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Bis(5-aminotetrazole-1-acetato-κO)-tetraaquacobalt(II) and *catena*-poly[[cadmium(II)]-bis(μ-5-amino-tetrazole-1-acetato-κ^3N^4:O,O′)]

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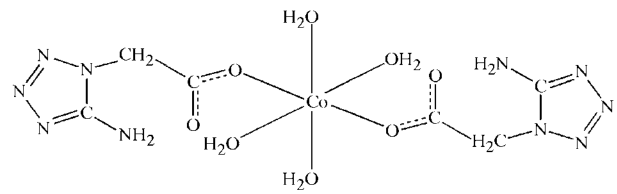
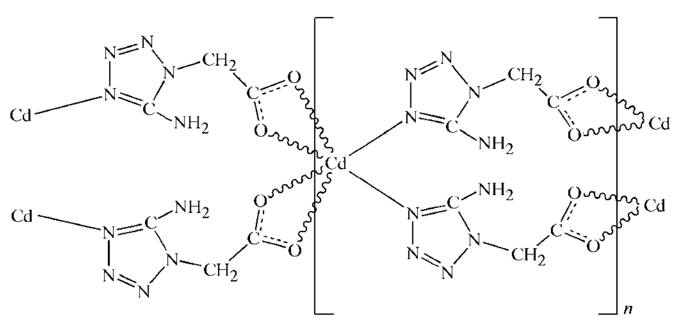
The Co^{II} atom in bis(5-aminotetrazole-1-acetato)tetraaqua-cobalt(II), $[Co(C_3H_4N_5O_2)_2(H_2O)_4]$, (I), is octahedrally coordinated by six O atoms from two 5-aminotetrazole-1-acetate (atza) ligands and four water molecules. The molecule has a crystallographic centre of symmetry located at the Co^{II} atom. The molecules of (I) are interlinked by hydrogen-bond interactions, forming a two-dimensional supramolecular network structure in the *ac* plane. The Cd^{II} atom in *catena*-poly[[cadmium(II)]-bis(μ-5-aminotetrazole-1-acetato], $[Cd(C_3H_4N_5O_2)_2]_n$, (II), lies on a twofold axis and is coordinated by two N atoms and four O atoms from four atza ligands to form a distorted octahedral coordination environment. The Cd^{II} centres are connected through tridentate atza bridging ligands to form a two-dimensional layered structure extending along the *ab* plane, which is further linked into a three-dimensional structure through hydrogen-bond interactions.

Comment

Coordination compounds containing a tetrazole group have been the subject of an intense research effort in recent years, owing to their unique structures and their potential applications in advanced materials (Ye *et al.*, 2006; Xiong *et al.*, 2002; Stagni *et al.*, 2006; Mautner *et al.*, 2004; Jiang *et al.*, 2004). Among numerous organic ligands containing a tetrazole group, 5-substituted tetrazolates [*e.g.* 5-methyl-, 5-ethyl-, 5-(2-pyridyl)-, 5-(3-pyridyl)- and 5-(4-pyridyl)tetrazolate] and 1-substituted tetrazoles [*e.g.* 1-acetato-, 1-phenyl-, 1-(2-chloroethyl)-, 1-methyl- and 1-ethyltetrazole] have already been studied, and a number of complexes containing these ligands have been reported (He *et al.*, 2005; Wu *et al.*, 2005, 2006; Xue *et al.*, 2002; Qu *et al.*, 2003; Zhao *et al.*, 2004; Wang *et al.*, 2005; Palazzi *et al.*, 2002). However, adducts of another class of 1,5-disubstituted tetrazoles have only been the subject of limited study with metal ions, and few coordination complexes with 1,5-disubstituted tetrazole ligands have been reported to date (Zhilin *et al.*, 2002; Gaponik *et al.*, 2005). Inspired by the pioneering work of Demko & Sharpless (2001, 2002), we have recently studied [2+3]-cycloaddition reactions of dicyandiamide with NaN_3 and $ZnCl_2$ as Lewis acids in aqueous solution to give 5-aminotetrazole (Hatz), and 5-aminotetrazole-1-acetic acid (Hatza) was obtained by the reaction of Hatz with chloroacetic acid in methanolic potassium hydroxide solution. Of interest to us is the coordination ability of the Hatza or atza ligands through the N and O electron-donating atoms, which allows it to serve as either a multidentate or a bridging ligand in supramolecular assemblies. To our knowledge, there is no synthetic and structural information on any complex of the Hatza or atza ligands. In this context, we carried out the reactions of Hatza with $CoCl_2\cdot6H_2O$ and $CdCl_2\cdot6H_2O$, and isolated two new coordination complexes, $[Co(atza)_2(H_2O)_4]$, (I), $[Cd(atza)_2]_n$, (II), respectively, and we report their crystal structures here.



