

Two mononuclear octahedral complexes with benzimidazole-2-carboxylate: supramolecular networks constructed by hydrogen bonds

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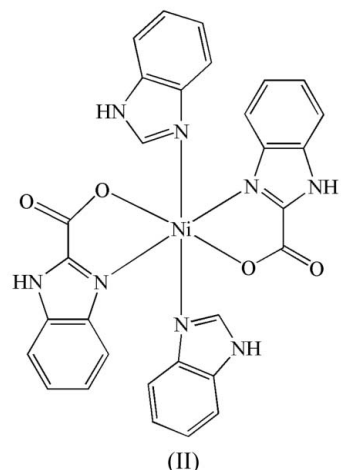
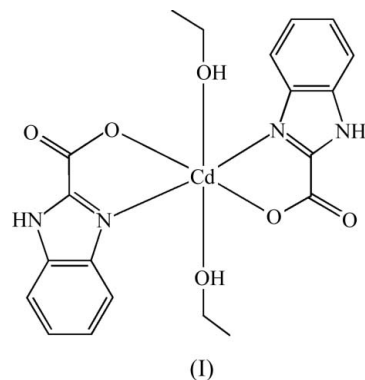
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The title compounds, *trans*-bis(1*H*-benzimidazole-2-carboxylato- κ^2N^3,O)bis(ethanol- κO)cadmium(II), [Cd(C₈H₅N₂O₂)₂(C₂H₆O)₂], (I), and *trans*-bis(1*H*-benzimidazole-2-carboxylato- κ^2N^3,O)bis(1*H*-benzimidazole-2-carboxylato- κ^2N^3,O)nickel(II), [Ni(C₈H₅N₂O₂)₂(C₇H₆N₂)₂], (II), are hydrogen-bonded supramolecular complexes. In (I), the Cd^{II} ion is six-coordinated by two O atoms from two ethanol molecules, and by two O and two N atoms from two bidentate benzimidazole-2-carboxylate (HBIC) ligands, giving a distorted octahedral geometry. The combination of O—H...O and N—H...O hydrogen bonds results in two-dimensional layers parallel to the *ab* plane. In (II), the six-coordinated Ni^{II} atom, which lies on an inversion centre, shows a similar distorted octahedral geometry to the Cd^{II} ion in (I); two benzimidazole molecules occupy the axial sites and the equatorial plane contains two chelating HBIC ligands. Pairs of N—H...O hydrogen bonds between pairs of HBIC anions connect adjacent Ni^{II} coordination units to form a one-dimensional chain parallel to the *a* axis. Moreover, these one-dimensional chains are further linked *via* N—H...O hydrogen bonds between HBIC anions and benzimidazole molecules to generate a three-dimensional supramolecular framework. The two compounds show quite different supramolecular networks, which may be explained by the fact that different co-ligands occupy the axial sites in the coordination units.

Comment

The design and construction of coordination architectures with unprecedented topologies have attracted considerable attention over recent decades (Moulton & Zaworotko, 2001; Roesky & Andruh, 2003). Discrete coordination assemblies are linked through numerous weak interactions, such as hydrogen bonds and π - π stacking, thereby resulting in higher-dimensional supramolecular networks with multiple structural

features and properties (Kitaura *et al.*, 2003; Custelcean *et al.*, 2006; Madalan *et al.*, 2006; Jiang *et al.*, 2008, 2009). It has been demonstrated that the number and orientation of weak attraction sites on the discrete building blocks have a significant effect on the resulting supramolecular structures. Thus, minor changes in interaction sites in the building blocks may affect the packing and even the overall network. Related studies will help us rationally design crystallized materials with desirable structures.



