Two polymeric nickel(II) complexes with aromatic benzene-1,2,4,5-tetracarboxylate and pyridine-2,5-dicarboxylate linkers

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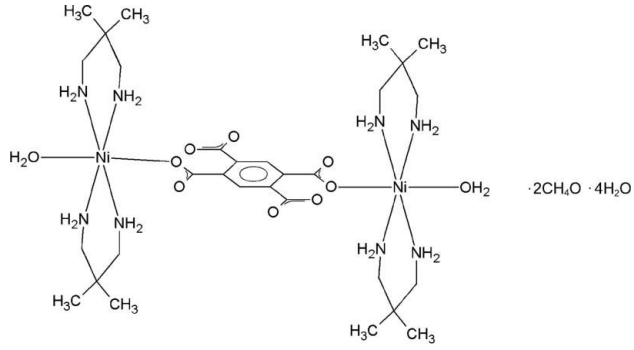
(μ-Benzene-1,2,4,5-tetracarboxylato-$\kappa^2O^1{:}O^4$)bis[aquabis-(2,2-methylpropane-1,3-diamine-κ^2N,N')nickel(II)] methanol disolvate tetrahydrate, $[Ni_2(C_{10}H_2O_8)(C_5H_{14}N_2)_4(H_2O)_2]\cdot 2CH_4O\cdot 4H_2O$, (I), is dinuclear, with elemental units built up around an inversion centre halving the benzene-1,2,4,5-tetracarboxylate (btc) anion, which bridges two symmetry-related Ni^{II} cations. The octahedral Ni polyhedron is completed by two chelating 2,2-methylpropane-1,3-diamine (dmpda) groups and a terminal aqua ligand. Two methanol and four water solvent molecules are involved in a number of N—H···O and O—H···O hydrogen bonds which define a strongly bound two-dimensional supramolecular structure. The structure of *catena*-poly[[[bis(2,2-methylpropane-1,3-diamine-κ^2N,N')nickel(II)]-μ-pyridine-2,5-dicarboxylato-$\kappa^3O^5{:}N,O^2$-[(2,2-methylpropane-1,3-diamine-κ^2N,N')nickel(II)]-μ-pyridine-2,5-dicarboxylato-$\kappa^3N,O^2{:}O^5$] octahydrate], $\{[Ni_2(C_7H_3NO_4)_2(C_5H_{14}N_2)_3]\cdot 8H_2O\}_n$, (II), is polymeric, forming twisted chains around three independent Ni centres, two of which lie on inversion centres and the third in a general position. There are three chelating dmpda ligands (one disordered over two equally populated positions), which are each attached to a different cation, and two pyridine-2,5-dicarboxylate (pdc) anions, both chelating the Ni centre in general positions through an –O—C—C—N– loop, while acting as bridges to the remaining two centrosymmetric Ni atoms. There are, in addition, eight noncoordinated water molecules in the structure, some of which are disordered.

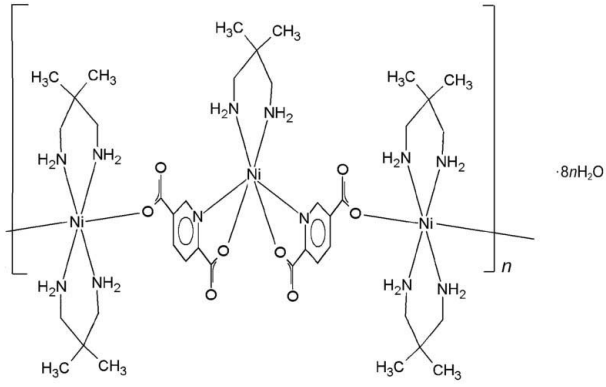
Comment

Multidimensional structures built up around metal centres bridged by carboxylate linkers are extremely appealing systems, both structurally, due to the variation in topologies to which they can give rise (Eddaoudi *et al.*, 2001) and for their potential applications, *viz.* in medicine, chemical separation and heterogeneous catalysis, and occasionally due to their eventual electronic or magnetic properties (Go *et al.*, 2005; Shi *et al.*, 2004).

