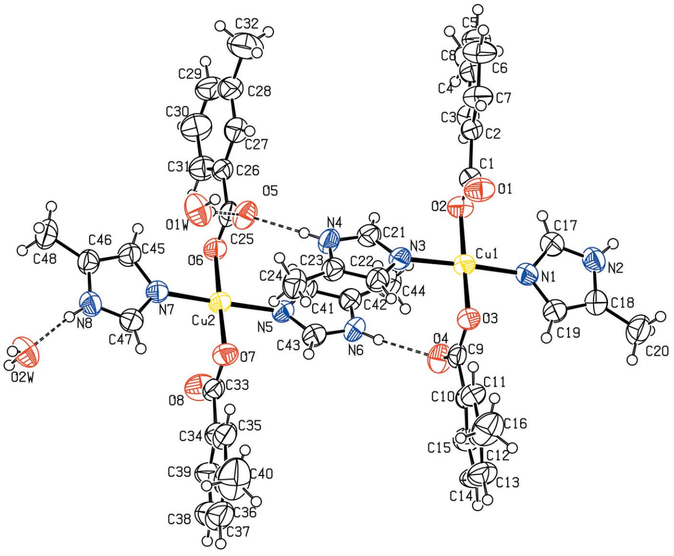

Figure 4
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.

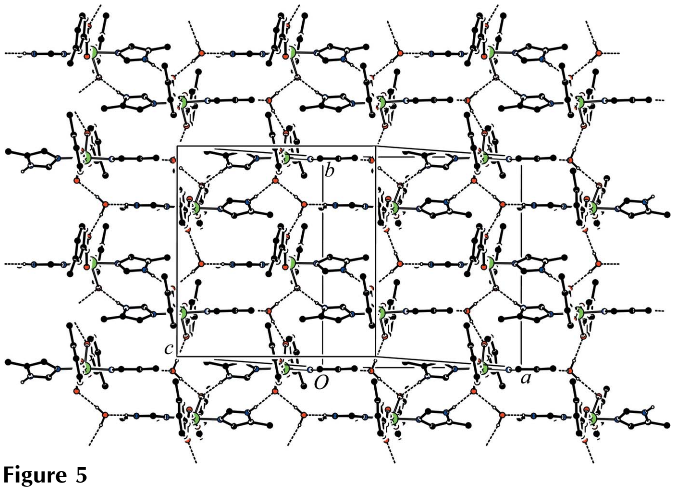

Figure 5
Part of the crystal structure of (II), showing the formation of the two-dimensional structure parallel to the (001) plane. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity.

When $\mathrm{H_2BDC}$ in (I) is replaced with 3-methylbenzoate (3-HMeBC), compound (II) is produced, wherein an analogous two-dimensional hydrogen-bonded structure in the (001) plane is formed. Compound (II) crystallizes in the monoclinic $P2_1/c$ space group with two symmetry-independent molecules in the asymmetric unit, which is thus composed of two $\mathrm{Cu^{2+}}$ ions, four 4-MeIM molecules, four $\mathrm{3\text{-}MeBC^{-}}$ anions and two solvent water molecules. Each $\mathrm{Cu^{2+}}$ centre is coordinated by two N atoms and two O atoms in a square-planar arrangement with an similar coordination environment to that in (I) (Table 2).

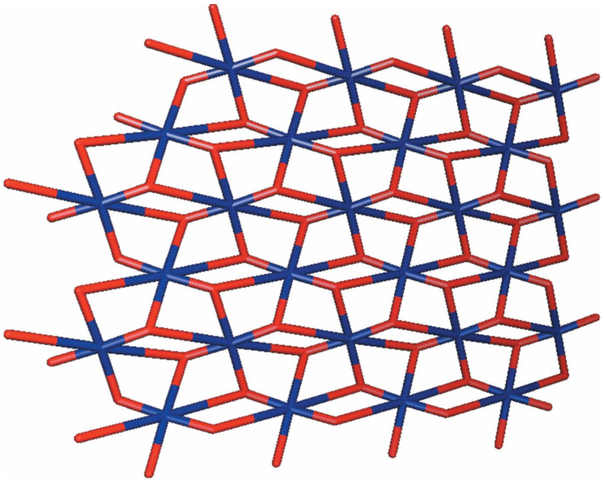

Figure 6
The $(4^3)_2(4^6,6^6,8^3)$ net of (II).