The assembly of complexes based on bis(chelating) bridging ligands has been of intense interest, mainly because of the multiple coordination modes of these ligands, intriguing structural features and the potential properties of the resulting complexes (Zhang, Cheng *et al.*, 2008; Zhang, Ma *et al.*, 2008; Colacio *et al.*, 2009; Mota *et al.*, 2010). For example, a great many magnetically ordered materials based on oxalate and its derivatives have been explored in recent years (Ruiz *et al.*, 1999; Xu *et al.*, 2007; Train *et al.*, 2008). Benzimidazole-2-carboxylic acid (H₂BIC) represents a new kind of bis-(chelating) bridging ligand and is less well explored than oxalate and its derivatives. Several complexes constructed from H₂BIC molecules have been investigated, and they exhibit low-dimensional structural features, such as mononuclear, discrete six-membered rings and a two-dimensional honeycomb network containing bowl-shaped voids (Dutta & Satapathi, 1981; Rettig *et al.*, 1999; Saczewski *et al.*, 2006; Zheng *et al.*, 2011). In this work, we present the structures and supramolecular assembly *via* hydrogen bonds of two new

complexes with HBIC ligands (HBIC is benzimidazole-2-carboxylate), namely, *trans*-bis(1*H*-benzimidazole-2-carboxylato- κ^2N^3,O)bis(ethanol- κO)cadmium(II), (I), and *trans*-bis(1*H*-benzimidazole- κN^3)bis(1*H*-benzimidazole-2-carboxylato- κ^2N^3,O)-nickel(II), (II). Both possess similar mononuclear structures and one-dimensional hydrogen-bonding chains, but different hydrogen bonds involving the group on the axial sites result in quite different higher-dimensional networks.

The molecule of complex (I) consists of one Cd^{II} ion, two HBIC anions and two ligated ethanol molecules (Fig. 1), while in complex (II), the asymmetric unit only contains half an Ni^{II} ion, one HBIC anion and one benzimidazole molecule, as the Ni^{II} ion lies on a crystallographic inversion centre (Fig. 2). (I) and (II) are mononuclear complexes, in which the metal centre displays a distorted octahedral coordination geometry completed by two N atoms and two O atoms from two bidentate chelating HBIC ligands in the equatorial plane, and two donors from the different co-ligands in axial sites [O atoms from two ethanol molecules in (I) and N atoms from two benzimidazole molecules in (II)]. Selected bond lengths and angles for the title compounds are listed in Tables 1 and 3; the *M*–O and *M*–N bond distances [*M* = Cd in (I) and Ni in (II)] are in the normal ranges (Sarma *et al.*, 2009; Yang & Wu, 2009). In (I), two *trans*-oriented HBIC ligands in equatorial positions are almost coplanar, with a dihedral angle between the Cd1/N1/O1 and Cd1/N3/O3 planes of 9.97°. The two ligated ethanol molecules occupy the axial sites and the axial O5–Cd1–O6 angle [179.94 (19)°] deviates only slightly from 180°.

In the title compounds, pairs of N–H...O hydrogen bonds are formed between pairs of HBIC anions from adjacent mononuclear building blocks [for (I): N2–H2...O4ⁱⁱ and N4–H4...O2ⁱⁱⁱ, symmetry codes: (ii) $x + 1, y - 1, z$; (iii) $x - 1, y + 1, z$; for (II): N2–H2...O2^{iv}, symmetry code: (iv) $-x + 1, -y, -z$], which yield centrosymmetric $R_2^2(10)$ rings. Thus, the connection of these hydrogen bonds leads to similar one-dimensional chain-like structures in both complexes (Fig. 3).

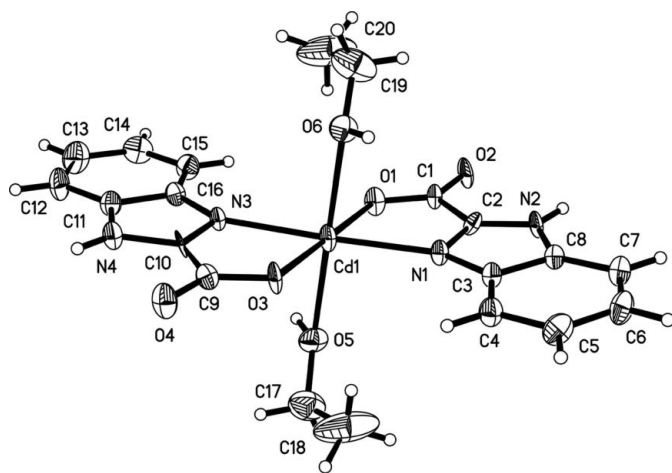


Figure 1

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. All H atoms are drawn as spheres of arbitrary radii.

