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## Crystal Structure

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

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The title complexes, hexaaquacobalt(II) bis( $\mu$-pyridine-2,6-dicarboxylato)bis[(pyridine-2,6-dicarboxylato)bismuthate(III)] dihydrate, $\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]\left[\mathrm{Bi}_{2}\left(\mathrm{C}_{7} \mathrm{H}_{4} \mathrm{NO}_{4}\right)_{4}\right] \cdot 2 \mathrm{H}_{2} \mathrm{O}$, (I), and hexaaquanickel(II) bis( $\mu$-pyridine-2,6-dicarboxylato)bis[(pyri-dine-2,6-dicarboxylato)bismuthate(III)] dihydrate, $\left[\mathrm{Ni}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]$ $\left[\mathrm{Bi}_{2}\left(\mathrm{C}_{7} \mathrm{H}_{4} \mathrm{NO}_{4}\right)_{4}\right] \cdot 2 \mathrm{H}_{2} \mathrm{O}$, (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 $M_{6}(M=\mathrm{Co}$ or Ni$)$ octahedral geometries. Two $\left[\mathrm{Bi}(\mathrm{pydc})_{2}\right]^{-}$ units (pydc is pyridine-2,6-dicarboxylate) are linked via bridging carboxylate groups into centrosymmetric $\left[\mathrm{Bi}_{2}-\right.$ $\left.(\text { pydc })_{4}\right]^{2-}$ dianions. The crystal packing reveals that the $\left[M\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ cations, $\left[\mathrm{Bi}_{2}(\text { pydc })_{4}\right]^{2-}$ anions and solvent water molecules form multiple hydrogen bonds to generate a supramolecular three-dimensional network. The formation of secondary $\mathrm{Bi} \cdots \mathrm{O}$ bonds between adjacent $\left[\mathrm{Bi}_{2}(\text { pydc })_{4}\right]^{2-}$ 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 $\left(\mathrm{H}_{2}\right.$ 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 $\mathrm{H}_{2}$ 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, $\mathrm{H}_{2}$ pydc acts as an $O, N, O^{\prime}$-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( $\mu$-pyridine-2,6-dicarboxylato)bis[(pyri-dine-2,6-dicarboxylato)bismuthate(III)] dihydrate, (I), and hexaaquanickel(II) bis( $\mu$-pyridine-2,6-dicarboxylato)bis[(pyri-dine-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 $\mathrm{Bi}(\mathrm{Hpydc})(\mathrm{pydc})$. 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 $\mathrm{Co}-\mathrm{O}$ and $\mathrm{Ni}-\mathrm{O}$ distances (Fig. 1 and Table 1) (Guo et al., 2008; Morzyk-Ociepa, 2007). The primary coordination environment of $\mathrm{Bi}^{\text {III }}$ includes seven donor atoms, six from two tridentate pydc ${ }^{2-}$ ligands and one bridging O atom from an adjacent symmetry-related complex. The pydc ${ }^{2-}$ ligand is coordinated to the $\mathrm{Bi}^{\mathrm{III}}$ centre in a conventional $O, N, O^{\prime}-$ 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 $\left[\mathrm{Bi}_{2}(\text { pydc })_{4}\right]^{2-}$ dimer (Fig. 1).