The presence of two potentially coordinating O atoms in the carboxylate group usually favours the stability of these compounds, and at the same time they assume different coordination modes to metallic centres (*syn–syn*, *syn–anti* and *anti–anti*), which can lead to a variety of structural types. In general, it appears that *syn–syn* conformations lead to binuclear compounds, while the remaining two conformations favour polymeric entities (Eddaoudi *et al.*, 2001, 2002; Roswell & Yaghi, 2004; Wang *et al.*, 1999; Whitlow, 1973). In addition, the presence of donor solvent molecules such as water, amines, *etc.*, in the vicinity of the COOH groups frequently promotes the formation of supramolecular structures through extended hydrogen-bonding networks, sometimes in the form of porous systems having applications in size-selective sorption, host–guest recognition, catalysis, *etc.* (Coughlin & Lippard, 1984; Colacio *et al.*, 1992, 1994).



(I)



(II)

We report here the structures of the title compounds, $[Ni_2(btc)(dmpda)_4(H_2O)_2]\cdot 2CH_4O\cdot 4H_2O$, (I) (Fig. 1), and $[Ni_2(pdc)_2(dmpda)_3]\cdot 8H_2O$, (II) (Fig. 2), where btc is the benzene-1,2,4,5-tetracarboxylate anion, pdc is the pyridine-2,5-dicarboxylate anion and dmpa is the 2,2-methylpropane-1,3-diamine ligand. Complexes (I) and (II) are based on the same Ni^{II} cation complexed to the same chelating dmpda ligand, but where different (though closely related) bridging

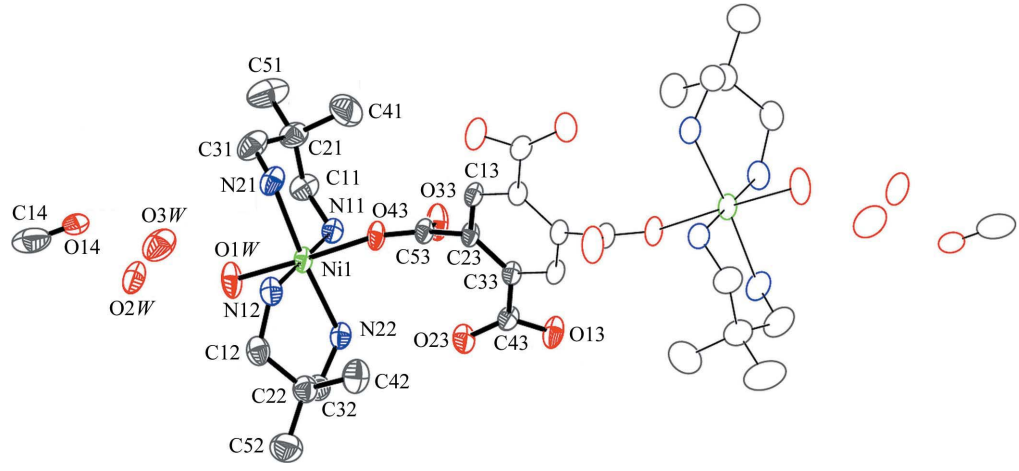


Figure 1
A molecular view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. The asymmetric unit is shown in bold. [Symmetry code: (i) $1-x, 1-y, 2-z$.]