However, further investigation indicates that these one-dimensional chains are arranged in a quite different manner through the linkage of intermolecular attractions, thereby resulting in quite different supramolecular frameworks, mainly due to the difference in the apical ligand of the metal centres.

In compound (I), two ligated ethanol molecules act as hydrogen-bond donors to form two hydrogen bonds with carboxylate O atoms (O1 and O3) of HBIC ligands from adjacent one-dimensional chains. The angle between the ethanol O–H group and the equatorial plane is 81° and this orientation of the hydrogen-bond donor favours the formation of a ring. Thus, intermolecular O5–H5...O3^v and O6–H6...O1^{vi} hydrogen bonds [symmetry codes: (v) $x + 1, y, z$; (vi) $x - 1, y, z$] between adjacent mononuclear building units, which generate $R_2^2(8)$ rings, serve to further link the one-dimensional chains into an extended two-dimensional supramolecular layer, which runs along the *ab* plane (Fig. 4). In the structure of (I), all potential strong hydrogen-bonding sites are involved in the formation of hydrogen bonds in the two-dimensional supramolecular network.

In compound (II), benzimidazole molecules occupying the axial sites also act as hydrogen-bond donors to generate N4–H4...O1^{vii} hydrogen bonds [symmetry code: (vii) $-x + 2, y + \frac{1}{2}, -z + \frac{1}{2}$] with carboxylate O atoms (O2) of HBIC anions. Although the angle between the benzimidazole N–H group and the equatorial plane is 45° and the orientation of the hydrogen-bond donor in (II) is not suitable for the formation of a hydrogen-bond ring, these hydrogen-bond interaction sites cannot be restrained in a two-dimensional layer, thereby resulting in a three-dimensional supramolecular network (Fig. 5).

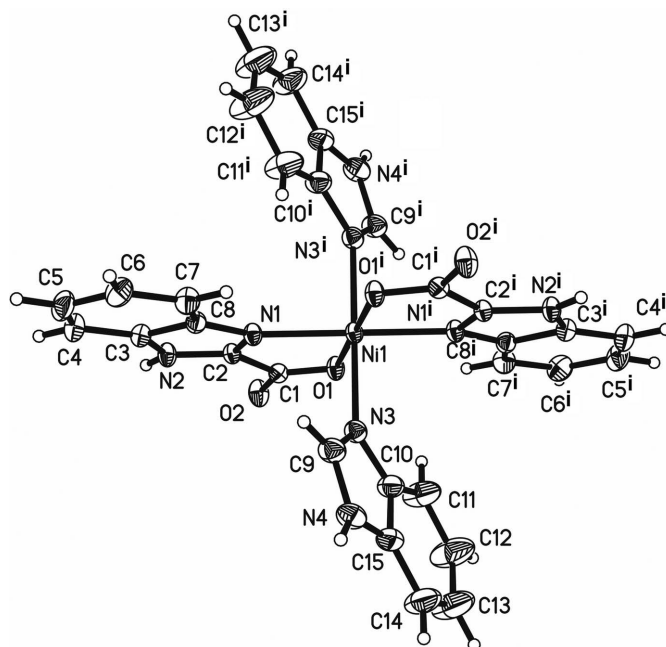


Figure 2

The molecular structure of (II), with displacement ellipsoids drawn at the 30% probability level. [Symmetry code: (i) $-x + 2, -y, -z$.]