(I)



(II)

The asymmetric unit of (I) contains half of the $[Co(atza)_2(H_2O)_4]$ molecule. As shown in Fig. 1, atom Co1 lies on an inversion centre and is coordinated by four O atoms [O1, O1^i, O3 and O3^i; symmetry code: (i) $-x, -y + 1, -z + 2$] from two atza ligands and two aqua ligands, located in the equatorial plane, and two O atoms (O4 and O4^i) from two aqua ligands in the apical sites, thereby forming a slightly distorted CoO_6 octahedral coordination geometry. The Co—O(carboxylate) distance [2.0768 (13) Å] is close to the values observed in $[CoL_2(H_2O)_4]$ [2.0653 (12) Å for L = 4-hydroxypyridine-2,6-dicarboxylate (Cui *et al.*, 2006) and 2.0663 (14) Å for L = 2-(methylthio)nicotinate (Miklos *et al.*, 2006)]. The Co—O(H_2O) distances [2.0828 (15) and 2.1451 (14) Å] are in the range observed in $[CoL_2(H_2O)_4]$ [2.0764 (13)–2.1266 (13) Å for L is 4-hydroxypyridine-2,6-dicarboxylate (Cui *et al.*, 2006) and 2.086 (16)–2.1846 (15) Å for L = 2-(methylthio)nicotinate (Miklos *et al.*, 2006)]. The *cisoid* angles of $[CoO_6]$ are in the range 87.52 (5)–92.18 (5)°, close to 90°. The atza anion in (I) acts only as a monodentate ligand *via* its one carboxylate O atom.

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In complex (I), six intermolecular hydrogen-bond interactions exist, *viz*. between water molecules and carboxylate O atoms [O4—H4*A*···O2^{i} and O3—H3*B*···O2^{iii}; symmetry code: (iii) $x - 1$, y, z], between water molecules and tetrazole N atoms [O3—H3*A*···N4^{ii} and O4—H4*B*···N2^{iv}; symmetry codes: (ii) $-x + 1$, $-y + 1$, $-z + 1$; (iv) $-x + 1$, $-y$, $-z + 2$], between an amino group and a tetrazole N atom (N5—H5*A*···N3^{iii}), and between an amino group and a carboxylate O atom (N5—H5*B*···O2^{ii}). Thus, the molecules of complex (I) are interlinked by these intermolecular hydrogen bonds, forming a two-dimensional supramolecular network structure in the *ac* plane (Fig. 2).

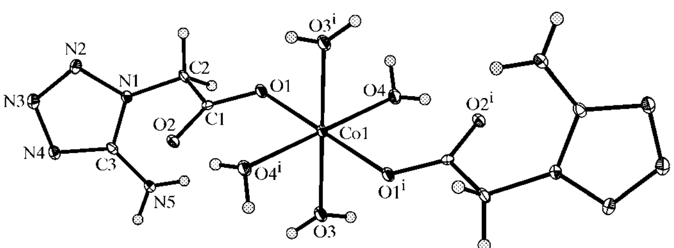

Figure 1
A view of the molecule of complex (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $-x$, $-y + 1$, $-z + 2$.]

