

## METAL-ORGANIC COMPOUNDS

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### A Hydrated Cobalt(II) Complex of Quinolinic Acid: *trans*-[Co(C<sub>7</sub>H<sub>4</sub>NO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]

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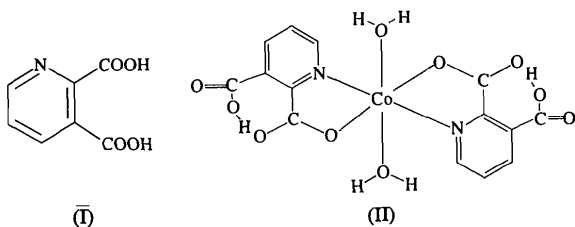
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#### Abstract

In *trans*-diaquabis(2,3-pyridinedicarboxylato-*N,O*)-cobalt(II), the Co atom lies on an inversion centre and has distorted octahedral coordination defined by two pyridine N atoms, two carboxylato O atoms and two water O atoms. The deprotonated carboxylate group at position 2 and the protonated carboxy group at position 3 are located nearly in the plane of the pyridine ring and are linked by an intramolecular hydrogen bond. The crystal structure is stabilized by intermolecular O—H···O hydrogen bonds between carboxy and water O atoms.

#### Comment

Quinolinic acid (pyridine-2,3-dicarboxylic acid), (I), is a well known tryptophan metabolite, a precursor of nicotinamide adenine dinucleotide (Murray, Granner, Mayes & Rodwell, 1993), has neurotoxic effects (Kalisch, Jhamandas, Boegman & Beninger, 1994; Espey, Moffett & Namboodiri, 1995) and is an agonist of the *N*-methyl-D-aspartate receptor (Mawatari, Oshida, Iinuma & Watanabe, 1995). It also forms chelate complexes with transition metals such as Mn, Co, Ni and Zn (Goher, Youssef, Zhou & Mak, 1993). It is important, therefore, to determine the crystal structures of the metal complexes of quinolinic acid in order to clarify its biological functions. Accordingly, the structure of the title complex, (II), a hydrated cobalt(II) complex of quinolinic acid, has been determined in this study.



The crystal structure of quinolinic acid has been analyzed by neutron diffraction (Kvick, Koetzle, Thomas & Takusagawa, 1974; Takusagawa & Koetzle, 1978)

and X-ray diffraction (Takusagawa, Hirotsu & Shimada, 1973), and the crystal structures of its Ni<sup>II</sup> and Mn<sup>II</sup> complexes have been reported previously (Goher, Youssef, Zhou & Mak, 1993). The molecular structure of (II) is shown in Fig. 1, with the unit-cell packing shown in Fig. 2. The Co<sup>II</sup> atom is coordinated octahedrally by two *trans* pyridine N atoms [Co(1)—N(1) 2.080 (2) Å], by two O atoms of the carboxylate groups at position 2 of (I) [Co(1)—O(1) 2.051 (2) Å] and by two *trans* water O atoms [Co(1)—O(5) 2.158 (2) Å]. The carboxy group at position 3 is not ionized and forms an intramolecular hydrogen bond to the carboxylate group at position 2, as observed in the structure of quinolinic acid itself [O(3)···O(2) 2.400 (2) Å]. This short O(3)···O(2) distance and the apparently long O(3)—H(4) bond (1.15 Å) correspond to a very strong and possibly symmetrical hydrogen bond. Both of the carboxy groups are nearly coplanar with the pyridine ring.

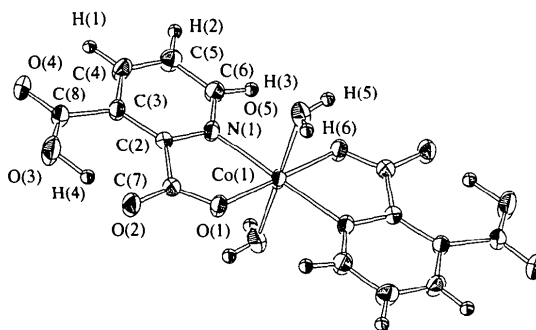


Fig. 1. An ORTEP drawing (Johnson, 1976) of the title compound with the atomic numbering scheme. Ellipsoids for non-H atoms correspond to 50% probability.