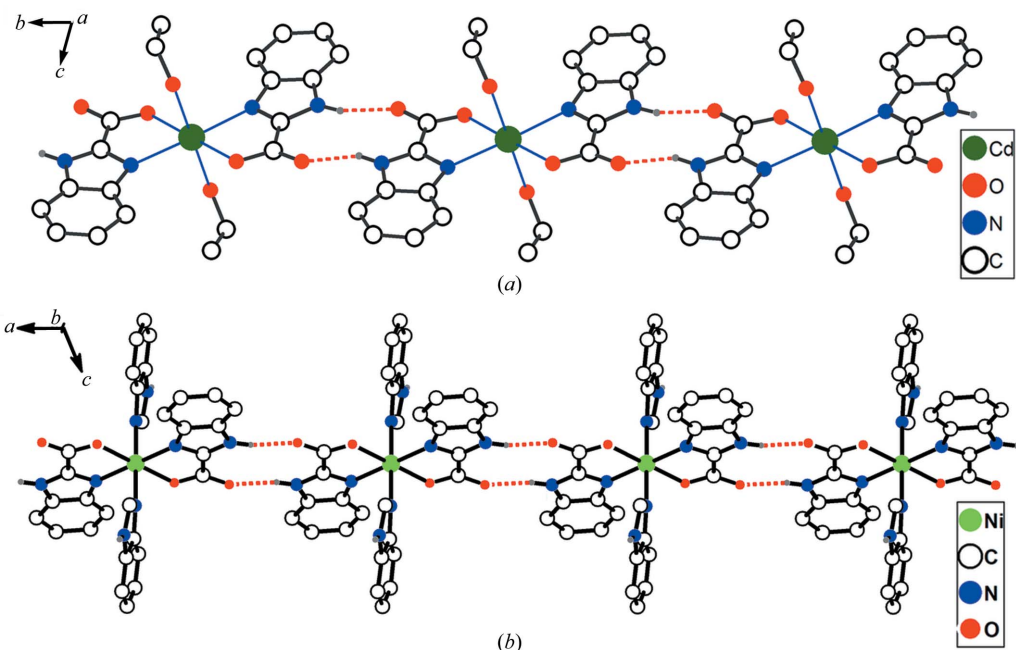


Figure 3
 (a) A packing diagram of (I), showing a one-dimensional chain formed by pairs of intermolecular hydrogen bonds (dashed lines). (b) A packing diagram of (II), showing a one-dimensional chain. Dashed lines represent N—H···O interactions.

The topological analysis approach was employed to better describe the structural characteristics of (II). The topology of this three-dimensional supramolecular framework can be simplified by considering the Ni^{II} coordination units as six-connected nodes and the intermolecular hydrogen bonds as two-connected linkers between these nodes. As a result, a three-dimensional network structure of 4¹².6³-pcu topology is formed.

IR spectra of the two compounds show characteristic absorptions for the carboxylate stretching vibrations. The characteristic bands of carboxylate groups are seen in the range 1648–1520 cm⁻¹ for asymmetric stretching and 1490–1458 cm⁻¹ for symmetric stretching (Zheng *et al.*, 2011). The absence of strong absorption peaks around 1700 cm⁻¹ indicates that all carboxyl groups (–COOH) are deprotonated. Moreover, a strong and broad absorption band at 3587 cm⁻¹ is

assigned to the $\nu(\text{O}–\text{H})$ vibration of ethanol molecules in complex (I).

In summary, two new complexes were constructed from the reaction between various metal salts and H₂BIC molecules with different co-ligands. They show a similar mononuclear structure, where the metal ions reside in a distorted octahedral coordination environment and in which two bidentate chelating HBIC anions occupy equatorial positions. However, intermolecular hydrogen bonds link discrete coordination units to form different supramolecular networks.

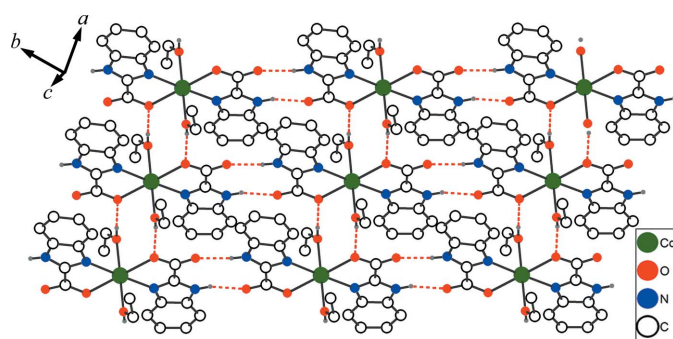


Figure 4
 A packing diagram of (I), showing the two-dimensional layer-like structure along the *ab* plane. Dashed lines represent hydrogen-bonding interactions.