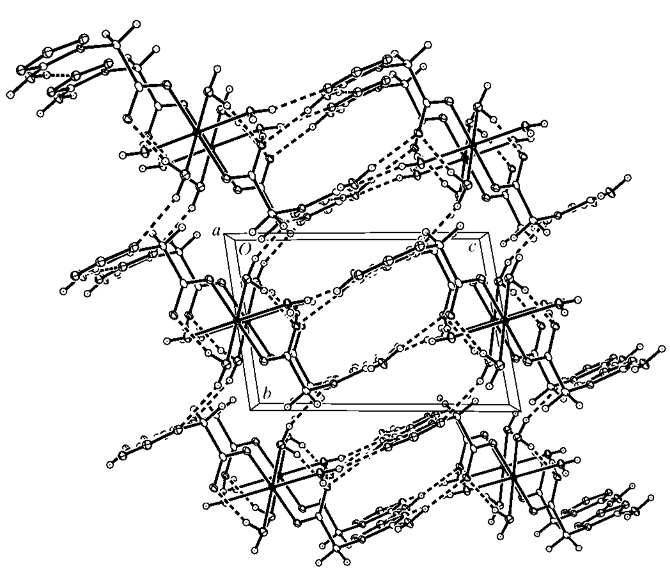

Figure 2
A cell packing diagram for (I).

The asymmetric unit of (II) contains one-half of a Cd^{II} atom and one atza ligand. As shown in Fig. 3, atom Cd1 resides on a twofold axis and is coordinated by two N atoms [N4^{i} and N4^{ii}; symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x + \frac{1}{2}, y - \frac{1}{2}, z$] and four O atoms [O1, O1^{iii}, O2 and O2^{iii}; symmetry code: (iii) $-x + 1$, y, $-z + \frac{1}{2}$] from four atza ligands. Two carboxylate groups chelate atom Cd1, with an O1—Cd1—O2 angle of 53.51 (5)°, leading to a severely distorted octahedral coordination geometry. The Cd—N(tetrazole) bond distance [2.2300 (16) Å] is shorter than those observed in [$Cd_3Cl_2L_2$-$(OH)_2$] [2.362 (12) Å; *L* is 5-(4-pyridyl)tetrazolate; Xue *et al.*, 2002], [Cd*L*(H_2O)]$_n$ [2.3245 (18)–2.372 (2) Å; *L* is 4-(tetrazolyl)benzenecarboxylate; Wang *et al.*, 2005] and [CdL_4-$(H_2O)_2$](dipicrate)·$2H_2O$ [2.334 (3) and 2.325 (2) Å; *L* is 5-amino-1,2,3,4-tetrazolyl; Zhang *et al.*, 2001]. The Cd—O(carboxylate) bond lengths [2.2692 (15) and 2.6037 (14) Å] are in the range observed in [Cd*L*(H_2O)]$_n$ [2.219 (2) and 2.478 (2) Å; *L* is 4-(tetrazolyl)benzenecarboxylate; Wang *et al.*, 2005], {[CdL_2(H_2O)]·0.5(3pa)}$_n$ [2.336 (8)–2.574 (7) Å; *L* is isonicotinate and 3pa is 1,4-di-3-pyridyl-2,3-diaza-1,3-buta-

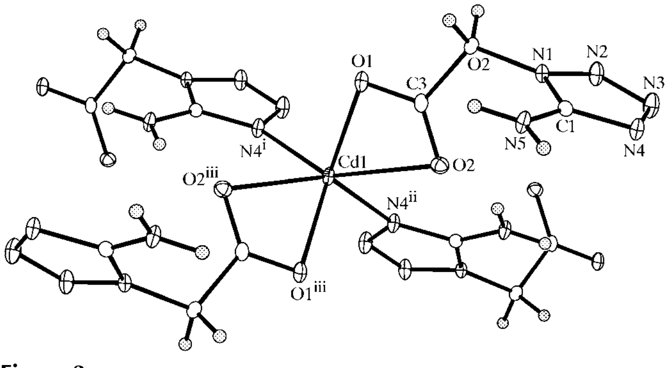

Figure 3
The coordination environment of the Cd^{II} atom of complex (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x + \frac{1}{2}, y - \frac{1}{2}, z$; (iii) $-x + 1, y, -z + \frac{1}{2}$.]

