

# A benzene-rich pseudopolymorph of bis[ $\mu$ -1,3-bis(pentafluorophenyl)propane-1,3-dionato]- $\kappa^3 O, O': O'$ ; $\kappa^3 O:-O, O'$ -bis[aqua[1,3-bis(pentafluorophenyl)propane-1,3-dionato- $\kappa^2 O, O'$ ]-nickel(II)] benzene tetrasolvate

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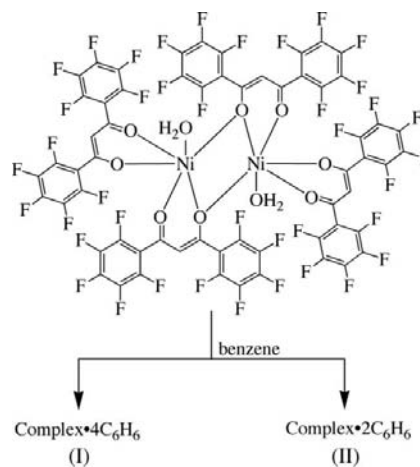
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The title complex comprises two Ni<sup>2+</sup> ions, four fluorinated ligands and two water molecules in a centrosymmetric dinuclear complex. This compound was crystallized from benzene–CH<sub>2</sub>Cl<sub>2</sub>, and two types of crystals, *viz.* the title benzene tetrasolvate, [Ni<sub>2</sub>(C<sub>15</sub>HF<sub>10</sub>O<sub>2</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 4C<sub>6</sub>H<sub>6</sub>, (I), and the previously reported benzene disolvate, [Ni<sub>2</sub>(C<sub>15</sub>HF<sub>10</sub>O<sub>2</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 2C<sub>6</sub>H<sub>6</sub>, (II) [Hori *et al.* (2009). *Bull. Chem. Soc. Jpn.*, **82**, 96–98], were obtained as pseudopolymorphs. In the crystal structure of (I), the four benzene solvent molecules interact closely with all the pentafluorophenyl groups of the complex through arene–perfluoroarene interactions. The molecular structures of the two compounds show essentially the same conformation, although the benzene molecules are accommodated in a columnar packing in (I), while they are isolated from each other in (II).

## Comment

Coordination complexes with dibenzoylmethane (dbm) and transition metals ( $M = \text{Co}^{\text{II}}$ , Ni<sup>II</sup>, Cu<sup>II</sup> or Pd<sup>II</sup>) form isomorphs of the flat mononuclear complex  $M(\text{dbm})_2$  (Vigato *et al.*, 2009; Soldatov *et al.*, 2001). While single crystals of  $M(\text{dbm})_2$  have no crystallization solvent molecules, coordination complexes of bis(pentafluorophenyl)propane-1,3-dione (*L*), which is fully fluorinated dbm, produce unique crystals which take in benzene molecules abundantly when crystallized from a benzene–CH<sub>2</sub>Cl<sub>2</sub> solvent mixture (Hori & Arii, 2007; Hori *et al.*, 2009). For example, single crystals of [Cu(*L*)<sub>2</sub>] were obtained as [Cu(*L*)<sub>2</sub>] $\cdot$ 3C<sub>6</sub>H<sub>6</sub> with 21 wt% benzene molecules. Complexation of *L* and Ni<sup>II</sup> ions gave a dinuclear nickel(II) complex, and single crystals were obtained as [Ni<sub>2</sub>(*L*)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 2C<sub>6</sub>H<sub>6</sub>, (II), with 8 wt% benzene molecules. These high capacities for solvent occlusion are explained by the