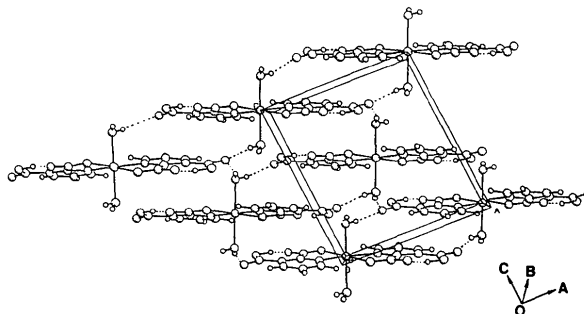


Fig. 2. A packing diagram of the title compound shown along the *a* axis of the unit cell, with intermolecular hydrogen bonds represented by dashed lines.

In the crystal structure, the molecules are connected by hydrogen bonds involving the carboxy group at position 3 of the pyridine ring and both H atoms of the coordinated water molecule: O(5)···O(4') 2.867 (2) Å

and O(5)··O(4<sup>ii</sup>) 2.814 (3) Å [symmetry codes: (i)  $-1+x, y, z$ ; (ii)  $\frac{5}{2}-x, -\frac{1}{2}+y, \frac{3}{2}-z$ ]. There are no significant contacts between adjacent pyridine rings.

C(5)	1.2724 (3)	0.4328 (3)	0.9586 (3)	2.6 (1)
C(6)	1.1630 (3)	0.3269 (3)	0.9872 (2)	2.35 (9)
C(7)	1.2575 (2)	-0.0976 (3)	0.8917 (2)	1.81 (8)
C(8)	1.5341 (2)	0.1367 (3)	0.8232 (2)	2.20 (9)

## Experimental

A light-brown prismatic crystal of the title compound was obtained by the slow evaporation at room temperature of an aqueous solution containing quinolinic acid and  $[\text{Co}(\text{NH}_4)_2(\text{SO}_4)_2] \cdot 6\text{H}_2\text{O}$  in a 2:1 molar ratio.

### Crystal data

$[\text{Co}(\text{C}_7\text{H}_4\text{NO}_4)_2(\text{H}_2\text{O})_2]$

$M_r = 427.19$

Monoclinic

$P2_1/n$

$a = 9.3096 (8) \text{ \AA}$

$b = 7.9319 (9) \text{ \AA}$

$c = 10.4302 (8) \text{ \AA}$

$\beta = 95.297 (7)^\circ$

$V = 766.9 (1) \text{ \AA}^3$

$Z = 2$

$D_x = 1.850 \text{ Mg m}^{-3}$

$D_m$  not measured

Mo  $K\alpha$  radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 24.75\text{--}25.00^\circ$

