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A new coordination mode of 6-methylnicotinic acid in *trans*-tetraaquabis(6-methylpyridine-3-carboxylato-*κO*)cobalt(II) tetrahydrate

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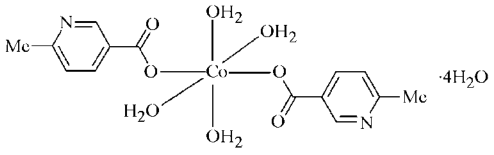
The title compound, $[Co(C_7H_6NO_2)_2(H_2O)_4]\cdot 4H_2O$, contains a Co^{II} ion lying on a crystallographic inversion centre. The Co^{II} ion is octahedrally coordinated by two 6-methylpyridine-3-carboxylate ligands in axial positions [Co—O = 2.0621 (9) Å] and by four water molecules in the equatorial plane [Co—O = 2.1169 (9) and 2.1223 (11) Å]. There are also four uncoordinated water molecules. The 6-methylpyridine-3-carboxylate ligands are bound to the Co^{II} ion in a monodentate manner through a carboxylate O atom. There is one strong intramolecular O—H···O hydrogen bond, and six strong intermolecular hydrogen bonds of type O—H···O and one of type O—H···N in the packing, resulting in a complex three-dimensional supramolecular structure.

Comment

As part of our wider research programme, we have recently studied (Popović *et al.*, 2006; Kukovec *et al.*, 2006; Kukovec, Popović, Pavlović & Rajić Linarić, 2007) the coordination modes of *N*,*O*-chelating ligands such as 3-hydroxy- and 6-hydroxypicolinic acids with late 3*d*-block metals, namely cobalt(II) and nickel(II). Complexes of these ligands with many transition metals have been extensively investigated owing to their biological significance and their great coordination potential.

In order to develop this structural diversity, we have extended our investigations to 3-methyl- and 6-methyl-substituted picolinic acid (Kukovec, Popović, Pavlović, Calhorda & Vaz, 2007). There are only a few such complexes reported in the literature, for example, complexes of zinc (Yoshikawa *et al.*, 2002; Pons *et al.*, 2004), cadmium (Kukovec, Popović & Pavlović, 2007), mercury(II) (González-Duarte *et al.*, 1998), cobalt(II) (March *et al.*, 2003) and silver (Leiva *et al.*, 1999), and a heteroleptic binuclear complex containing Cr^{III} and Sn^{IV} (Xu *et al.*, 2006). Consequently, we began to study more systematically the structural features of transition metal complexes derived from 6-methylnicotinic acid, as there are few structural data on complexes of nicotinic acid derivatives containing electron-donating substituents. To the best of our knowledge, only two such complexes, both with copper(I), have been reported (Aakeröy *et al.*, 2000).

The title compound, (I), contains a Co^{II} ion lying on a crystallographic inversion centre. The Co^{II} ion is octahedrally coordinated by two 6-methylpyridine-3-carboxylate ligands in the apical positions and by four water molecules in the equatorial plane (Table 1 and Fig. 1). The bond angles around the Co centre lie within the range 87–93° for the formally *cis* pairs of ligating atoms (Table 1). There are also four uncoordinated water molecules in (I). The 6-methylpyridine-3-carboxylate ligands are bound to the Co^{II} ion in a monodentate mode through a carboxylate O atom. This coordination mode has not been reported previously. There are only two polymeric copper(I) complexes reported hitherto containing 6-methylnicotinic acid bound to Cu^{I} through the pyridine N atom (Aakeröy *et al.*, 2000). By contrast, several papers (Waizumi *et al.*, 1998; Jia *et al.*, 2002; Yu *et al.*, 2006) report a cobalt(II) complex of nicotinic acid, $[Co(nic)_2(H_2O)_4]$, where the nicotinate ligand (nic) is bound to cobalt(II) through the pyridine N atom.