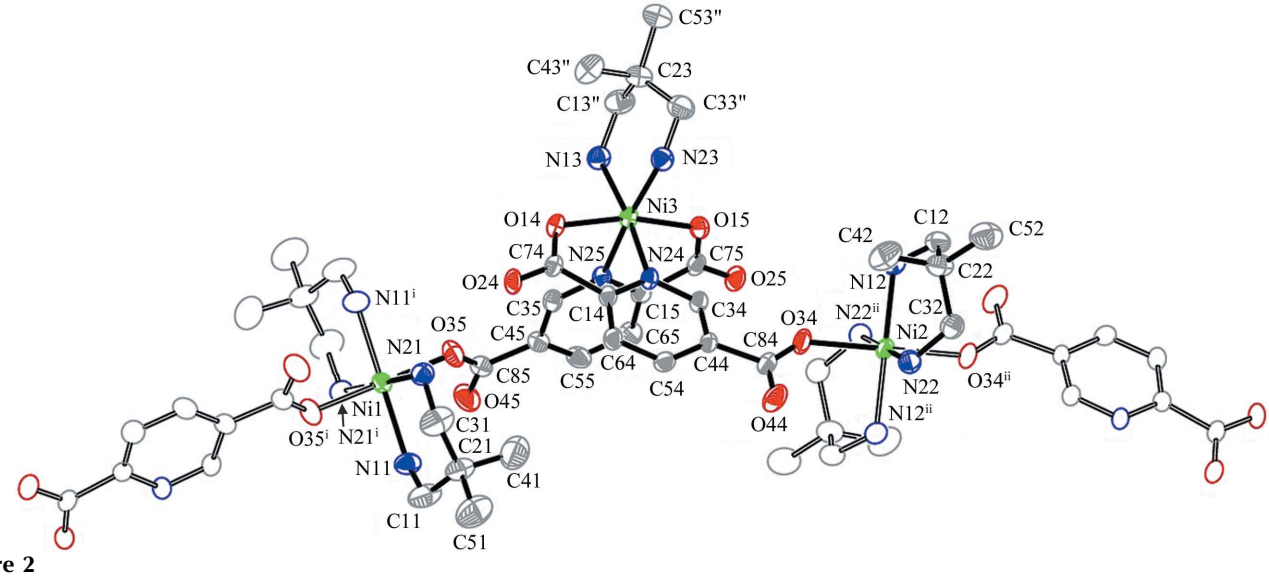


Figure 2
A molecular view of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms and water solvent molecules have been omitted for clarity. The asymmetric unit is shown in bold. Doubly primed atoms are in the disordered dmpa ligand. [Symmetry codes: (i) $1-x, 2-y, 1-z$; (ii) $-x, -y, -z$.]

agents have been used to link the metal centres, *viz.* btc in (I) and pdc in (II). Although both polycarboxylates behave in a rather similar fashion (basically as one-dimensional linkers), the resulting structures are different in a number of interesting aspects.

Compound (I) is basically constructed out of dinuclear units built up around an inversion centre, and the asymmetric unit is one half of such a unit. The inversion centre bisects the btc anion, which therefore bridges two opposite symmetry-related Ni^{II} cations, involving in this linkage only two carboxylate O atoms (one on each side) out of the eight available; the remaining six are in principle free to take part in hydrogen bonding (see below). Two dmpda groups chelate the metal centre through their amine groups, contributing four N atoms towards the octahedral environment of the metal, the sixth position being occupied by a terminal aqua ligand. The Ni—N bonds lie in a narrow range of 2.089 (3)–2.114 (3) Å, while the two Ni—O bond lengths are less similar at 2.081 (2) Å for O_{aqua} and 2.173 (2) Å for O_{btc}. Finally, the structure contains one methanol and two water solvent molecules (Table 1). As a result, there are 15 H atoms potentially available for hydrogen bonding: six from the three water molecules, eight from the four amino groups and one from the methanol unit. Of these, 14 form significant interactions, generating a very complex hydrogen-bonding scheme leading to a two-dimensional structure lying parallel to (100) (Fig. 3). These sheets are well separated along [100] and interact only weakly.