$\mu = 1.177 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Prism

$0.3 \times 0.3 \times 0.3 \text{ mm}$

Brown

### Data collection

Rigaku AFC-5R diffractometer

$\omega$ - $2\theta$  scans

Absorption correction: none

1995 measured reflections

1886 independent reflections

1604 observed reflections

$[I > 2\sigma(I)]$

$R_{\text{int}} = 0.015$

$\theta_{\text{max}} = 27.50^\circ$

$h = 0 \rightarrow 12$

$k = 0 \rightarrow 10$

$l = -13 \rightarrow 13$

3 standard reflections

monitored every 150

reflections

intensity decay: none

### Refinement

Refinement on  $F^2$

$R = 0.032$

$wR = 0.056$

$S = 2.73$

1604 reflections

124 parameters

H-atom parameters not refined; positions from  $\Delta\rho$  maps

$w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{\text{max}} = 0.020$

$\Delta\rho_{\text{max}} = 0.42 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.58 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$B_{\text{eq}} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	$x$	$y$	$z$	$B_{\text{eq}}$
Co(1)	1	0	1	1.82 (2)
O(1)	1.1406 (2)	-0.1580 (2)	0.9188 (2)	2.17 (6)
O(2)	1.3558 (2)	-0.1871 (2)	0.8519 (2)	2.67 (7)
O(3)	1.5515 (2)	-0.0176 (2)	0.7901 (2)	3.6 (1)
O(4)	1.6292 (2)	0.2411 (2)	0.8112 (2)	2.94 (7)
O(5)	0.8942 (2)	0.0567 (2)	0.8122 (2)	2.55 (7)
N(1)	1.1669 (2)	0.1617 (2)	0.9623 (2)	1.88 (7)
C(2)	1.2797 (2)	0.0925 (3)	0.9098 (2)	1.66 (8)
C(3)	1.3969 (2)	0.1924 (3)	0.8799 (2)	1.83 (8)
C(4)	1.3882 (3)	0.3647 (3)	0.9051 (2)	2.31 (9)

Table 2. Selected geometric parameters ( $\text{\AA}, ^\circ$ )

Co(1)—O(1)	2.051 (2)	N(1)—C(6)	1.337 (3)
Co(1)—O(5)	2.158 (2)	C(2)—C(3)	1.407 (3)
Co(1)—N(1)	2.080 (2)	C(2)—C(7)	1.531 (3)
O(1)—C(7)	1.246 (3)	C(3)—C(4)	1.396 (3)
O(2)—C(7)	1.259 (3)	C(3)—C(8)	1.522 (3)
O(3)—C(8)	1.286 (3)	C(4)—C(5)	1.369 (3)
O(4)—C(8)	1.227 (3)	C(5)—C(6)	1.374 (3)
N(1)—C(2)	1.346 (3)		
O(1)—Co(1)—O(5)	90.45 (6)	C(2)—C(3)—C(8)	128.2 (2)
O(1)—Co(1)—N(1)	77.44 (7)	C(4)—C(3)—C(8)	115.1 (2)
O(5)—Co(1)—N(1)	89.22 (7)	C(3)—C(4)—C(5)	121.7 (2)
Co(1)—O(1)—C(7)	117.6 (1)	C(4)—C(5)—C(6)	118.3 (2)
Co(1)—N(1)—C(2)	116.8 (1)	N(1)—C(6)—C(5)	121.6 (2)
Co(1)—N(1)—C(6)	122.3 (1)	O(1)—C(7)—O(2)	122.3 (2)
C(2)—N(1)—C(6)	121.0 (2)	O(1)—C(7)—C(2)	117.5 (2)
N(1)—C(2)—C(3)	120.7 (2)	O(2)—C(7)—C(2)	120.2 (2)
N(1)—C(2)—C(7)	110.5 (2)	O(3)—C(8)—O(4)	120.3 (2)
C(3)—C(2)—C(7)	128.7 (2)	O(3)—C(8)—C(3)	120.8 (2)
C(2)—C(3)—C(4)	116.7 (2)	O(4)—C(8)—C(3)	118.9 (2)

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985) and *DIREDF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MUI229). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Manganese Cupferronate

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### Abstract

In the title compound, bis(*N*-nitroso-*N*-phenylhydroxylaminato)manganese, [Mn(C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>], the Mn<sup>II</sup> ion has distorted octahedral coordination defined by four O atoms from two cupferron ligands and two O atoms of the nitroso groups of two adjacent cupferron ligands [Mn—O 2.142(2)–2.198(2) Å]. Each nitroso O atom coordinates to two Mn<sup>II</sup> ions resulting in an (—Mn—O—Mn—)<sub>n</sub> network. The plane of the nitrosohydroxylaminato group is nearly coplanar with that of the phenyl ring.

