Acta Crystallographica Section C Crystal Structure Communications ISSN 0108-2701

Hexaaquacobalt(II) and hexaaquanickel(II) bis(µ-pyridine-2,6-dicarboxylato)bis[(pyridine-2,6-dicarboxylato)bismuthate(III)] dihydrate

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Received 15 October 2010 Accepted 20 December 2010 Online 5 February 2011

The title complexes, hexaaquacobalt(II) bis(μ -pyridine-2,6dicarboxylato)bis[(pyridine-2,6-dicarboxylato)bismuthate-(III)] dihydrate, $[Co(H_2O)_6][Bi_2(C_7H_4NO_4)_4]\cdot 2H_2O$, (I), and hexaaquanickel(II) bis(μ -pyridine-2,6-dicarboxylato)bis[(pyridine-2,6-dicarboxylato)bismuthate(III)] dihydrate, [Ni(H₂O)₆]- $[Bi_2(C_7H_4NO_4)_4]$ ·2H₂O, (II), are isomorphous and crystallize in the triclinic space group $P\overline{1}$. The transition metal ions are located on the inversion centre and adopt slightly distorted MO_6 (M = Co or Ni) octahedral geometries. Two $[Bi(pydc)_2]^$ units (pydc is pyridine-2,6-dicarboxylate) are linked via bridging carboxylate groups into centrosymmetric [Bi2- $(pydc)_4$ ²⁻ dianions. The crystal packing reveals that the $[M(H_2O)_6]^{2+}$ cations, $[Bi_2(pydc)_4]^{2-}$ anions and solvent water molecules form multiple hydrogen bonds to generate a supramolecular three-dimensional network. The formation of secondary Bi \cdots O bonds between adjacent $[Bi_2(pydc)_4]^{2-1}$ 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 (H₂pydc) 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 H₂pydc (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, H₂pydc acts as an O.N.O'-donor ligand to the metal ion to form fivemembered 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(µ-pyridine-2,6-dicarboxylato)bis[(pyridine-2,6-dicarboxylato)bismuthate(III)] dihydrate, (I), and hexaaquanickel(II) bis(μ -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 Bi(Hpydc)(pydc). Both compounds crystallize in the triclinic system (space group $P\overline{1}$) 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 Co-O and Ni-O distances (Fig. 1 and Table 1) (Guo et al., 2008; Morzyk-Ociepa, 2007). The primary coordination environment of Bi^{III} includes seven donor atoms, six from two tridentate pydc²⁻ ligands and one bridging O atom from an adjacent symmetry-related complex. The pydc²⁻ ligand is coordinated to the Bi^{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 $[Bi_2(pydc)_4]^{2-}$ dimer (Fig. 1).

The bridging C11–O11–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 Bi^{III} complexes with dipicolinate ligands (Stavila *et al.*, 2006). According to the nomenclature proposed by Serezhkin *et al.* (2009), the coordination type of



Figure 1

A view of the molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level. [Symmetry code: (A) -x + 1, -y + 1, -z + 1.] [A view of the molecular structure of (II) is available in the *Supplementary material*.]

the bridging aminocarboxylate ligand in (I) and (II) can be represented as T^{101} , indicating that one pydc²⁻ ion acts as a tridentate ligand towards one Bi^{III} atom and as a monodentate ligand towards the other. This type of coordination of the pvdc²⁻ ligand is also found in complexes of Tl^I, Pb^{II} and some lanthanides (Serezhkin et al., 2009). The nonbridging pydc²⁻ group has a coordination of type T^{001} , which represents the most frequent coordination mode in dipicolinate complexes and is typically adopted by the $bis(pydc^{2-})$ complexes of the first- and second-row transition metals. The crystal structures of other Bi^{III} complexes with H₂pydc exhibit similar coordination features. The dimeric structure of [Bi(Hpydc)(pydc)-(DMSO)]₂ (DMSO is dimethyl sulfoxide; Zevaco et al., 1992) displays octacoordinated Bi^{III} atoms surrounded by six donor atoms from the H_n pydc⁽²⁻ⁿ⁾⁻ ions, a bridging O atom from an adjacent complex and one O atom from a DMSO molecule. $\{[BiCl(H_2O)(pydc)]_2\}_n$ (Ranjbar *et al.*, 2001) contains only one pydc²⁻ group per Bi^{III} atom, with an additional chloride ligand to complete a pentagonal-bipyramidal environment. In $(pydaH)_2[Bi_2(pydc)_4(H_2O)_2]\cdot 4H_2O$ (pyda is pyridine-2,6-diamine; Ranjbar et al., 2003) and (phenH)₂[Bi₂(pydc)₄-(H₂O)₂]·5H₂O (phen is 1,10-phenanthroline; Sheshmani et al., 2005), the Bi^{III} centres are coordinated by two pydc²⁻ ions, a bridging carboxylate O atom and a water molecule. Interestingly, no Bi^{III}-OH₂ bonds were found in (creatH)₂[Bi₂-(pvdc)₄]·4H₂O (creatH is creatinine or 2-amino-1-methyl-5Himidazol-4-one; Agbabozorg et al., 2008). We have recently synthesized and determined the crystal structures of two bismuth(III) dipicolinate complexes with thiourea (tu) and thiosemicarbazide (tsc) (Stavila et al., 2009), viz. [Bi₆(pydc)₈- $(Hpydc)_2(tu)_8$ and $[Bi_2(pydc)_3(tsc)(H_2O)_2]\cdot H_2O$, which contain Bi-S bonds. In $[Bi_6(pydc)_8(Hpydc)_2(tu)_8]$, there are three independent Bi^{III} atoms connected by means of bridging