The bridging $\mathrm{C} 11-\mathrm{O} 11-\mathrm{O} 12$ 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 $\mathrm{Bi}^{\mathrm{III}}$ 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 $\mathrm{T}^{101}$, indicating that one pydc ${ }^{2-}$ ion acts as a tridentate ligand towards one $\mathrm{Bi}^{\mathrm{III}}$ atom and as a monodentate ligand towards the other. This type of coordination of the pydc ${ }^{2-}$ ligand is also found in complexes of $\mathrm{Tl}^{\mathrm{I}}, \mathrm{Pb}^{\mathrm{II}}$ and some lanthanides (Serezhkin et al., 2009). The nonbridging pydc ${ }^{2-}$ group has a coordination of type $\mathrm{T}^{001}$, which represents the most frequent coordination mode in dipicolinate complexes and is typically adopted by the bis $\left(\operatorname{pydc}^{2-}\right)$ complexes of the first- and second-row transition metals. The crystal structures of other $\mathrm{Bi}^{\mathrm{III}}$ complexes with $\mathrm{H}_{2}$ pydc exhibit similar coordination features. The dimeric structure of $[\mathrm{Bi}(\mathrm{Hpydc})(\mathrm{pydc})-$ (DMSO) $]_{2}$ (DMSO is dimethyl sulfoxide; Zevaco et al., 1992) displays octacoordinated $\mathrm{Bi}^{\mathrm{III}}$ atoms surrounded by six donor atoms from the $\mathrm{H}_{n}$ pydc $^{(2-n)-}$ ions, a bridging O atom from an adjacent complex and one O atom from a DMSO molecule. $\left\{\left[\mathrm{BiCl}\left(\mathrm{H}_{2} \mathrm{O}\right)(\text { pydc })\right]_{2}\right\}_{n}$ (Ranjbar et al., 2001) contains only one pydc ${ }^{2-}$ group per $\mathrm{Bi}^{\text {III }}$ atom, with an additional chloride ligand to complete a pentagonal-bipyramidal environment. In (pydaH) $)_{2}\left[\mathrm{Bi}_{2}(\text { pydc })_{4}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right] \cdot 4 \mathrm{H}_{2} \mathrm{O}$ (pyda is pyridine-2,6-diamine; Ranjbar et al., 2003) and (phenH) $)_{2}\left[\mathrm{Bi}_{2}(\text { pydc })_{4}{ }^{-}\right.$ $\left.\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right] \cdot 5 \mathrm{H}_{2} \mathrm{O}$ (phen is 1,10-phenanthroline; Sheshmani et al., 2005), the $\mathrm{Bi}^{\text {III }}$ centres are coordinated by two pydc ${ }^{2-}$ ions, a bridging carboxylate O atom and a water molecule. Interestingly, no $\mathrm{Bi}^{\mathrm{III}}-\mathrm{OH}_{2}$ bonds were found in (creatH) $)_{2}\left[\mathrm{Bi}_{2}-\right.$ (pydc) $\left.)_{4}\right] \cdot 4 \mathrm{H}_{2} \mathrm{O}$ (creatH is creatinine or 2-amino-1-methyl-5 H -imidazol-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. [ $\mathrm{Bi}_{6}(\text { pydc })_{8^{-}}$ $\left.(\mathrm{Hpydc})_{2}(\mathrm{tu})_{8}\right]$ and $\left[\mathrm{Bi}_{2}(\text { pydc })_{3}(\mathrm{tsc})\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right] \cdot \mathrm{H}_{2} \mathrm{O}$, which contain $\mathrm{Bi}-\mathrm{S}$ bonds. In $\left[\mathrm{Bi}_{6}(\text { pydc })_{8}(\mathrm{Hpydc})_{2}(\mathrm{tu})_{8}\right]$, there are three independent $\mathrm{Bi}^{\mathrm{III}}$ atoms connected by means of bridging


Figure 2
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 $\mathrm{Bi}_{6}$ units, while $\left[\mathrm{Bi}_{2}(\text { pydc })_{3}(\mathrm{tsc})\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right] \cdot \mathrm{H}_{2} \mathrm{O}$ is a coordination polymer generated by bridging carboxylate groups.

The $\mathrm{Bi} \cdots \mathrm{Bi}$ distances in the $\left\{\left[\mathrm{Bi}(\mathrm{pydc})_{2}\right]_{2}\right\}^{2-}$ dimers here are 4.2240 (9) and 4.2194 (9) $\AA$ for (I) and (II), respectively, which is somewhat shorter than the sum of the van der Waals radii ( $4.8 \AA$; Emsley, 1989). The transition metal and $\mathrm{Bi}^{\mathrm{III}}$ 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 $\mathrm{Bi}-\mathrm{N}$ distances found in the $\left[\mathrm{Bi}_{2}(\text { pydc })_{4}\right]^{2-}$ dimer correlate well with those in other structurally characterized $\mathrm{Bi}^{\mathrm{III}}$ complexes with pydc ${ }^{2-}$ ligands (Stavila et al., 2006). The $\mathrm{Bi}-\mathrm{O}$ distances are asymmetric, with the longest distance being to the bridging atom O11 [2.682 (3) and 2.688 (3) $\AA$ for (I) and (II), respectively], which is situated closer to the adjacent $\mathrm{Bi}^{\text {III }}$ 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 $\left[\mathrm{Bi}_{2}(\text { pydc })_{4}\right]^{2-}$ complexes joined into chains by secondary $\mathrm{Bi} \cdots \mathrm{O} 24^{i i}$ bonds [3.122 (4) and 3.085 (3) $\AA$ for (I) and (II), respectively; symmetry code: (ii) $x-1, y, z$ ]. The layers are held together by a network of nearly linear $\mathrm{O}-\mathrm{H} \cdots \mathrm{O}$ hydrogen bonds with medium to long $\mathrm{O} \cdots \mathrm{O}$ 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 $\mathrm{Bi}-\mathrm{O}$ 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 ( $466 \mathrm{mg}, 1.0 \mathrm{mmol}$ ) and pyridine-2,6-dicarboxylic acid $(668 \mathrm{mg}$, 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 $\mathrm{Co}^{\mathrm{II}}-\mathrm{Bi}^{\mathrm{III}}$ and $\mathrm{Ni}^{\mathrm{II}}-$ $\mathrm{Bi}^{\mathrm{III}}$ 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