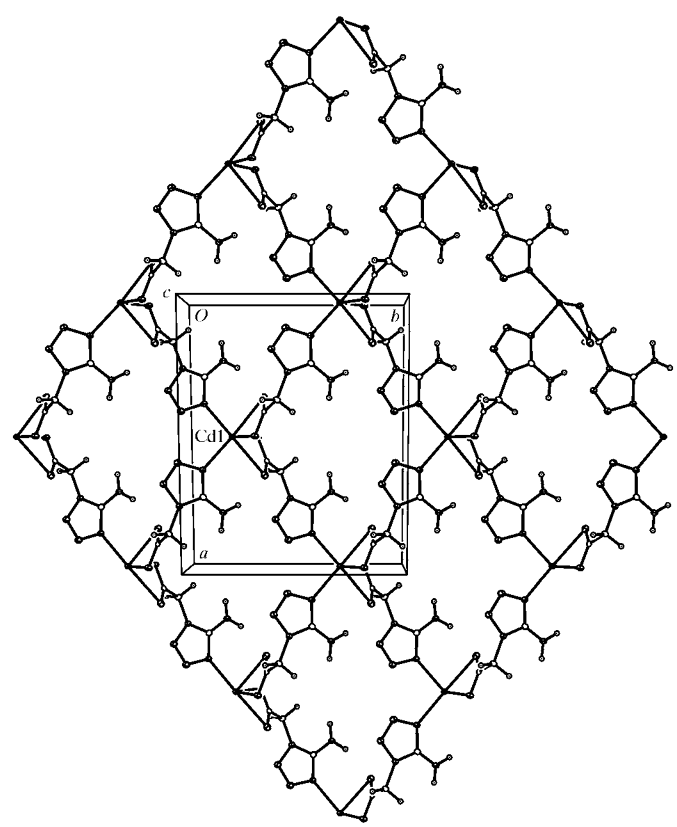

Figure 4
A view of the two-dimensional network of (II).

diene; Granifo & Baggio, 2007] and $[CdL_2(H_2O)_2]_n$ [2.255 (4)–2.724 (5) Å; L is nicotinate; Zhang *et al.*, 2004].

Each atza ligand in (II) acts as a tridentate ligand, chelating one Cd^{II} atom through its carboxylate O atoms while simultaneously binding to a second Cd^{II} atom through a tetrazole N atom, forming a two-dimensional neutral (4,4)-network extending along the *ab* plane (Fig. 4). The network contains a rhombus grid (28-membered rings) with a Cd^{II} atom at each corner and an atza ligand at each edge connecting two Cd^{II} atoms. The edge lengths are equal, with a value of 8.5977 (18) Å. The diagonal lengths of the rhombus grid are 10.625 (13) and 13.520 (4) Å, and the angles of the rhombus are 76.326 (2) and 103.67 (2)°. The rhombus grid sheets are stacked together in an offset fashion along the *c* direction, in an ...*A*–*B*–*A*–*B*... sequence (Fig. 5).

Within the two-dimensional layer, one hydrogen-bond interaction is formed between an amino group and a carboxylate O atom [N5—H5*B*···O2^{v}; symmetry code: (v) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$]. Adjacent two-dimensional layers are further connected by two hydrogen-bonding interactions between an amino group, a methylene group and a carboxylate O atom [N5—H5*A*···O1^{iv} and C2—H2*B*···O1^{iv}; symmetry code: (iv) $-x + 1, -y + 1, -z + 1$], forming a three-dimensional supramolecular structure (Fig. 5).

