metal-organic papers

Redetermination of *trans*-diaquabis(picolinato-κ²*N*,*O*)cobalt(II) dihydrate

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The crystal structure of the title compound, [Co(C₆H₄NO₂)₂(H₂O)₂]·2H₂O, has been reinvestigated with improved precision [previous reports: Chang *et al.* (1972). *J. Coord. Chem.* **2**, 31–34; Lumme *et al.* (1969). *Suom. Kemistil. B*, **42**, 270]. In the title compound, the Co atom is located on an inversion center and its coordination can be described as slightly distorted octahedral, equatorially *trans*-coordinated by two N and O atoms of two picolinate ligands and axially coordinated by two O atoms of the water molecules. Intermolecular O—H···O and C—H···O hydrogen-bonding interactions result in the formation of an intricate three-dimensional network.

Comment

Picolinic acid (pyridine-2-carboxylic acid) is a well known terminal tryptophan metabolite (Mahler & Cordes, 1971). It has biological activity to induce apoptosis in leukemia HL-60 cells, which is cell death characterized by DNA fragmentation (Ogata *et al.*, 2000). Pyridine-2-carboxylic acid and its analogs have been used increasingly in the synthesis of high-nuclearity transition metallacrowns with high spin values which could be used as single-molecule magnets (Sessoli *et al.*, 1993; Thomas *et al.*, 1996; Aubin *et al.*, 1996; Gatteschi *et al.*, 2000; Winpenny, 1999; Liu *et al.*, 2001). We report here a redetermination of the crystal structure of the title compound, (I), which has been determined previously by Chang *et al.* (1972) with a higher *R* value (0.097) and atom H8 removed from the atom list for suspected coordinate error(s) (Cambridge Structural Database, Version 5.26; Allen, 2002), and by Lumme *et al.* (1969) with no *R* value given.

(I)
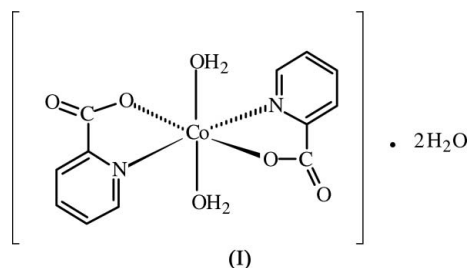
The complex molecule of (I) lies on an inversion center and thus the asymmetric unit contains only one half-complex. The coordination of the Co atom located on the inversion center is slightly distorted octahedral (Fig. 1). The Co atom is *trans*-coordinated by two carboxylic O atoms (O1) and two pyridine N atoms (N1) from two picolinate ligands and two O atoms (O1*W*) of two water molecules. The equatorial plane consists of N and O atoms from the two picolinate ligands and the axial
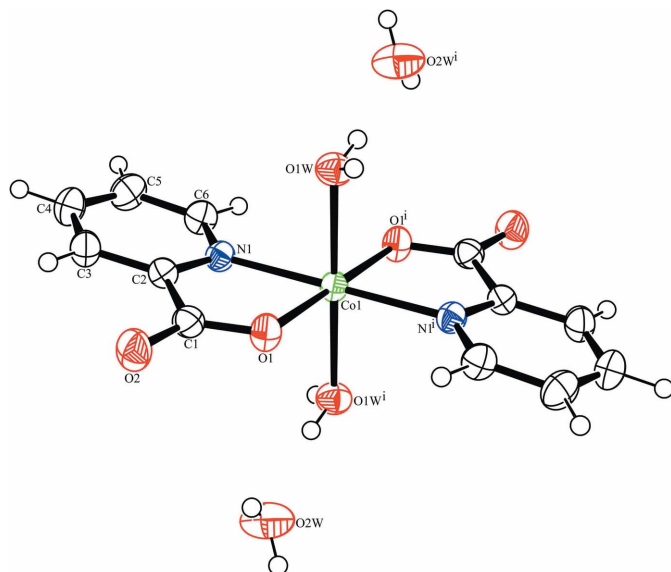
Figure 1
An *ORTEP-3* (Farrugia, 1997) drawing of the structure of (I), showing the atomic numbering. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level [symmetry code: (i) $1 - x$, $1 - y$, $1 - z$].
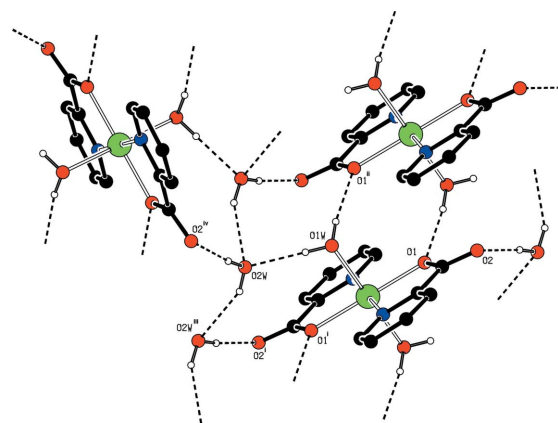