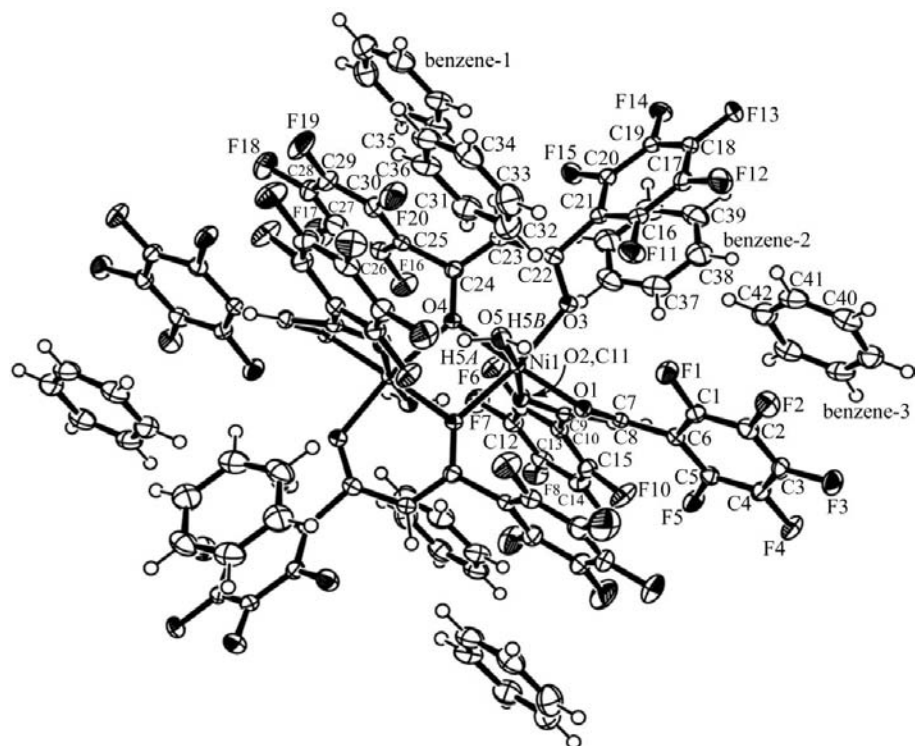
arene–perfluoroarene interaction, which is currently well known as an electrostatic interaction (Patrick & Prosser, 1960; Williams, 1993), between the pentafluorophenyl groups of the complex and the benzene molecules. In the crystal structure of (II) (Hori *et al.*, 2009), however, the pentafluorophenyl groups are in close contact not only with benzene molecules but also with other pentafluorophenyl groups by  $\pi$ – $\pi$  stacking.



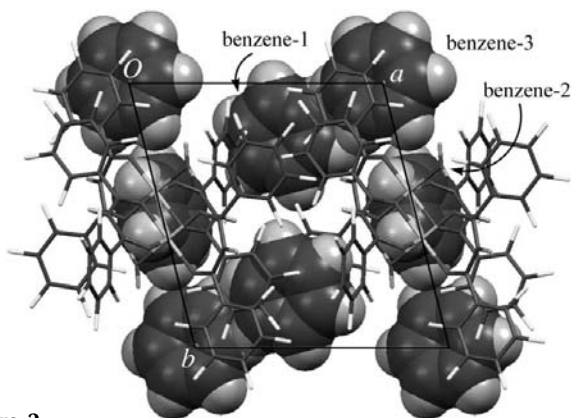
During detailed analysis of a series of complexes showing arene–perfluoroarene interactions, we accidentally found the title unique pseudopolymorph example of [Ni<sub>2</sub>(*L*)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 4C<sub>6</sub>H<sub>6</sub>, (I), with 15 wt% benzene molecules. Four benzene molecules are included in one complex unit. In this study, the two crystal forms, (I) and (II), are compared and discussed in relation to the arene–perfluoroarene interaction.

Two types of green crystals were obtained from a benzene–CH<sub>2</sub>Cl<sub>2</sub> mixture. The shapes of the crystals were mainly blocks, but a few crystals showed prismatic forms. Most crystals were monoclinic,  $P2_1/n$ , with unit-cell dimensions corresponding with those reported for (II) (Hori *et al.*, 2009):  $a = 11.5848$  (5) Å,  $b = 16.1079$  (6) Å,  $c = 18.0508$  (7) Å,  $\beta = 99.050$  (1)°,  $V = 3326.5$  (2) Å<sup>3</sup> and  $Z = 2$ . However, we found a crystal with different parameters, namely triclinic,  $P\bar{1}$ ,  $a = 12.0236$  (13) Å,  $b = 12.4384$  (14) Å,  $c = 14.0058$  (15) Å,  $\alpha = 82.980$  (1)°,  $\beta = 73.411$  (1)°,  $\gamma = 74.536$  (1)°,  $V = 1932.4$  (4) Å<sup>3</sup> and  $Z = 1$ . This is the benzene-rich pseudopolymorph (I). Unfortunately, we could not control the ratio of the products to isolate pure (I).

