

## Hexaaquacobalt(II) and hexaaquanickel(II) bis( $\mu$ -pyridine-2,6-dicarboxylato)bis[(pyridine-2,6-dicarboxylato)bismuthate(III)] dihydrate

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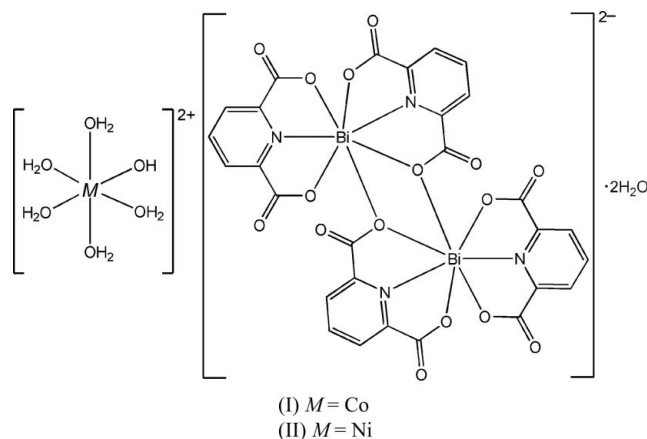
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The title complexes, hexaaquacobalt(II) bis( $\mu$ -pyridine-2,6-dicarboxylato)bis[(pyridine-2,6-dicarboxylato)bismuthate(III)] dihydrate,  $[\text{Co}(\text{H}_2\text{O})_6][\text{Bi}_2(\text{C}_7\text{H}_4\text{NO}_4)_4]\cdot 2\text{H}_2\text{O}$ , (I), and hexaaquanickel(II) bis( $\mu$ -pyridine-2,6-dicarboxylato)bis[(pyridine-2,6-dicarboxylato)bismuthate(III)] dihydrate,  $[\text{Ni}(\text{H}_2\text{O})_6][\text{Bi}_2(\text{C}_7\text{H}_4\text{NO}_4)_4]\cdot 2\text{H}_2\text{O}$ , (II), are isomorphous and crystallize in the triclinic space group  $P\bar{1}$ . The transition metal ions are located on the inversion centre and adopt slightly distorted  $\text{MO}_6$  ( $M = \text{Co}$  or  $\text{Ni}$ ) octahedral geometries. Two  $[\text{Bi}(\text{pydc})_2]^-$  units (pydc is pyridine-2,6-dicarboxylate) are linked *via* bridging carboxylate groups into centrosymmetric  $[\text{Bi}_2(\text{pydc})_4]^{2-}$  dianions. The crystal packing reveals that the  $[\text{M}(\text{H}_2\text{O})_6]^{2+}$  cations,  $[\text{Bi}_2(\text{pydc})_4]^{2-}$  anions and solvent water molecules form multiple hydrogen bonds to generate a supramolecular three-dimensional network. The formation of secondary  $\text{Bi}\cdots\text{O}$  bonds between adjacent  $[\text{Bi}_2(\text{pydc})_4]^{2-}$  dimers provides an additional supramolecular synthon that directs and facilitates the crystal packing of both (I) and (II).

### Comment

Compounds of bismuth(III) with aminopolycarboxylate ligands have been of interest over the past few decades, mainly due to their high stability in aqueous solutions and their rich structural chemistry (Stavila *et al.*, 2006). The bismuth(III) centre is highly acidic and can achieve coordination numbers as high as 10 (Briand & Burford, 2000; Stavila *et al.*, 2006). Pyridine-2,6-dicarboxylic acid ( $\text{H}_2\text{pydc}$ ) is a versatile chelating ligand and its metal complexes have been intensively explored in the context of their biological activity (Hwang *et al.*, 2003) and rich coordination chemistry (Serezhkin *et al.*, 2009). Bismuth(III) is known to form stable chelate complexes with  $\text{H}_2\text{pydc}$  (or its anions), and several crystal structures have been reported to date (Agbabozorg *et al.*, 2008; Ranjbar *et al.*,

2001, 2003; Sheshmani *et al.*, 2005). In these structures,  $\text{H}_2\text{pydc}$  acts as an  $O,N,O'$ -donor ligand to the metal ion to form five-membered metallocycles. This high coordination capacity, coupled with the ability to link to metal centres in a variety of bridging modes, makes aminopolycarboxylate ligands attractive for the assembly of mixed-metal complexes. Previously, we have described several transition metal–bismuth complexes based on ethylenediaminetetraacetate and nitrilotriacetate ligands (Bachman *et al.*, 2003; Stavila *et al.*, 2000, 2002, 2003; Stavila, Gulea, Shova *et al.*, 2004; Stavila, Gulea, Popa *et al.*, 2004). We report here the crystal structures of the first transition metal–bismuth pyridine-2,6-dicarboxylates, namely hexaaquacobalt(II) bis( $\mu$ -pyridine-2,6-dicarboxylato)bis[(pyridine-2,6-dicarboxylato)bismuthate(III)] dihydrate, (I), and hexaaquanickel(II) bis( $\mu$ -pyridine-2,6-dicarboxylato)bis[(pyridine-2,6-dicarboxylato)bismuthate(III)] dihydrate, (II).