(I)

The Co—O(water) bond distance found here corresponds to the values found in the literature (Waizumi *et al.*, 1998; Jia *et al.*, 2002; Yu *et al.*, 2006). However, nicotinic acid *N*-oxide (N-nicO) is bound in a monodenate manner through a carboxylate O atom to the Co^{II} ion, as with 6-methylnicotinic acid in (I), in the similar complex $[Co(N\text{-}nicO)_2(H_2O)_4]$ (Knuuttila, 1983); the Co—O(carboxylate) bond distance in (I) is slightly shorter than the analogous bond in the latter complex [2.102 (1) Å; Knuuttila, 1983], while the Co—O(water) bond distances are slightly longer [2.072 (1) and 2.113 (2) Å; Knuuttila, 1983].

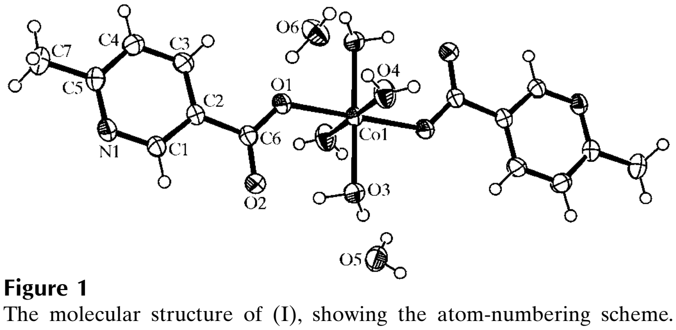


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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There are two polymeric cobalt(II) complexes with nicotinic acid, both with the carboxylate group bound in a bidentate manner to one Co^{II} ion (Yeh *et al.*, 2004; Feng *et al.*, 2006). One Co—O(carboxylate) bond distance in these complexes [2.054 (6) (Feng *et al.*, 2006) and 2.059 (6) Å (Yeh *et al.*, 2004)] corresponds to that in (I), while the other is significantly longer [2.441 (6) (Feng *et al.*, 2006) and 2.291 (7) Å (Yeh *et al.*, 2004)].

Two similar dinuclear cobalt(II) complexes (Ayyappan *et al.*, 2001; Xu *et al.*, 2007), containing a bridging water ligand, contain nicotinic acid bound in three different coordination modes, *viz*. monodentate through a carboxylate O atom or the pyridine N atom, and bidentate through carboxylate O atoms bridging two Co^{II} ions. The Co—O(carboxylate) bond distance in (I) is similar to various Co—O bond distances [in the ranges 2.052 (4)–2.112 (4) (Ayyappan *et al.*, 2001) and 2.035 (2)–2.136 (2) Å (Xu *et al.*, 2007)] in these cobalt(II) complexes. The carboxylate group geometry is not affected by coordination of one carboxylate O atom to the Co^{II} ion since the O1—C6 and O2—C6 bond distances of the carboxylate group [1.2573 (14) and 1.2595 (15) Å] are very similar.

There is one strong intramolecular hydrogen bond of type O—H⋯O, formed by coordinated water atom O3 and uncoordinated carboxylate atom O2, as well as six strong intermolecular hydrogen bonds of O—H⋯O type and one of O—H⋯N type in the packing of (I) (Table 2 and Fig. 2). Three of these are formed by coordinated water atoms O3 or O4 as donors and the uncoordinated water atoms O5 or O6 as acceptors, two are formed by water atoms O5 or O6 as donors and water atoms O3 or O2 as acceptors, and one is formed between water atom O6 and the pyridine N atom. There is also an intermolecular O—H⋯O hydrogen bond between water atoms O5 and O6. Thus, each of atoms O3, O4, O5 and O6 acts as a double donor, while only atoms O5 and O6 act as a double acceptor. The uncoordinated carboxylate atom O2, acting as a double acceptor, is the only O atom in the complex that participates in hydrogen-bond formation (Table 2). This complex hydrogen-bonding scheme links the molecular components into a three-dimensional supramolecular structure.