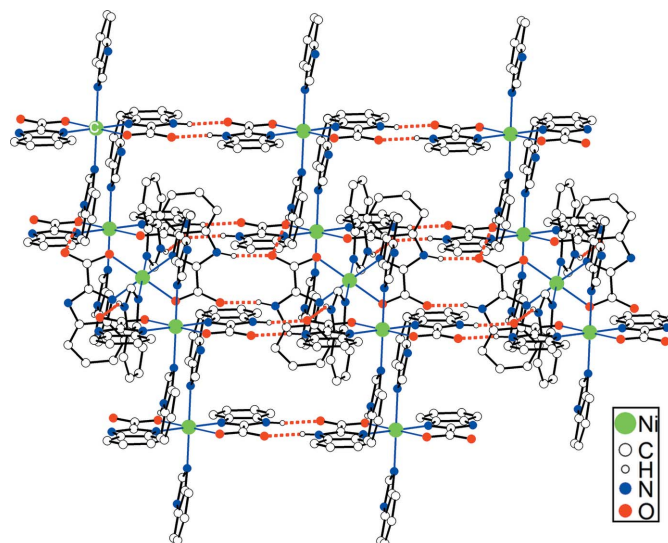


Figure 5
 A packing diagram of (II), showing the three-dimensional supramolecular network formed by intermolecular hydrogen bonds (dashed lines).

Experimental

For the synthesis of complex (I), benzimidazole-2-carboxylic acid (H₂BIC, 16.2 mg, 0.10 mmol) was dissolved in water (5 ml) and the pH was adjusted to about 8 with NaOH solution. A solution of Cd(ClO₄)₂·6H₂O (41.9 mg, 0.10 mmol) in ethanol (5 ml) was then layered on the aqueous H₂BIC solution. The system was left for about two months at room temperature and colourless block-shaped crystals of (I) were obtained by filtration (yield 56%). IR (KBr pellet, ν, cm⁻¹): 3587 (s), 3100 (s), 1648 (s), 1582 (w), 1520 (s), 1484 (m), 1458 (s), 1391 (m), 1331 (s), 1212 (w), 1147 (w), 1018 (s), 994 (w), 948 (w), 911 (w), 857 (m), 819 (m), 757 (s), 631 (w), 593 (w), 547 (w), 436 (w).

For the preparation of (II), a mixture of NiCl₂·6H₂O (23.8 mg, 0.10 mmol), H₂BIC (16.2 mg, 0.10 mmol) and benzimidazole (11.8 mg, 0.10 mmol) in H₂O–C₂H₅OH (3:1 v/v, 4 ml) was sealed in a sample bottle reactor (10 ml) and heated at 383 K under autogenous pressure for 48 h. After the sample had been cooled to room temperature at a rate of 5 K h⁻¹, block-shaped pale-purple crystals of (II) were collected (yield 68%). IR (KBr pellet, ν, cm⁻¹): 3098 (s), 1627 (s), 1614 (s), 1523 (m), 1490 (m), 1464 (s), 1391 (s), 1372 (w), 1343 (s), 1302 (w), 1273 (w), 1145 (w), 1023 (m), 966 (w), 914 (w), 858 (w), 823 (m), 766 (w), 743 (s), 637 (w), 597 (w), 433 (w).

Compound (I)

Crystal data

[Cd(C₈H₅N₂O₂)₂(C₂H₆O)₂] $\gamma = 78.54 (3)^\circ$
M_r = 526.82 $V = 1081.7 (4) \text{ \AA}^3$
 Triclinic, *P* $\bar{1}$ $Z = 2$
a = 5.4761 (11) Å $\text{Mo } K\alpha$ radiation
b = 10.477 (2) Å $\mu = 1.05 \text{ mm}^{-1}$
c = 19.896 (4) Å $T = 298 \text{ K}$
 $\alpha = 75.31 (3)^\circ$ $0.35 \times 0.28 \times 0.22 \text{ mm}$
 $\beta = 88.67 (3)^\circ$

Data collection

Bruker SMART APEXII CCD 5344 measured reflections
 area-detector diffractometer 3804 independent reflections
 Absorption correction: multi-scan 3228 reflections with $I > 2\sigma(I)$
 (SADABS; Bruker, 2002) $R_{\text{int}} = 0.021$
 $T_{\text{min}} = 0.709, T_{\text{max}} = 0.801$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$ 12 restraints
 $wR(F^2) = 0.161$ H-atom parameters constrained
 $S = 1.17$ $\Delta\rho_{\text{max}} = 0.93 \text{ e \AA}^{-3}$
 3804 reflections $\Delta\rho_{\text{min}} = -1.26 \text{ e \AA}^{-3}$
 270 parameters