The structure of the entire complex and the surrounding benzene molecules of (I) is shown in Fig. 1. The asymmetric unit contains one-half of the complex, one whole benzene molecule (C31–C36, benzene-1), and two half-benzene molecules (C37–C39, benzene-2; C40–C42, benzene-3). The complex is centrosymmetric and comprises two Ni<sup>II</sup> ions, four *L* ligands and two water molecules in a dinuclear nickel(II) complex. The compositions of the complexes in (I) and (II) are exactly the same. The same coordination mode exhibited by these complexes is also known for Ni<sup>II</sup> ions and acetylacetonate ligands (Tahir *et al.*, 2007). The geometries around the metal centres are pseudo-octahedral. The metal–metal separation is 3.115 Å in (I) and 3.139 Å in (II). The coordi-


**Figure 1**

The entire dinuclear nickel(II) complex, (I), shown with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.


**Figure 2**

A crystal packing view of (I), projected along the *c* axis, showing the columnar arrangement of the benzene molecules linked by arene-perfluoroarene interactions between the pentafluorophenyl groups and the benzene solvent molecules.

nation geometries of atom Ni1 in (I) and (II) are very similar, as are the C=O bond lengths (Table 1).

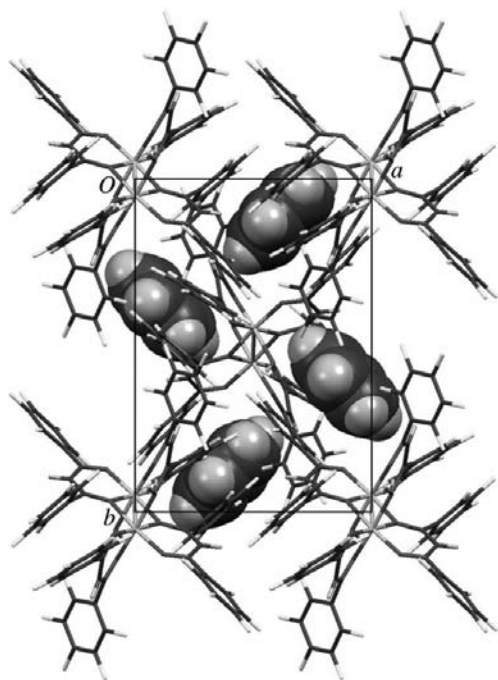
The pentafluorophenyl groups of (I) and (II) are highly twisted with respect to the coordination plane, as shown by the torsion angles in Table 1; the C5–C6–C7–C8 and C23–C24–C25–C30 torsion angles are almost the same. Thus, the direction and angles of the intramolecular  $\pi$ – $\pi$  stacking between the two corresponding pentafluorophenyl rings, *viz.* C1–C6 and C25–C30, are essentially the same. In the structure of (II), the C10–C15 ring is surrounded by four pentafluorophenyl groups of other molecules and no significant plane-to-

plane stacking is observed. In contrast, all the pentafluorophenyl rings have intermolecular stacking with benzene molecules in the structure of (I). In particular, six pentafluorophenyl rings of the complex and three benzene molecules (two benzene-1 and one benzene-3) are stacked in columns along the *c* axis. The remaining two pentafluorophenyl rings (C16–C21) and benzene-2 are perpendicularly aligned with respect to the other rings.

The packing structures of (I) and (II) are shown in Figs. 2 and 3, respectively. In the crystal structure of (I), cavities exist along the *b* axis, and benzene-2 and benzene-3 are packed alternately in these cavities with the benzene planes twisted. No strong intermolecular interactions are observed between the benzene molecules in the cavities; the closest intermolecular H···H distances of the benzene molecules are around 2.78–2.93 Å. The cavity is surrounded by pentafluorophenyl rings from four directions to stabilize the benzene positions. The benzene-2 and benzene-3 molecules are sandwiched between the

C16–C21 and C1–C6 pentafluorophenyl rings, respectively. Both of the average intermolecular plane-to-plane distances are around 3.5 Å, and the shortest F···C and C···C distances are 3.072 (2) [F15···C38(1 – *x*, 1 – *y*, 1 – *z*)] and 3.306 (3) Å [C1···C42(*x*, –1 + *y*, *z*)], indicating arene-perfluoroarene interaction. Benzene-1 is also stabilized between the C10–C15 and C25–C30 pentafluorophenyl rings, and the average distance of the intermolecular stacking is around 3.5 Å. C–H···F interactions (Thalladi *et al.*, 1998) are also observed as intermolecular interactions between the benzene and pentafluorophenyl rings, *e.g.* the F20···H31(1 – *x*, 1 – *y*, –*z*) and F20···H36(1 – *x*, 1 – *y*, –*z*) distances are 2.61 and 2.55 Å, respectively. Additionally, C–F··· $\pi$  interactions are observed between the pentafluorophenyl rings; the F14···C15(–*x*, 1 – *y*, 1 – *z*), F13···C12(–*x*, 1 – *y*, 1 – *z*) and F13···C13(–*x*, 1 – *y*, 1 – *z*) intermolecular distances are 3.155 (3), 2.951 (2) and 2.981 (3) Å, respectively.