Compounds (I) and (II) were obtained under slightly acidic reaction conditions by dissolution of freshly prepared cobalt(II) or nickel(II) hydroxycarbonates in a saturated solution of  $\text{Bi}(\text{Hpydc})(\text{pydc})$ . Both compounds crystallize in the triclinic system (space group  $P\bar{1}$ ) and they are essentially isomorphous. The transition metal rests on the inversion centre and is coordinated to six water molecules in a slightly distorted octahedral coordination geometry with typical  $\text{Co}-\text{O}$  and  $\text{Ni}-\text{O}$  distances (Fig. 1 and Table 1) (Guo *et al.*, 2008; Morzyk-Ociepa, 2007). The primary coordination environment of  $\text{Bi}^{\text{III}}$  includes seven donor atoms, six from two tridentate  $\text{pydc}^{2-}$  ligands and one bridging O atom from an adjacent symmetry-related complex. The  $\text{pydc}^{2-}$  ligand is coordinated to the  $\text{Bi}^{\text{III}}$  centre in a conventional  $O,N,O'$ -tridentate fashion *via* the N atom and two O atoms, one from each of the two carboxylate groups. Atom Bi1 and its symmetry-related counterpart constitute the anionic part of the molecule, forming a centrosymmetric  $[\text{Bi}_2(\text{pydc})_4]^{2-}$  dimer (Fig. 1).

The bridging  $\text{C11}-\text{O11}-\text{O12}$  carboxylate group in (I) and (II) displays a monoatomic bidentate  $\eta^0:\eta^2:\mu_2$ -type coordination, which represents the most common bridging motif in structurally characterized  $\text{Bi}^{\text{III}}$  complexes with dipicolinate ligands (Stavila *et al.*, 2006). According to the nomenclature proposed by Serezhkin *et al.* (2009), the coordination type of



## Experimental

All reagents were obtained commercially. Bismuth(III) oxide (466 mg, 1.0 mmol) and pyridine-2,6-dicarboxylic acid (668 mg, 4.0 mmol) were stirred under reflux in water (400 ml) until most of the oxide had dissolved. The filtered solution was reacted with freshly prepared cobalt(II) or nickel(II) basic carbonate, obtained upon reaction of aqueous solutions of the transition metal nitrates with excess sodium carbonate. The solutions of the  $\text{Co}^{\text{II}}\text{--Bi}^{\text{III}}$  and  $\text{Ni}^{\text{II}}\text{--Bi}^{\text{III}}$  compounds were filtered and allowed to stand for crystallization at ambient temperature. Light-pink crystals of (I) and light-green crystals of (II) were obtained after 3–4 weeks.

### Compound (I)

#### Crystal data

$[\text{Co}(\text{H}_2\text{O})_6][\text{Bi}_2(\text{C}_7\text{H}_4\text{NO}_4)_4]\cdot 2\text{H}_2\text{O}$   $\gamma = 97.44 (3)^\circ$   
 $M_r = 1281.43$   $V = 892.1 (3) \text{ \AA}^3$   
 Triclinic,  $P\bar{1}$   $Z = 1$   
 $a = 7.2966 (15) \text{ \AA}$   $\text{Mo } K\alpha$  radiation  
 $b = 11.184 (2) \text{ \AA}$   $\mu = 10.40 \text{ mm}^{-1}$   
 $c = 12.004 (2) \text{ \AA}$   $T = 293 \text{ K}$   
 $\alpha = 112.99 (3)^\circ$   $0.21 \times 0.16 \times 0.11 \text{ mm}$   
 $\beta = 90.67 (3)^\circ$

#### Data collection

Bruker CCD 1000 area-detector diffractometer 10685 measured reflections  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996) 4176 independent reflections  
 $T_{\text{min}} = 0.219$ ,  $T_{\text{max}} = 0.394$  3914 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.035$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$  H atoms treated by a mixture of independent and constrained refinement  
 $wR(F^2) = 0.063$   $\Delta\rho_{\text{max}} = 1.10 \text{ e \AA}^{-3}$   
 $S = 1.07$   $\Delta\rho_{\text{min}} = -1.73 \text{ e \AA}^{-3}$   
 4176 reflections  
 292 parameters  
 12 restraints

### Compound (II)

#### Crystal data

$[\text{Ni}(\text{H}_2\text{O})_6][\text{Bi}_2(\text{C}_7\text{H}_4\text{NO}_4)_4]\cdot 2\text{H}_2\text{O}$   $\gamma = 97.33 (3)^\circ$   
 $M_r = 1281.21$   $V = 891.0 (3) \text{ \AA}^3$   
 Triclinic,  $P\bar{1}$   $Z = 1$   
 $a = 7.2615 (15) \text{ \AA}$   $\text{Mo } K\alpha$  radiation  
 $b = 11.210 (2) \text{ \AA}$   $\mu = 10.48 \text{ mm}^{-1}$   
 $c = 12.014 (2) \text{ \AA}$   $T = 293 \text{ K}$   
 $\alpha = 112.96 (3)^\circ$   $0.17 \times 0.14 \times 0.12 \text{ mm}$   
 $\beta = 90.79 (3)^\circ$