$\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]\left[\mathrm{Bi}_{2}\left(\mathrm{C}_{7} \mathrm{H}_{4} \mathrm{NO}_{4}\right)_{4}\right] \cdot 2 \mathrm{H}_{2} \mathrm{O}$
$M_{r}=1281.43$
Triclinic, $P \overline{1}$
$a=7.2966$ (15) $\AA$
$b=11.184$ (2) $\AA$
$c=12.004$ (2) $\AA$
$\alpha=112.99(3)^{\circ}$
$\beta=90.67$ (3) ${ }^{\circ}$

## Data collection

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

## Refinement

$R\left[F^{2}>2 \sigma\left(F^{2}\right)\right]=0.024$
$w R\left(F^{2}\right)=0.063$
$S=1.07$
4176 reflections
292 parameters
12 restraints

## Compound (II)

## Crystal data

$\left[\mathrm{Ni}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]\left[\mathrm{Bi}_{2}\left(\mathrm{C}_{7} \mathrm{H}_{4} \mathrm{NO}_{4}\right)_{4}\right] \cdot 2 \mathrm{H}_{2} \mathrm{O}$
$M_{r}=1281.21$
Triclinic, $P \overline{1}$
$a=7.2615$ (15) $\AA$
$b=11.210$ (2) $\AA$
$c=12.014$ (2) $\AA$
$\alpha=112.96(3)^{\circ}$
$\beta=90.79$ (3) ${ }^{\circ}$

## Data collection

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

## Refinement

$R\left[F^{2}>2 \sigma\left(F^{2}\right)\right]=0.021$
$w R\left(F^{2}\right)=0.050$
$S=1.06$
4214 reflections
292 parameters
12 restraints
10920 measured reflections 4214 independent reflections 3837 reflections with $I>2 \sigma(I)$ $R_{\text {int }}=0.030$

H atoms treated by a mixture of independent and constrained refinement
$\Delta \rho_{\max }=1.06 \mathrm{e}^{\AA^{-3}}$
$\Delta \rho_{\min }=-0.85 \mathrm{e}_{\mathrm{m}} \mathrm{\AA}^{-3}$

$$
\begin{aligned}
& \gamma=97.44(3)^{\circ} \\
& V=892.1(3) \AA^{3} \\
& Z=1 \\
& \text { Mo } K \alpha \text { radiation } \\
& \mu=10.40 \mathrm{~mm}^{-1} \\
& T=293 \mathrm{~K} \\
& 0.21 \times 0.16 \times 0.11 \mathrm{~mm}
\end{aligned}
$$

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
$\Delta \rho_{\max }=1.10$ e $\AA^{-3}$
$\Delta \rho_{\min }=-1.73 \mathrm{e}^{\AA^{-3}}$
$\gamma=97.33(3)^{\circ}$
$V=891.0(3) \AA^{3}$
$Z=1$
Mo $K \alpha$ radiation
$\mu=10.48 \mathrm{~mm}^{-1}$
$T=293 \mathrm{~K}$
$0.17 \times 0.14 \times 0.12 \mathrm{~mm}$

Table 1
Selected geometric parameters for (I) and (II) $\left(\AA{ }^{\circ},^{\circ}\right)$.

|  | $(\mathrm{I})(M=\mathrm{Co})$ | $(\mathrm{II})(M=\mathrm{Ni})$ |
| :--- | :--- | :--- |
| $M 1-\mathrm{O} 1$ | $2.094(3)$ | $2.063(3)$ |
| $M 1-\mathrm{O} 2$ | $2.084(3)$ | $2.049(3)$ |
| $M 1-\mathrm{O} 3$ | $2.044(3)$ | $2.024(3)$ |
| 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 | $2.498(3)$ | $2.277(3)$ |
| Bi1-O23 | $2.269(3)$ | $2.504(3)$ |
| Bi1-O11 | $2.493(3)$ | $3.085(3)$ |
| Bi1-O24 | $3.122(4)$ |  |
|  |  | $62.04(8)$ |
| N1-Bi1-O11 | $62.07(10)$ | $67.39(9)$ |
| N1-Bi1-O13 | $67.02(11)$ | $73.46(10)$ |
| N1-Bi1-O23 | $73.56(11)$ | $65.72(9)$ |
| N2-Bi1-O21 | $65.75(11)$ | $68.68(9)$ |
| N2-Bi1-O23 | $68.79(11)$ | $79.49(10)$ |
| O11-Bi1-O23 | $72.66(11)$ | $78.75(9)$ |
| O13-Bi1-O21 | $78.84(11)$ | $93.28(10)$ |
| O13-Bi1-O23 | $93.19(12)$ |  |