Figure 2
View showing the formation of a chain of rings through O—H···O hydrogen bonding. H atoms bonded to C atoms have been omitted. Hydrogen bonds are shown as dashed lines. [Symmetry code: (i) $1 - x$, $1 - y$, $1 - z$; (ii) $-x + 1$, $-y + 2$, $-z + 1$; (iii) $-x + 1$, $y - \frac{1}{2}$, $\frac{1}{2} - z$; (iv) x, $\frac{3}{2} - y$, $z - \frac{1}{2}$.]

positions are occupied by the water molecules. The bond lengths around the metal [Co—O1 = 2.065 (1) Å, Co—N1 = 2.119 (1) Å and Co—O1W = 2.138 (1) Å] fall into normal ranges.

There is an intricate hydrogen bonding network generated by O—H···O and C—H···O interactions. Atom O1W acts as a hydrogen-bond donor to water atom O2W and to carboxylate atom O1($-x + 1$, $-y + 2$, $-z + 1$), whereas O2W acts as a hydrogen-bond donor to the symmetry-related water molecule O2W($-x + 1$, $y - \frac{1}{2}$, $\frac{1}{2} - z$) and to the second carboxylate atom O2(x, $\frac{3}{2} - y$, $z - \frac{1}{2}$), so generating by translation a $C_3^3 C(6) C_3^3 C(8) C_2^2 (9) R_4^3 (10) R_3^3 (10)$ chain of rings (Bernstein *et al.*, 1995) running parallel to the [001] direction (Table 1 and Fig. 2). In addition, atom C3 of the pyridine ring acts as a hydrogen-bond donor to the carboxylate atom
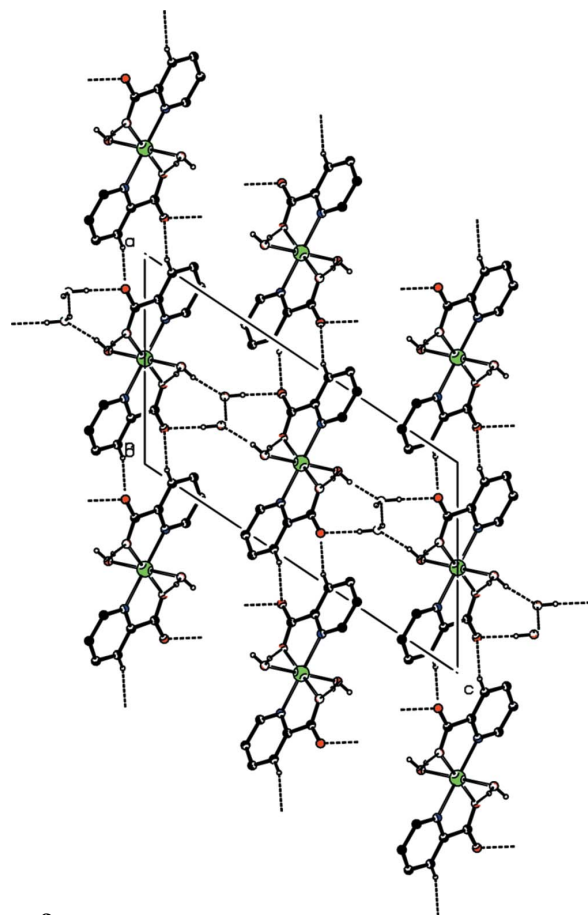

Figure 3
View down the *b* axis, showing the interconnection between the chains of rings. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted.