The network formed by hydrogen-bonding interactions (dashed lines) in (I). Aromatic H atoms have been omitted for clarity. The network in (II) is essentially identical.

carboxylate groups into hexanuclear Bi_6 units, while $[Bi_2(pydc)_3(tsc)(H_2O)_2] \cdot H_2O$ is a coordination polymer generated by bridging carboxylate groups.

The Bi···Bi distances in the { $[Bi(pydc)_2]_2$ ²⁻ dimers here are 4.2240 (9) and 4.2194 (9) Å for (I) and (II), respectively, which is somewhat shorter than the sum of the van der Waals radii (4.8 Å; Emsley, 1989). The transition metal and Bi^{III} atoms in (I) and (II) are separated by 6.3950 (13) and 6.3821 (13) Å, respectively. The interatomic distances and bond angles in (I) and (II) are statistically about the same (Table 1). The Bi–N distances found in the $[Bi_2(pydc)_4]^{2-}$ dimer correlate well with those in other structurally characterized Bi^{III} complexes with $pydc^{2-}$ ligands (Stavila *et al.*, 2006). The Bi–O distances are asymmetric, with the longest distance being to the bridging atom O11 [2.682 (3) and 2.688 (3) Å for (I) and (II), respectively], which is situated closer to the adjacent Bi^{III} atom of the dimer at 2.493 (3) and 2.504 (2) Å, respectively.

The extended three-dimensional structure of (I) and (II) shows layers of anions alternating with layers of cations along the *b* axis. Each anion layer contains dimeric $[Bi_2(pydc)_4]^{2-}$ complexes joined into chains by secondary $Bi \cdots O24^{ii}$ bonds [3.122 (4) and 3.085 (3) Å for (I) and (II), respectively; symmetry code: (ii) x - 1, y, z]. The layers are held together by a network of nearly linear $O-H\cdots O$ hydrogen bonds with medium to long $O\cdots O$ separations (Fig. 2, and Tables 2 and 3). The H atoms of all water molecules in the structure are involved in hydrogen bonds with the O atoms of other water molecules or carboxylate O atoms. The hydrogen bonds, secondary Bi-O bonds and electrostatic interactions between the cations and anions are the major packing forces that stabilize the crystal structures of compounds (I) and (II).

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 Co^{II} -Bi^{III} and Ni^{II}-Bi^{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

$$\begin{split} & [\mathrm{Co}(\mathrm{H}_2\mathrm{O})_6][\mathrm{Bi}_2(\mathrm{C}_7\mathrm{H}_4\mathrm{NO}_4)_4]\cdot 2\mathrm{H}_2\mathrm{O} \\ & M_r = 1281.43 \\ & \mathrm{Triclinic}, \ P\overline{1} \\ & a = 7.2966 \ (15) \ \text{\AA} \\ & b = 11.184 \ (2) \ \text{\AA} \\ & c = 12.004 \ (2) \ \text{\AA} \\ & \alpha = 112.99 \ (3)^{\circ} \\ & \beta = 90.67 \ (3)^{\circ} \end{split}$$

Data collection

Bruker CCD 1000 area-detector diffractometer Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) $T_{\rm min} = 0.219, T_{\rm max} = 0.394$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.024$ $wR(F^2) = 0.063$ S = 1.074176 reflections 292 parameters 12 restraints

Compound (II)

Crystal data

 $[\text{Ni}(\text{H}_2\text{O})_6][\text{Bi}_2(\text{C}_7\text{H}_4\text{NO}_4)_4]\cdot2\text{H}_2\text{O}$ $M_r = 1281.21$ Triclinic, $P\overline{1}$ a = 7.2615 (15) Å b = 11.210 (2) Å c = 12.014 (2) Å a = 112.96 (3)° $\beta = 90.79$ (3)°