### Comment

As part of a series of studies aimed at clarifying the interaction modes of *N*-nitroso compounds with biologically important metal ions, the crystal structures of the Ni<sup>II</sup> and Al<sup>III</sup> complexes of cupferron, *N*-nitroso-*N*-phenylhydroxylamine, (I), have been determined (Okabe & Tamaki, 1995; Okabe, Tamaki, Suga & Kohyama, 1995). The structures of the related complexes iron cupferronate (van der Helm, Merritt & Degeilh, 1965), (*N*-nitroso-*N*-phenylhydroxylaminato-*O*,*O'*)bis(triphenylphosphine)copper(I) (Charalambous, Haines, Harris, Henrick & Taylor, 1984) and bis(cupferronato)copper(II) (Elerman, Atakol, Svoboda & Geselle, 1995) have been reported previously. In the

present study, the crystal structure of the Mn<sup>II</sup> complex of cupferron, (II), has been determined in order to clarify the binding scheme of the nitroso group to the Mn<sup>II</sup> ion.

The molecular structure of the title complex is illustrated in Fig. 1. The four O atoms of two cupferron ligands (*A* and *B*) coordinate to the Mn<sup>II</sup> ion and two O atoms of the nitroso groups of two adjacent cupferron ligands also coordinate to it from axial and equatorial directions. In each ligand, the plane of the nitrosohydroxylaminato group is nearly coplanar with that of the phenyl ring [O(1A)—N(1A)—N(2A)—O(2A) –0.7(4), O(1A)—N(1A)—C(1A)—C(6A) –16.9(5), O(1B)—N(1B)—N(2B)—O(2B) –0.7(4) and O(1B)—N(1B)—C(1B)—C(6B) 1.2(5)°] and the planes of the *A* and *B* ligands are nearly perpendicular to each other [O(1A)—

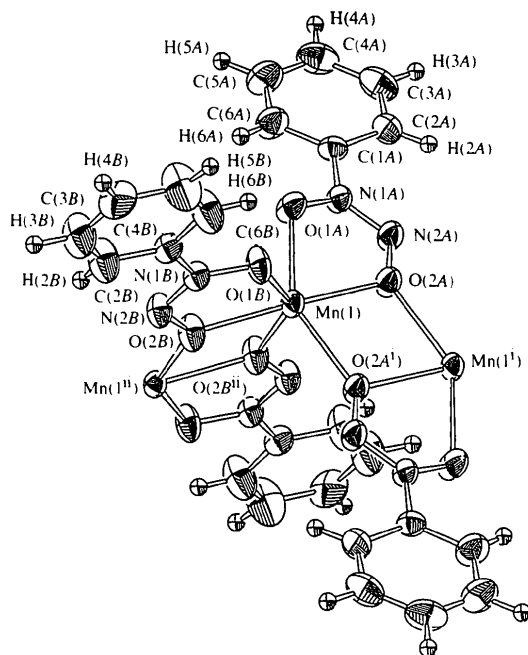


Fig. 1. An ORTEP (Johnson, 1976) drawing of the title compound with the atomic numbering scheme. Ellipsoids for non-H atoms correspond to 50% probability. Symmetry codes are as given in Table 2.

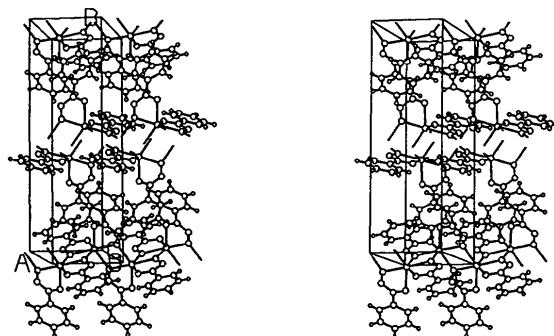


Fig. 2. Stereoview of the unit-cell packing of the title compound.