The structure of (II) is more complex. There are three independent Ni^{II} centres, two (Ni1 and Ni2) lying on inversion centres and the third (Ni3) in a general position but displaying noncrystallographic twofold pseudosymmetry. This is shown in Fig. 4, which displays a fit of the group on to its rotated image

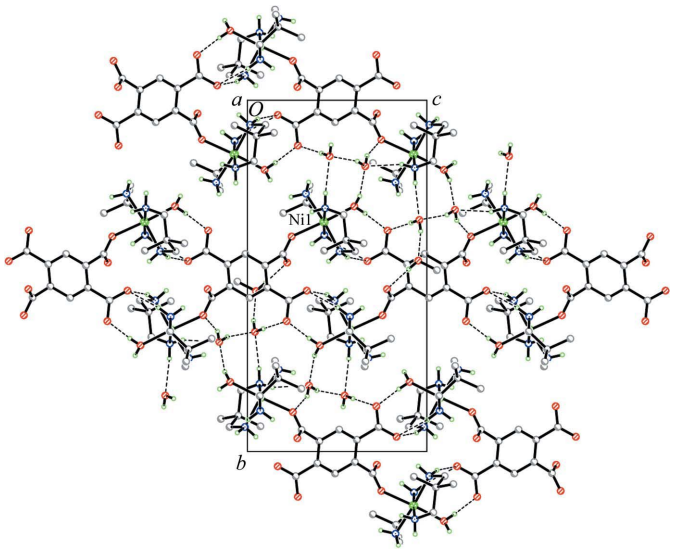


Figure 3
A packing view of (I), projected down [100], showing the two-dimensional hydrogen-bonded structure parallel to (100). Methyl groups and carbon-bound H atoms have been omitted for clarity.

around an axis bisecting the $N_{dmpda}—Ni—N_{dmpda}$ angle and passing through the cation. The largest deviation corresponds to the C75/C74 pair, with a misfit of 0.14 Å. There are also three dmpda ligands, each one identified herein by a different terminal digit and attached to a different cation: unit 1 to Ni1, unit 2 to Ni2, and unit 3, disordered over two equally populated positions, to Ni3. Completion of the coordination is achieved by two pdc anions (terminal digits 4 and 5), both of them chelating atom Ni3 through an –O—C—C—N– loop, while acting as bridges to the remaining two centrosymmetric Ni centres (one Ni each). The resulting polyhedra are rather regular, as is usual in nickel structural chemistry. Irrespective of the type of ligand (X = C, O or N), the range of Ni—X distances is narrow [Ni1 2.064 (3)–2.091 (3) Å; Ni2 2.076 (3)–2.089 (3) Å; Ni3 2.040 (3)–2.113 (3) Å]. The bond angles in the centrosymmetric polyhedra are also tightly bunched around ideal values [Ni1 90±3.23 (14)°; Ni2 90±4.05 (14)°], with those for Ni3 being more dispersed due to the closed pdc chelating bite [*cis* 77.88 (11)–96.03 (13)°; *trans* 167.91 (10)–175.03 (12)°].

This *N*,*O*-chelating bite in (II) is a typical binding behaviour for pyridine-2,5-dicarboxylate. Out of a total of 173 cases where the ligand coordinates a metal (Cambridge Structural Database, February 2009 update; Allen, 2002), 168 have combinations of the aforementioned chelating bite plus a diversity of μ_2-, μ_3- and μ_4-bridging modes; in particular, a total of 40 correspond to the μ_2-*N*,*O*:*O*′ type displayed in (II). In only five structures does the pyridine N atom not participate in coordination.

The bridging mode exerted by both pdc anions leads to a zigzag chain structure of the ···Ni1···Ni3···Ni2···Ni3···Ni1··· type (with Ni1 and Ni2 lying on inversion centres and Ni3 on a general position) running parallel to the [121] direction (Fig. 5). These chains propagate in a rather non-interacting way and the space between them is filled by eight

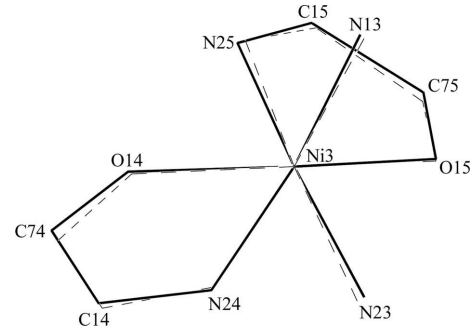


Figure 4
Schematic drawing of the Ni3 coordination polyhedron in (II) fitted to its twofold rotated image.