Data collection

Bruker CCD 1000 area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 1996) T_{min} = 0.269, T_{max} = 0.366

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.021$ $wR(F^2) = 0.050$ S = 1.064214 reflections 292 parameters 12 restraints Mo $K\alpha$ radiation $\mu = 10.40 \text{ mm}^{-1}$ T = 293 K $0.21 \times 0.16 \times 0.11 \text{ mm}$

 $\gamma = 97.44 \ (3)^{\circ}$

Z = 1

V = 892.1 (3) Å³

10685 measured reflections 4176 independent reflections 3914 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.035$

H atoms treated by a mixture of independent and constrained refinement $\Delta \rho_{\rm max} = 1.10 \text{ e } \text{\AA}^{-3}$ $\Delta \rho_{\rm min} = -1.73 \text{ e } \text{\AA}^{-3}$

$$\begin{split} \gamma &= 97.33 \; (3)^{\circ} \\ V &= 891.0 \; (3) \; \text{\AA}^3 \\ Z &= 1 \\ \text{Mo } K\alpha \; \text{radiation} \\ \mu &= 10.48 \; \text{mm}^{-1} \\ T &= 293 \; \text{K} \\ 0.17 \; \times \; 0.14 \; \times \; 0.12 \; \text{mm} \end{split}$$

10920 measured reflections 4214 independent reflections 3837 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.030$

Table 1

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

	(I) $(M = \text{Co})$	(II) $(M = Ni)$
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 ⁱ	2.493 (3)	2.504 (3)
Bi1···O24 ⁱⁱ	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 (Å, $^{\circ}$) for (I).

$D - H \cdot \cdot \cdot A$	D-H	$H \cdots A$	$D \cdots A$	$D - \mathbf{H} \cdots A$
$\begin{array}{c} O1 - H1A \cdots O12^{i} \\ O1 - H1B \cdots O12^{ii} \\ O2 - H2A \cdots O4^{iii} \\ O2 - H2B \cdots O21^{iv} \\ O3 - H3A \cdots O22^{iv} \\ O3 - H3B \cdots O14^{v} \end{array}$	$\begin{array}{c} 0.836 \ (10) \\ 0.835 \ (10) \\ 0.836 \ (10) \\ 0.837 \ (10) \\ 0.839 \ (10) \\ 0.841 \ (10) \end{array}$	2.04 (2) 2.079 (12) 1.778 (14) 2.002 (11) 1.807 (17) 1.958 (17)	2.848 (5) 2.913 (5) 2.607 (6) 2.839 (5) 2.631 (5) 2.785 (5)	163 (6) 177 (6) 171 (6) 178 (5) 167 (6) 167 (6)
$\begin{array}{c} O4 - H4B \cdots O14^{\text{vi}} \\ O4 - H4B \cdots O24^{\text{vii}} \end{array}$	0.840(10) 0.839(10)	2.11 (6) 2.07 (2)	2.885 (7) 2.898 (7)	153 (12) 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 (Å, °) for (II).

$D - H \cdots A$	D-H	$H \cdots A$	$D \cdots A$	$D - \mathbf{H} \cdots A$
$O1-H1A\cdots O12^{i}$ $O1-H1B\cdots O12^{ii}$	0.832(10) 0.835(10)	2.030(13) 2.095(11)	2.856(4) 2 927(4)	172 (5) 174 (4)
$O2 - H2A \cdots O4^{iii}$ $O2 - H2B \cdots O21^{iv}$	0.839(10) 0.838(10)	1.771(11) 2.023(13)	2.608(5) 2.852(4)	175 (4) 170 (4)
$O3-H3A\cdots O22^{iv}$ $O3-H3B\cdots O14^{v}$	0.839(10) 0.835(10)	1.803(11) 2.04(3)	2.632(1) 2.634(4) 2.796(4)	170 (4) 151 (4)
$\begin{array}{c} O4 - H4A \cdots O14^{vi} \\ O4 - H4B \cdots O24^{vii} \end{array}$	0.835(10) 0.837(10)	2.19 (6) 2.15 (4)	2.895 (6) 2.944 (6)	142 (8) 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 C-H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. Water H atoms were found in a difference Fourier map and included in the refinement with the restraints O-H = 0.84 (1) Å and $H \cdots H \ge 1.33$ (1) Å, and with $U_{iso}(H) = 1.2U_{eq}(O)$.

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,

metal-organic compounds

2008); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The authors acknowledge financial support from CRDF (award No. MOE2-2850-CS-06) and the Robert A. Welch Foundation (C-0976).

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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