O2($-x$, $2 - y$, $1 - z$), generating an $R_2^2(10)$ ring linking the chains into a three-dimensional network (Fig. 3).

Experimental

A solution of picolinic acid (2.4 mmol, 0.29 g) in absolute ethanol (20 ml) was added dropwise with stirring to a solution of cobalt(II) acetate tetrahydrate (1.2 mmol, 0.30 g) in absolute ethanol (20 ml). The mixture was heated to 333 K in a temperature-controlled bath and stirred for 4 h. The reaction mixture was then cooled to room temperature. The orange crystals which formed were filtered off and washed with 10 ml of water and dried in air (yield 75%, based on Co). Chemical analyses found for $C_{12}H_{16}N_2NiO_8$: C 38.41, H 4.30, N 7.47%; calculated: C 37.92, H 4.17, N 7.35%.

Crystal data

$[Co(C_6H_4NO_2)_2(H_2O)_2]\cdot 2H_2O$	$D_x = 1.682$ Mg m^{-3}
$M_r = 375.20$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 14007
$a = 9.8093$ (9) Å	data
$b = 5.1846$ (3) Å	$\theta = 2.5$–$27.9°$
$c = 17.5233$ (16) Å	$\mu = 1.20$ mm^{-1}
$\beta = 123.780$ (6)°	$T = 296$ (2) K
$V = 740.74$ (11) Å^3	Plate, orange
$Z = 2$	$0.37 \times 0.19 \times 0.02$ mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: integration
  (X-$RED32$; Stoe & Cie, 2002)
  $T_{min} = 0.879$, $T_{max} = 0.961$
12035 measured reflections
1760 independent reflections

1441 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$
$\theta_{max} = 27.9°$
$h = -12 \rightarrow 12$
$k = -6 \rightarrow 6$
$l = -23 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.063$
$S = 1.03$
1760 reflections
118 parameters
H atoms treated by a mixture of
  independent and constrained
  refinement

$w = 1/[\sigma^2(F_o^2) + (0.0389P)^2 + 0.0458P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1W—H1A⋯O1^i	0.847 (9)	1.892 (10)	2.7300 (17)	169.9 (19)
O1W—H1B⋯O2W	0.84 (2)	1.956 (10)	2.7900 (19)	171 (2)
O2W—H2A⋯O2W^{ii}	0.832 (10)	2.150 (15)	2.9264 (18)	155 (3)
O2W—H2B⋯O2^{iii}	0.841 (10)	1.853 (10)	2.6891 (19)	173 (3)
C3—H3⋯O2^{iv}	0.93	2.54	3.447 (2)	166

Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (iv) $-x, -y+2, -z+1$.

C-bound H atoms were positioned geometrically and were treated as riding on their parent atoms, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The water H atoms were refined using bond restraints: O—H = 0.85 (1) Å, H⋯H = 1.39 Å and $U_{iso}(H) = 1.5U_{eq}(O)$.

Data collection: X-$AREA$ (Stoe & Cie, 2002); cell refinement: X-$AREA$; data reduction: X-$RED32$ (Stoe & Cie, 2002); program(s) used to solve structure: $SHELXS97$ (Sheldrick, 1997); program(s) used to refine structure: $SHELXL97$ (Sheldrick, 1997); molecular graphics: $ORTEP$-3 for $Windows$ (Farrugia, 1997) and $PLATON$ (Spek, 2003); software used to prepare material for publication: $WinGX$ (Farrugia, 1999).

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