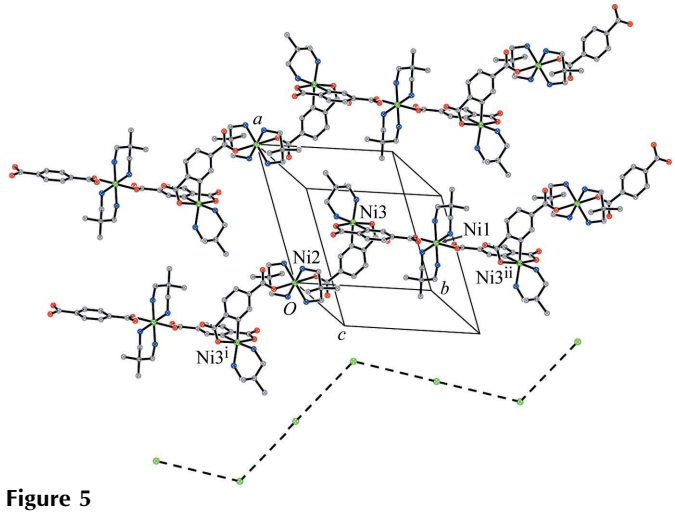


Figure 5
The upper part shows a packing view of (II), projected down [001]* and showing the zigzag chain structure of Ni^{II} centres. H atoms and water solvent molecules have been omitted for clarity. [Symmetry codes: (i) $-x$, $-y$, $-z$; (ii) $-x+1$, $-y+2$, $-z+1$.] The lower part is a schematic representation of a chain of Ni^{II} centres.

independent solvent water molecules (two of them heavily disordered). In spite of not having been able to determine the positions of the water H atoms with certainty (they have not been included in the model), the large number of short O···O contacts present in the structure, with a minimum of three contacts below 3.00 Å per solvent water molecule (see supplementary material for the most relevant ones), strongly suggests a very complex hydrogen-bonding scheme involving them and connecting the chains together. The strength of the interaction involving the water molecules in (II) contrasts with the much feebler participation displayed by the N—H groups; only half of the available N—H groups are involved in (extremely weak) N—H···O interactions (Table 2).

Experimental

For the synthesis of complex (I), benzene-1,2,4,5-tetracarboxylic acid (H4btc; 0.254 g, 1 mmol) was added slowly to an aqueous solution (20 ml) of NaOH (0.16 g, 4 mmol). Nickel acetate tetrahydrate (0.497 g, 2 mmol) was dissolved in water (20 ml) and added to the above solution. The resulting mixture was stirred for 10 min, followed by the addition of a methanolic solution (15 ml) of 2,2-dimethyl-

propane-1,3-diamine (dmpda; 0.204 g, 2 mmol). Single crystals of (I) suitable for X-ray diffraction studies were obtained by slow concentration of the solution. Complex (II) was obtained in the same way, using pyridine-2,5-dicarboxylic acid (H_2pdc) (0.167 g, 1 mmol) and NaOH (0.080 g, 2 mmol).

Compound (I)

Crystal data

$[Ni_2(C_{10}H_2O_8)(C_5H_{14}N_2)_4(H_2O)_2]\cdot 2CH_4O\cdot 4H_2O$
M_r = 948.44
Monoclinic, $P2_1/c$
a = 10.6492 (10) Å
b = 20.914 (2) Å
c = 11.3422 (11) Å
β = 109.662 (2)°
V = 2378.8 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.86 mm^{-1}
T = 295 K
0.44 × 0.25 × 0.18 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.72, T_{max} = 0.86
19918 measured reflections
5385 independent reflections
3837 reflections with $I > 2\sigma(I)$
R_{int} = 0.048

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.146
S = 1.03
5385 reflections
267 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.70 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Compound (II)