#### Data collection

Bruker CCD 1000 area-detector diffractometer 10920 measured reflections  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996) 4214 independent reflections  
 $T_{\text{min}} = 0.269$ ,  $T_{\text{max}} = 0.366$  3837 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.030$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$  H atoms treated by a mixture of independent and constrained refinement  
 $wR(F^2) = 0.050$   $\Delta\rho_{\text{max}} = 1.06 \text{ e \AA}^{-3}$   
 $S = 1.06$   $\Delta\rho_{\text{min}} = -0.85 \text{ e \AA}^{-3}$   
 4214 reflections  
 292 parameters  
 12 restraints

**Table 1**

Selected geometric parameters for (I) and (II) ( $\text{\AA}$ ,  $^\circ$ ).

	(I) ( $M = \text{Co}$ )	(II) ( $M = \text{Ni}$ )
M1—O1	2.094 (3)	2.063 (3)
M1—O2	2.084 (3)	2.049 (3)
M1—O3	2.044 (3)	2.024 (3)
Bi1—N1	2.494 (3)	2.497 (3)
Bi1—N2	2.372 (3)	2.378 (3)
Bi1—O11	2.682 (3)	2.688 (3)
Bi1—O13	2.307 (3)	2.310 (3)
Bi1—O21	2.498 (3)	2.510 (3)
Bi1—O23	2.269 (3)	2.277 (3)
Bi1—O11 <sup>i</sup>	2.493 (3)	2.504 (3)
Bi1···O24 <sup>ii</sup>	3.122 (4)	3.085 (3)
N1—Bi1—O11	62.07 (10)	62.04 (8)
N1—Bi1—O13	67.02 (11)	67.39 (9)
N1—Bi1—O23	73.56 (11)	73.46 (10)
N2—Bi1—O21	65.75 (11)	65.72 (9)
N2—Bi1—O23	68.79 (11)	68.68 (9)
O11—Bi1—O23	72.66 (11)	79.49 (10)
O13—Bi1—O21	78.84 (11)	78.75 (9)
O13—Bi1—O23	93.19 (12)	93.28 (10)

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

**Table 2**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for (I).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O1—H1A···O12 <sup>i</sup>	0.836 (10)	2.04 (2)	2.848 (5)	163 (6)
O1—H1B···O12 <sup>ii</sup>	0.835 (10)	2.079 (12)	2.913 (5)	177 (6)
O2—H2A···O4 <sup>iii</sup>	0.836 (10)	1.778 (14)	2.607 (6)	171 (6)
O2—H2B···O21 <sup>iv</sup>	0.837 (10)	2.002 (11)	2.839 (5)	178 (5)
O3—H3A···O22 <sup>iv</sup>	0.839 (10)	1.807 (17)	2.631 (5)	167 (6)
O3—H3B···O14 <sup>v</sup>	0.841 (10)	1.958 (17)	2.785 (5)	167 (6)
O4—H4A···O14 <sup>vi</sup>	0.840 (10)	2.11 (6)	2.885 (7)	153 (12)
O4—H4B···O24 <sup>vii</sup>	0.839 (10)	2.07 (2)	2.898 (7)	171 (11)

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

**Table 3**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for (II).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O1—H1A···O12 <sup>i</sup>	0.832 (10)	2.030 (13)	2.856 (4)	172 (5)
O1—H1B···O12 <sup>ii</sup>	0.835 (10)	2.095 (11)	2.927 (4)	174 (4)
O2—H2A···O4 <sup>iii</sup>	0.839 (10)	1.771 (11)	2.608 (5)	175 (4)
O2—H2B···O21 <sup>iv</sup>	0.838 (10)	2.023 (13)	2.852 (4)	170 (4)
O3—H3A···O22 <sup>iv</sup>	0.839 (10)	1.803 (11)	2.634 (4)	170 (4)
O3—H3B···O14 <sup>v</sup>	0.835 (10)	2.04 (3)	2.796 (4)	151 (4)
O4—H4A···O14 <sup>vi</sup>	0.835 (10)	2.19 (6)	2.895 (6)	142 (8)
O4—H4B···O24 <sup>vii</sup>	0.837 (10)	2.15 (4)	2.944 (6)	157 (8)

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

C-bound H atoms were located in calculated positions and constrained to ride on their parent atoms, with  $\text{C—H} = 0.93 \text{ \AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . Water H atoms were found in a difference Fourier map and included in the refinement with the restraints  $\text{O—H} = 0.84 (1) \text{ \AA}$  and  $\text{H}\cdots\text{H} \geq 1.33 (1) \text{ \AA}$ , and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ .

For both compounds, data collection: XSCANS (Bruker, 1997); cell refinement: XSCANS; data reduction: SHELXTL (Sheldrick, 2008); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick,

2008); molecular graphics: *SHELXTL*; 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: SQ3274). Services for accessing these data are described at the back of the journal.

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