The crystal structure of (I) contains two types of benzene molecule; benzene-2 and benzene-3 are packed alternately in the cavity, and benzene-1 is adjacently packed in the same direction as benzene-3. In the crystal structure of (II), on the other hand, the benzene molecules are three-dimensionally isolated by pentafluorophenyl rings of the complex, as shown in Fig. 3. The benzene molecule is sandwiched by two pentafluorophenyl rings, *viz.* C16–C21 and C25–C30, and the intermolecular plane-to-plane distances are around 3.4 Å. In both (I) and (II), the benzene molecules are stabilized by the arene-perfluoroarene interaction through a strong host-guest interaction.



**Figure 3**  
A crystal packing view of (II) (Hori *et al.*, 2009), projected along the *c* axis.

## Experimental

The dinuclear nickel(II) complex was prepared as reported by Hori *et al.* (2009). The result of the elemental analysis showed the formation of the complex (calculated for  $C_{60}H_8F_{40}Ni_2O_{10}$ : C 40.81, H 0.46%; found: C 40.98, H 0.47%). The complex was crystallized from  $CH_2Cl_2$  by the gas-phase diffusion of benzene to give green crystals of (I) and (II), in principle optically indistinguishable from each other and suitable for X-ray structural work.

**Table 1**

Comparison of selected bond lengths (Å) for (I) and (II).

	(I)	(II)
Ni1—O1	1.9804 (13)	1.9842 (11)
Ni1—O2	1.9974 (13)	2.0138 (12)
Ni1—O3	2.0003 (13)	2.0087 (12)
Ni1—O4	2.0401 (13)	2.0231 (11)
Ni1—O4 <sup>i</sup>	2.0922 (13)	2.1224 (12)
Ni1—O5	2.0854 (14)	2.0829 (13)
O1—C7	1.267 (2)	1.266 (2)
O2—C9	1.278 (2)	1.271 (2)
O3—C22	1.251 (2)	1.252 (2)
O4—C24	1.288 (2)	1.293 (2)
C5—C6—C7—C8	34.0 (3)	37.9 (2)
C8—C9—C10—C15	31.2 (3)	64.5 (2)
C20—C21—C22—C23	51.3 (3)	36.0 (2)
C23—C24—C25—C30	67.1 (3)	67.2 (2)

Symmetry code: (i)  $-x, -y + 1, -z$  in (I) and  $-x + 1, -y, -z$  in (II).

## Crystal data

$[Ni_2(C_{15}HF_{10}O_2)_4(H_2O)_2] \cdot 4C_6H_6$   
 $M_r = 2078.48$   
 Triclinic,  $P\bar{1}$   
 $a = 12.0236$  (13) Å  
 $b = 12.4384$  (14) Å  
 $c = 14.0058$  (15) Å  
 $\alpha = 82.980$  (1)°  
 $\beta = 73.411$  (1)°  
 $\gamma = 74.536$  (1)°  
 $V = 1932.4$  (4) Å<sup>3</sup>  
 $Z = 1$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.65$  mm<sup>-1</sup>  
 $T = 100$  K  
 $0.25 \times 0.20 \times 0.15$  mm

## Data collection

Bruker APEXII CCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Sheldrick 1996)  
 $T_{min} = 0.855, T_{max} = 0.909$   
 21369 measured reflections  
 8387 independent reflections  
 6817 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.023$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$   
 $wR(F^2) = 0.087$   
 $S = 1.03$   
 8387 reflections  
 621 parameters  
 H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{max} = 0.41$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.29$  e Å<sup>-3</sup>

H atoms attached to C atoms were refined as riding on their idealized positions, with C—H = 0.95 Å and  $U_{iso}(H) = 1.2U_{eq}(C)$ . Water atoms H5A and H5B were located in a difference Fourier density map and were refined freely [O—H5A = 0.88 (3) Å and O5—H5B = 0.99 (4) Å].

Data collection: APEX2 (Bruker, 2006); cell refinement: SAINT (Bruker, 2006); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3106). Services for accessing these data are described at the back of the journal.

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