In conclusion, under the same experimental conditions, the reaction of atza with Co^{II} and Cd^{II} ions gives two compounds with distinctly different structures. In compound (I), atza acts as a monodentate ligand to coordinate the Co^{II} ion, while in (II), atza acts as a tridentate bridging ligand to coordinate the Cd^{II} ion. Further work is to be undertaken, reacting atza with other metal ions to study its coordination modes.

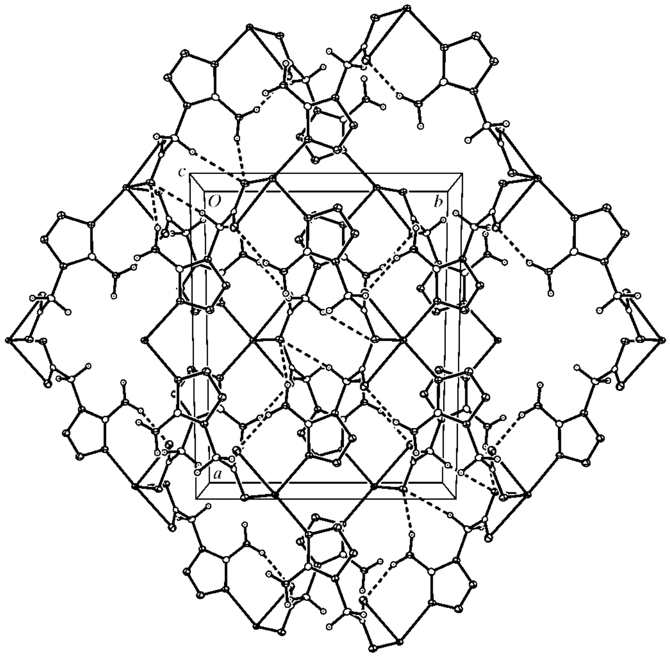

Figure 5
The three-dimensional network of (II) formed by hydrogen-bonding interactions (dashed lines).

Experimental

Hatza (0.0143 g, 0.1 mmol) was dissolved in distilled water (3 ml). The pH of the solution was adjusted to 5.0 using KOH solution, and a solution of $CoCl_2\cdot6H_2O$ (0.0238 g, 0.1 mmol) in distilled water (2 ml) was added. The mixture was stirred at room temperature for 3 h and then filtered. Slow evaporation of the solvent gave pink crystals of (I) (yield 80%). Analysis found: C 17.48, H 3.85, N 33.67%; calculated for $C_6H_{16}CoN_{10}O_8$: C 17.36, H 3.88, N 33.74%. IR (KBr, ν, cm^{-1}): 1655 (*m*), 1609 (*s*), 1582 (*s*), 1485 (*m*), 1435 (*m*), 1393 (*s*), 1327 (*m*), 1296 (*w*), 1134 (*w*), 1065 (*w*), 1015 (*w*), 949 (*w*), 829 (*s*), 768 (*m*), 737 (*w*), 694 (*m*), 577 (*w*). Compound (II) was prepared in a similar manner to (I), except that $CdCl_2\cdot6H_2O$ (0.0291 g, 0.1 mmol) was used instead of $CoCl_2\cdot6H_2O$ (yield 78%). Analysis found: C 18.24, H 2.05, N 35.45%; calculated for $C_6H_8CdN_{10}O_4$: C 18.17, H 2.03, N 35.32%. IR (KBr, ν, cm^{-1}): 1657 (*s*), 1634 (*s*), 1611 (*s*), 1591 (*s*), 1526 (*w*), 1495 (*m*), 1439 (*m*), 1404 (*s*), 1323 (*m*), 1292 (*w*), 1271 (*w*), 1134 (*w*), 1103 (*m*), 1074 (*w*), 1016 (*w*), 953 (*m*), 826 (*m*), 758 (*w*), 698 (*m*).