In the structure of (II), two neutral [Cu(4-MeIM)$_2$(3-MeBC)$_2$] molecules are held together *via* N4—H4$\cdots$O5 and N6—H6*A*$\cdots$O4 hydrogen bonds, leading to a dimeric pair, which links two discrete water molecules (O1*W* and O2*W*) through O1*W*—H1*WA*$\cdots$O5 and N8—H8$\cdots$O2*W* hydrogen bonds to form the asymmetric unit (Fig. 4 and Table 3). In fact, each [Cu(4-MeIM)$_2$(3-MeBC)$_2$]$_2$ dimeric pair interacts with six surrounding water molecules, while each water molecule bridges three dimeric units to form a two-dimensional (001) sheet (Fig. 5 and Table 3). In addition, there are complex strong π–π interactions to stabilize the crystal stacking [$Cg1\cdots Cg8^{\rm iii}$ = 3.8847 (18) Å, $Cg2\cdots Cg7$ = 3.5422 (18) Å, $Cg4\cdots Cg4^{\rm iv}$ = 3.733 (2) Å and $Cg9\cdots Cg10^{\rm v}$ = 3.783 (2) Å; Table 4]. If the dimeric pairs and water molecules are considered as six- and three-connected nodes, respectively, compound (II) can be simplified as a two-dimensional $(4^3)_2(4^6,6^6,8^3)$ net (Öhrström & Larsson, 2005) (Fig. 6) and the connectivities are 3 and 6. Every three-connected node binds to three six-connected nodes, each of which connects to six other three-connected nodes, giving the stoichiometry ratio 2:1 of three- to six-connected nodes.

We conclude that 4-MeIM coordinates to the Cu^{2+} ion as a monodentate ligand because the steric hindrance of the methyl group leads the N—H donor to interact with other hydrogen-bond acceptors *via* hydrogen bonds, while H$_2$BDC and 3-MeBC carboxylate ligands not only have strong coordination abilities but also are good hydrogen-bond acceptors. The successful combination of their metal-coordinating ability and hydrogen-bonding function results in two two-dimensional frameworks. Thus, a rational change of the substituent group in the organic ligand can construct similar hydrogen-bonded networks with different topologies.

Experimental

CuCl$_2$·2H$_2$O (0.17 g, 1.0 mmol) was added slowly to an aqueous solution (15 ml) of H$_2$BDC (0.16 g, 1.0 mmol) and NaOH (0.04 g, 1.0 mmol) and the mixture was refluxed for 30 min. An ethanol solution (10 ml) containing 4-MeIM (0.08 g, 1.0 mmol) was then added slowly with continuous stirring. The resulting solution was refluxed for 3 h, filtered and left to stand for crystallization. After 10 d, blue crystals of (I) suitable for single-crystal X-ray diffraction were obtained. Compound (II) was synthesized in a similar manner to compound (I), but H$_2$BDC was replaced with 3-MeBC (0.14 g, 1.0 mmol). After 4 d, blue crystals of (II) were obtained.

Compound (I)

Crystal data

[Cu(C$_8$H$_5$O$_4$)$_2$(C$_4$H$_6$N$_2$)$_2$]
M_r = 558.01
Triclinic, $P\overline{1}$
a = 7.3188 (6) Å
b = 8.5847 (7) Å
c = 10.1033 (8) Å
α = 96.487 (1)°
β = 98.756 (2)°
γ = 107.620 (1)°
V = 589.37 (8) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.99 mm^{-1}
T = 292 K
0.23 × 0.20 × 0.15 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\rm min}$ = 0.805, $T_{\rm max}$ = 0.866
3304 measured reflections
2290 independent reflections
2155 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.011

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.069
S = 1.00
2290 reflections
178 parameters
14 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max}$ = 0.33 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.26 e Å^{-3}

Compound (II)

Crystal data

[Cu(C$_8$H$_7$O$_2$)$_2$(C$_4$H$_6$N$_2$)$_2$]·H$_2$O
M_r = 516.04
Monoclinic, $P2_1/c$
a = 14.3860 (2) Å
b = 15.2620 (4) Å
c = 24.6922 (5) Å
β = 113.288 (2)°
V = 4979.71 (18) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.92 mm^{-1}
T = 292 K
0.28 × 0.25 × 0.20 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\rm min}$ = 0.783, $T_{\rm max}$ = 0.838
27494 measured reflections
9780 independent reflections
5859 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.048

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.108
S = 0.98
9780 reflections
653 parameters
38 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max}$ = 0.50 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.28 e Å^{-3}

For both compounds, H atoms bonded to N atoms, carboxyl O atoms and water O atoms were located in difference maps and refined isotropically, with distances restrained to N—H = 0.86 (3) Å, O—H = 0.82 (3) Å and H$\cdots$H = 1.34 (3) Å. All remaining H atoms were positioned geometrically, with C—H = 0.93 (aromatic) or 0.96 Å (methyl), and refined as riding, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C aromatic) or 1.5$U_{\rm eq}$(C methyl).