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

Table 2
Hydrogen-bond geometry ( $\AA,^{\circ}$ ) for (I).

| $D-\mathrm{H} \cdots A$ | D-H | H $\cdots$ A | $D \cdots A$ | $D-\mathrm{H} \cdots A$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{O} 1-\mathrm{H} 1 A \cdots \mathrm{O} 12^{\text {i }}$ | 0.836 (10) | 2.04 (2) | 2.848 (5) | 163 (6) |
| $\mathrm{O} 1-\mathrm{H} 1 B \cdots \mathrm{O} 2^{\text {ii }}$ | 0.835 (10) | 2.079 (12) | 2.913 (5) | 177 (6) |
| $\mathrm{O} 2-\mathrm{H} 2 A \cdots \mathrm{O} 4^{\text {iii }}$ | 0.836 (10) | 1.778 (14) | 2.607 (6) | 171 (6) |
| $\mathrm{O} 2-\mathrm{H} 2 B \cdots \mathrm{O} 2{ }^{\text {iv }}$ | 0.837 (10) | 2.002 (11) | 2.839 (5) | 178 (5) |
| $\mathrm{O} 3-\mathrm{H} 3 A \cdots \mathrm{O} 22^{\text {iv }}$ | 0.839 (10) | 1.807 (17) | 2.631 (5) | 167 (6) |
| $\mathrm{O} 3-\mathrm{H} 3 \mathrm{~B} \cdots \mathrm{O} 14^{\mathrm{v}}$ | 0.841 (10) | 1.958 (17) | 2.785 (5) | 167 (6) |
| $\mathrm{O} 4-\mathrm{H} 4 A \cdots \mathrm{O} 14^{\text {vi }}$ | 0.840 (10) | 2.11 (6) | 2.885 (7) | 153 (12) |
| $\mathrm{O} 4-\mathrm{H} 4 \mathrm{~B} \cdots \mathrm{O} 24^{\text {vii }}$ | 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 ( $\AA,^{\circ}$ ) for (II).

| $D-\mathrm{H} \cdots A$ | $D-\mathrm{H}$ | $\mathrm{H} \cdots A$ | $D \cdots A$ | $D-\mathrm{H} \cdots A$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{O} 1-\mathrm{H} 14 \cdots \mathrm{O} 12{ }^{\text {i }}$ | 0.832 (10) | 2.030 (13) | 2.856 (4) | 172 (5) |
| $\mathrm{O} 1-\mathrm{H} 1 B \cdots \mathrm{O} 12^{\text {ii }}$ | 0.835 (10) | 2.095 (11) | 2.927 (4) | 174 (4) |
| $\mathrm{O} 2-\mathrm{H} 2 A \cdots \mathrm{O} 4^{\text {iii }}$ | 0.839 (10) | 1.771 (11) | 2.608 (5) | 175 (4) |
| $\mathrm{O} 2-\mathrm{H} 2 B \cdots \mathrm{O} 21^{\text {iv }}$ | 0.838 (10) | 2.023 (13) | 2.852 (4) | 170 (4) |
| $\mathrm{O} 3-\mathrm{H} 3 A \cdots \mathrm{O} 22^{\text {iv }}$ | 0.839 (10) | 1.803 (11) | 2.634 (4) | 170 (4) |
| $\mathrm{O} 3-\mathrm{H} 3 \mathrm{~B} \cdots \mathrm{O} 14^{\mathrm{v}}$ | 0.835 (10) | 2.04 (3) | 2.796 (4) | 151 (4) |
| $\mathrm{O} 4-\mathrm{H} 4 A \cdots \mathrm{O} 14^{\text {vi }}$ | 0.835 (10) | 2.19 (6) | 2.895 (6) | 142 (8) |
| $\mathrm{O} 4-\mathrm{H} 4 \mathrm{~B} \cdots \mathrm{O} 24^{\text {vii }}$ | 0.837 (10) | 2.15 (4) | 2.944 (6) | 157 (8) | constrained to ride on their parent atoms, with $\mathrm{C}-\mathrm{H}=0.93 \AA$ and $U_{\text {iso }}(\mathrm{H})=1.2 U_{\text {eq }}(\mathrm{C})$. Water H atoms were found in a difference Fourier map and included in the refinement with the restraints $\mathrm{O}-\mathrm{H}=0.84(1) \AA$ and $\mathrm{H} \cdots \mathrm{H} \geq 1.33(1) \AA$, and with $U_{\text {iso }}(\mathrm{H})=$ $1.2 U_{\mathrm{eq}}(\mathrm{O})$.

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.

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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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