Crystal data

$[Ni_2(C_7H_3NO_4)_2(C_5H_{14}N_2)_3]\cdot 8H_2O$
M_r = 898.30
Triclinic, $P\overline{1}$
a = 12.269 (3) Å
b = 13.622 (3) Å
c = 15.171 (4) Å
α = 105.25 (3)°
β = 98.02 (2)°
γ = 111.25 (3)°
V = 2200.8 (12) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.93 mm^{-1}
T = 295 K
0.40 × 0.38 × 0.32 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.68, T_{max} = 0.74
18893 measured reflections
9619 independent reflections
6322 reflections with $I > 2\sigma(I)$
R_{int} = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.192
S = 0.98
9619 reflections
568 parameters
93 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.70 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

H atoms bonded to C or N atoms were positioned geometrically and treated as riding atoms, with C—H = 0.93–0.97 Å and N—H = 0.90 Å. In (I), H atoms bonded to O atoms were located in a difference map and refined with restrained distances [O—H = 0.85 (1) Å and H···H = 1.30 (2) Å] and kept riding in the final cycles. In structure (II), H atoms bonded to O atoms could not be confidently found and accordingly were not included in the model. In spite of this, a large number of short $O_{water}\cdots O_{any}$ distances clearly attributable to hydrogen bonding are present in the structure (see supplementary material). In all cases, U_{iso}(H) = 1.2 or 1.5U_{eq}(parent). The structure of (II) presents some disorder; one of the three chelating dmpda ligands is disordered over two nearly equally populated positions, as is one of the water solvent molecules (O7*WA*/O7*WB*). A second water molecule appears to be much more severely disordered, and could only be modelled as five complementary fragments, each with low site occupancy (O8*WA* to O8*WE*). The site-occupation factors of the disordered water O atoms were refined for a few cycles and then kept fixed, while those of the disordered dmpda ligand were refined continuously with the occupation factor sum for the two conformations constrained to unity. Some soft metric and atomic displacement parameter restraints were applied to the disordered atoms of the dmpda ligand [using the SADI and DELU instructions in *SHELXL97* (Sheldrick, 2008) with standard uncertainties of 0.01 Å and 0.01 Å^{-2}, respectively].

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

D—H···A	D—H	H···A	D···A	D—H···A
O14—H14···O33^{i}	0.85	1.95	2.800 (5)	179
N11—H11*A*···O33	0.90	2.08	2.883 (3)	149
N11—H11*B*···O23^{ii}	0.90	2.11	3.005 (3)	170
N21—H21*A*···O13^{i}	0.90	2.34	3.111 (4)	143
N12—H12*A*···O2*W*^{iii}	0.90	2.19	3.012 (3)	152
N12—H12*B*···O3*W*	0.90	2.25	3.124 (4)	165
N22—H22*A*···O23^{ii}	0.90	2.25	3.122 (3)	164
N22—H22*B*···O23	0.90	2.20	3.086 (3)	167
O1*W*—H1*WA*···O2*W*	0.85	1.90	2.706 (3)	157
O1*W*—H1*WB*···O13^{ii}	0.85	1.82	2.664 (3)	174
O2*W*—H2*WA*···O43^{iv}	0.85	1.96	2.761 (3)	157
O2*W*—H2*WB*···O3*W*	0.85	1.95	2.740 (4)	155
O3*W*—H3*WA*···O13^{i}	0.85	1.89	2.723 (4)	167
O3*W*—H3*WB*···O14	0.85	1.92	2.739 (5)	161

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N11—H11*C*···O2*W*^{i}	0.90	2.39	3.127 (6)	139
N12—H12*D*···O3*W*^{ii}	0.90	2.56	3.423 (6)	160
N13—H13*G*···O25^{iii}	0.90	2.42	3.297 (4)	165
N13—H13*H*···O7*WA*^{ii}	0.90	2.40	3.256 (4)	159
N23—H23*H*···O3*W*^{ii}	0.90	2.33	3.196 (6)	160

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

For both compounds, data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SAINT-NT* (Bruker, 2002); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL-NT* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL-NT* and *PLATON* (Spek, 2009).

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