Compound (I)

Crystal data

$[Co(C_3H_4N_5O_2)_2(H_2O)_4]$
$M_r = 415.22$
Triclinic, $P\overline{1}$
$a = 6.0869 (9)$ Å
$b = 6.5376 (9)$ Å
$c = 9.4896 (15)$ Å
$\alpha = 79.302 (8)°$
$\beta = 83.344 (9)°$
$\gamma = 76.137 (8)°$
$V = 359.24 (9)$ Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 1.26$ mm^{-1}
$T = 193 (2)$ K
0.41 × 0.37 × 0.18 mm

Data collection

Rigaku Mercury diffractometer
Absorption correction: multi-scan (Jacobson, 1998)
$T_{min} = 0.598, T_{max} = 0.804$
3493 measured reflections
1296 independent reflections
1245 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.070$
$S = 1.05$
1296 reflections
140 parameters
4 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.47$ e Å^{-3}

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

Co1—O1	2.0768 (13)	Co1—O4	2.1451 (14)
Co1—O3	2.0828 (15)		
O1—Co1—O3	92.50 (6)	O3—Co1—O4	92.31 (6)
O1—Co1—O4	87.90 (6)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4*A*···O2^{i}	0.881 (18)	1.86 (2)	2.704 (2)	161 (3)
N5—H5*B*···O2^{ii}	0.83 (3)	2.00 (3)	2.835 (2)	175 (2)
N5—H5*A*···N3^{iii}	0.86 (3)	2.21 (3)	3.047 (3)	166 (2)
O4—H4*B*···N2^{iv}	0.881 (18)	2.26 (2)	3.108 (2)	161 (3)
O3—H3*B*···O2^{iii}	0.812 (10)	1.930 (12)	2.731 (2)	169 (3)
O3—H3*A*···N4^{ii}	0.811 (10)	2.099 (13)	2.889 (2)	164 (3)

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

Compound (II)

Crystal data

$[Cd(C_3H_4N_5O_2)_2]$	V = 1227.0 (6) Å^3
M_r = 396.62	Z = 4
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
a = 13.520 (4) Å	μ = 1.82 mm^{-1}
b = 10.625 (3) Å	T = 193 (2) K
c = 8.877 (3) Å	0.47 × 0.38 × 0.37 mm
β = 105.808 (5)°	

Data collection

Rigaku Mercury diffractometer	5638 measured reflections
Absorption correction: multi-scan (Jacobson, 1998)	1124 independent reflections
T_{min} = 0.439, T_{max} = 0.512	1097 reflections with $I > 2\sigma(I)$
	R_{int} = 0.020

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.016	98 parameters
$wR(F^2)$ = 0.044	H-atom parameters constrained
S = 1.02	$\Delta\rho_{max}$ = 0.45 e Å^{-3}
1124 reflections	$\Delta\rho_{min}$ = −0.44 e Å^{-3}

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

Cd1—N4^{i}	2.2300 (16)	Cd1—O2	2.6037 (14)
Cd1—O1	2.2692 (15)		
N4^{i}—Cd1—N4^{ii}	100.49 (8)	N4^{i}—Cd1—O2	85.77 (5)
N4^{i}—Cd1—O1	121.98 (5)	N4^{ii}—Cd1—O2	147.77 (5)
N4^{ii}—Cd1—O1	98.16 (6)	O1—Cd1—O2	53.52 (5)
O1—Cd1—O1^{iii}	116.65 (7)	O2^{iii}—Cd1—O2	105.71 (6)
O1—Cd1—O2^{iii}	87.73 (5)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N5—H5A···O1^{iv}	0.88	2.06	2.889 (2)	157.6
N5—H5B···O2^{v}	0.88	2.02	2.847 (2)	156.6
C2—H2B···O1^{iv}	0.99	2.57	3.426 (2)	145

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

Carbon- and nitrogen-bound H atoms were positioned geometrically (C—H = 0.99 Å and N—H = 0.88 Å) and were included in the refinement in the riding-model approximation, with U_{iso}(H) = $1.2U_{eq}$(C). Water H atoms were located in a difference Fourier map and were refined with a distance restraint of O—H = 0.84 (1) Å.

For both compounds, data collection: *CrystalClear* (Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3110). Services for accessing these data are described at the back of the journal.

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