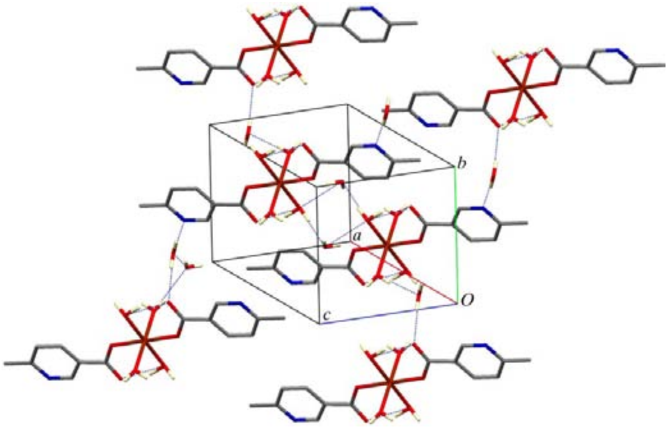

Figure 2
The crystal packing of (I), showing the three-dimensional hydrogen-bond network (represented by thin lines) formed by hydrogen bonds of the O—H⋯O type between water molecules, and between water molecules and carboxylate atom O2. The O—H⋯N hydrogen bond between water atom O6 and pyridine atom N1 also takes part in the network.

Experimental

A solution of 6-methylnicotinic acid (0.10 g, 0.70 mmol) in water (10 ml) was added to a solution of cobalt(II) acetate tetrahydrate (0.09 g, 0.36 mmol) in water (5 ml). The pH value of the resulting pink solution was 6, and concentrated ammonia solution was added dropwise until the pH of the solution was 7. The solution was left to stand for a month until a pink crystalline product, (I), was formed. This was filtered off, washed with a small portion of water and dried in air (yield 0.11 g, 64.7%). IR (KBr pellet, cm^{-1}): 3390 (*s*), 1604 (*s*), 1549 (*s*), 1404 (*s*), 1370 (*m*), 1286 (*m*), 1037 (*m*), 852 (*m*), 787 (*m*), 720 (*m*), 668 (*m*), 653 (*m*), 634 (*m*).

Crystal data

$[Co(C_7H_6NO_2)_2(H_2O)_4]\cdot 4H_2O$
$M_r = 475.31$
Triclinic, $P\bar{1}$
$a = 7.0284$ (2) Å
$b = 7.3655$ (2) Å
$c = 11.4912$ (4) Å
$\alpha = 86.829$ (2)°
$\beta = 78.746$ (3)°
$\gamma = 65.357$ (3)°
$V = 530.07$ (3) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 0.87$ mm^{-1}
$T = 296$ (2) K
0.53 × 0.33 × 0.07 mm

Data collection

Oxford Diffraction Xcalibur2 diffractometer with Sapphire-3 CCD detector
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2007)
$T_{min} = 0.720$, $T_{max} = 0.940$
14868 measured reflections
3062 independent reflections
2783 reflections with $I > 2\sigma(I)$
$R_{int} = 0.016$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.089$
$S = 1.12$
3062 reflections
166 parameters
8 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.82$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—O1	2.0621 (9)	O1—C6	1.2572 (14)
Co1—O3	2.1169 (9)	O2—C6	1.2595 (15)
Co1—O4	2.1223 (11)		
O1—Co1—O3	92.11 (4)	O3—Co1—O4	88.41 (5)
O1—Co1—O4	88.30 (4)		

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O3—H31⋯O5	0.90 (3)	1.93 (3)	2.821 (2)	174 (3)
O3—H32⋯O2	0.94 (2)	1.73 (3)	2.633 (2)	159 (3)
O4—H41⋯O6	0.81 (2)	1.97 (2)	2.774 (2)	171 (2)
O4—H42⋯O5^{ii}	0.78 (2)	2.11 (2)	2.878 (2)	169 (2)
O5—H51⋯O3^{iii}	0.79 (3)	2.28 (3)	2.984 (2)	148 (3)
O5—H52⋯O6^{i}	0.83 (4)	1.97 (4)	2.772 (2)	163 (3)
O6—H61⋯N1^{iv}	0.92 (2)	1.88 (2)	2.799 (2)	176 (2)
O6—H62⋯O2^{ii}	0.82 (3)	1.96 (3)	2.771 (2)	175 (3)

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

H atoms bonded to C atoms were introduced in calculated positions and refined using a riding model [C—H = 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) for aromatic H atoms, and C—H = 0.96 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) for methyl H atoms]. H atoms belonging to water molecules were found in difference Fourier maps, and the O—H distances were restrained to an average value of 0.90 (5) Å during refinement using the *SHELXL97* (Sheldrick, 1997) DFIX instruction.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3165). Services for accessing these data are described at the back of the journal.

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