Table 1

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

Cd1–N1	2.254 (5)	Cd1–O3	2.327 (4)
Cd1–N3	2.265 (5)	Cd1–O5	2.354 (5)
Cd1–O1	2.317 (4)	Cd1–O6	2.372 (5)
N1–Cd1–N3	177.57 (17)	O1–Cd1–O5	89.37 (17)
N1–Cd1–O1	74.26 (16)	O3–Cd1–O5	91.10 (17)
N3–Cd1–O1	105.53 (16)	N1–Cd1–O6	86.32 (18)
N1–Cd1–O3	105.98 (16)	N3–Cd1–O6	91.26 (17)
N3–Cd1–O3	74.21 (15)	O1–Cd1–O6	90.58 (17)
O1–Cd1–O3	179.45 (15)	O3–Cd1–O6	88.95 (17)
N1–Cd1–O5	93.64 (18)	O5–Cd1–O6	179.94 (19)
N3–Cd1–O5	88.78 (18)		

Table 2

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

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N2–H2···O4 ⁱ	0.86	1.94	2.743 (6)	155
N4–H4A···O2 ⁱⁱ	0.86	1.94	2.761 (6)	158
O5–H5A···O3 ⁱⁱⁱ	0.85	1.91	2.678 (6)	150
O6–H6A···O1 ^{iv}	0.85	1.85	2.678 (6)	164

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

Table 3

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

Ni1–N1	2.0492 (17)	Ni1–O1	2.0915 (14)
Ni1–N3	2.1181 (18)		
N1–Ni1–O1 ⁱ	99.52 (6)	O1–Ni1–N3	91.52 (7)
N1–Ni1–N3	89.17 (7)	O1–Ni1–N3 ⁱ	88.48 (7)

Symmetry code: (i) $-x + 2, -y, -z$.

Table 4

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

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N4–H4A···O1 ⁱⁱ	0.86	2.56	3.111 (2)	123
N4–H4A···O2 ⁱⁱ	0.86	2.25	3.030 (3)	150
N2–H2···O2 ⁱⁱⁱ	0.86	1.91	2.753 (2)	167

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

Compound (II)

Crystal data

[Ni(C₈H₅N₂O₂)₂(C₇H₆N₂)₂] $V = 1419.5 (5) \text{ \AA}^3$
M_r = 617.27 $Z = 2$
 Monoclinic, *P*₂₁/*c* $\text{Mo } K\alpha$ radiation
a = 10.321 (2) Å $\mu = 0.74 \text{ mm}^{-1}$
b = 12.923 (3) Å $T = 298 \text{ K}$
c = 11.495 (2) Å $0.42 \times 0.35 \times 0.26 \text{ mm}$
 $\beta = 112.21 (3)^\circ$

Data collection

Bruker SMART APEXII CCD 7496 measured reflections
 area-detector diffractometer 2787 independent reflections
 Absorption correction: multi-scan 2374 reflections with $I > 2\sigma(I)$
 (SADABS; Bruker, 2002) $R_{\text{int}} = 0.022$
 $T_{\text{min}} = 0.748, T_{\text{max}} = 0.832$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$ 6 restraints
 $wR(F^2) = 0.096$ H-atom parameters constrained
 $S = 1.09$ $\Delta\rho_{\text{max}} = 0.79 \text{ e \AA}^{-3}$
 2787 reflections $\Delta\rho_{\text{min}} = -0.48 \text{ e \AA}^{-3}$
 184 parameters

A SIMU instruction (SHELXL97; Sheldrick, 2008) was used for several C atoms with large displacement parameters in the refinement of both structures. The H atoms of the ethanol molecules were located in difference Fourier maps and the others were placed in calculated positions and refined as riding atoms, with isotropic displacement parameters [C–H = 0.97 (methyl), 0.96 (methylene) or 0.93 Å (aromatic) and N–H = 0.86 Å; $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}), 1.2U_{\text{eq}}(\text{N})$ or $1.5U_{\text{eq}}(\text{O})$].

For both compounds, data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Bruker, 2004); 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: QS3005). Services for accessing these data are described at the back of the journal.

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