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O2^{i}	0.81 (2)	2.16 (2)	2.965 (3)	170 (2)
O4—H4···O2^{ii}	0.82 (2)	1.86 (2)	2.632 (2)	156 (3)

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

Table 2
Selected geometric parameters (Å, °) for (II).

Cu1—N1	1.985 (2)	Cu2—N7	1.984 (2)
Cu1—N3	1.982 (2)	Cu1—O2	2.011 (2)
Cu1—O3	1.9534 (19)	Cu2—O6	1.9654 (19)
Cu2—N5	1.990 (2)	Cu2—O7	1.9759 (19)
O3—Cu1—N1	89.73 (9)	O6—Cu2—O7	177.84 (9)
O3—Cu1—N3	90.14 (9)	O6—Cu2—N5	90.08 (9)
O2—Cu1—O3	177.26 (9)	O6—Cu2—N7	89.07 (9)
N1—Cu1—N3	175.37 (10)	O7—Cu2—N5	89.87 (9)
N1—Cu1—O2	90.56 (9)	O7—Cu2—N7	90.91 (9)
N3—Cu1—O2	89.80 (9)	N5—Cu2—N7	178.27 (10)

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009) and *TOPOS* (Blatov *et al.*, 2000); software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KU3016). Services for accessing these data are described at the back of the journal.

Table 3
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···O5	0.81 (3)	2.04 (3)	2.824 (3)	163 (3)
O1*W*—H1*WB*···O8^{i}	0.81 (3)	1.876 (11)	2.690 (3)	176 (3)
N2—H2···O1*W*^{ii}	0.84 (3)	1.88 (3)	2.719 (4)	177 (3)
N4—H4···O5	0.846 (10)	1.989 (11)	2.832 (3)	174 (3)
N6—H6*A*···O4	0.842 (10)	2.106 (11)	2.946 (3)	175 (3)
N8—H8···O2*W*	0.85 (3)	1.86 (3)	2.701 (4)	171 (4)
O2*W*—H2*WA*···O4^{iii}	0.81 (3)	2.028 (16)	2.792 (3)	156 (3)
O2*W*—H2*WB*···O1^{iv}	0.815 (10)	1.887 (12)	2.693 (3)	170 (3)

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

Table 4
Geometry of π–π stacking interactions (Å, °) for compounds (I) and (II).

In (I), *Cg*3 and *Cg*4 are the centroids of the N1/C1/N2/C2–C3 and C5–C10 rings, respectively. In (II), *Cg*1, *Cg*2, *Cg*4, *Cg*7, *Cg*8, *Cg*9 and *Cg*10 are the centroids of rings N1/C17/N2/C18/C19, N3/C21/N4/C22/C23, C10–C15, N5/C41/C42/N6/C43, N7/C45/C46/N8/C47, C26–C30 and C34–C39, respectively. *CgI*···*CgJ* is the distance between ring centroids *I* and *J*, α is the dihedral angle between planes *I* and *J*, β is the angle between *CgI*→*CgJ* and the normal to plane *I*, γ is the angle between *CgI*→*CgJ* and the normal to plane *J*, $CgI_{\rm perp}$ is the perpendicular distance of *CgI* from ring *J* and $CgJ_{\rm perp}$ is the perpendicular distance of *CgJ* from ring *I*.

CgI···*CgJ*	*CgI*···*CgJ*	α	β	γ	$CgI_{\rm perp}$	$CgJ_{\rm perp}$
(I)						
*Cg*3···*Cg*3^{i}	3.4192 (14)	0.00	18.98	18.98	3.233	3.233
*Cg*4···*Cg*4^{ii}	3.7526 (15)	0.00	19.58	19.58	3.536	3.536
(II)						
*Cg*1···*Cg*8^{iii}	3.8847 (18)	2.28	29.80	31.95	3.296	3.371
*Cg*2···*Cg*7	3.5422 (18)	2.15	24.27	22.27	3.278	3.229
*Cg*4···*Cg*4^{iv}	3.733 (2)	0.00	14.46	14.46	3.615	3.615
*Cg*9···*Cg*10^{v}	3.783 (2)	5.05	14.72	14.53	3.662	3.659

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

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