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People's Republic of ChinaCorrespondence e-mail:
shangao67@yahoo.com**Key indicators**Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$
 R factor = 0.045
 wR factor = 0.128
Data-to-parameter ratio = 15.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**Diaquadiformatodipyridinecobalt(II)**

The Co^{II} atom in the title complex, $[\text{Co}(\text{CHO}_2)_2(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})_2]$, has an octahedral coordination geometry involving two O atoms of formate ligands, two pyridine N atoms and two water molecules. The Co atom lies on an inversion center. A supramolecular three-dimensional network structure is constructed by hydrogen bonds and π - π stacking interactions.

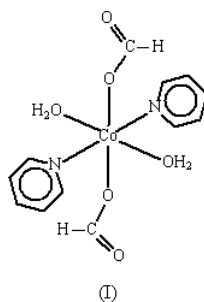
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Comment

Many structures of cobalt(II) complexes containing pyridine and organic carboxylic acids have been reported, in which the organic carboxylic acids mainly focus on acetic acid (Ye *et al.*, 2000; Lu *et al.*, 1998; Sumner *et al.*, 1985, 1988; Coucouvanis *et al.*, 1995), benzoic acid (Davies *et al.*, 1977), terephthalic acid (Pan *et al.*, 2000; Groeneman *et al.*, 1999) and 1,3,5-benzenetricarboxylic acid (Plater *et al.*, 1999). However, the complexes of pyridine and formic acid are less well documented. In the present study, the reaction of cobalt dichloride hexahydrate, pyridine, formic acid and benzene-1,4-dioxyacetic acid under basic conditions gave the title complex, (I), whose crystal structure is reported here.



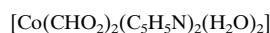
As shown in Fig. 1, the title complex has a mononuclear structure, in which each formate group is bonded to the Co^{II} atom in a monodentate fashion and the Co^{II} atom lies on a center of symmetry. The Co^{II} atom exists in an octahedral coordination environment, defined by two O atoms of different formate ligands [$\text{Co}-\text{O} = 2.081(2)\text{ \AA}$], two pyridine N atoms [$\text{Co}-\text{N} = 2.159(2)\text{ \AA}$] and two water molecules [$\text{Co}-\text{O} = 2.143(2)\text{ \AA}$]. The *cis* angles around the Co atom range from $86.70(7)$ to $93.30(7)^\circ$. The C6—O1 distance [$1.236(3)\text{ \AA}$] is slightly shorter than C6—O2 [$1.253(3)\text{ \AA}$], and the O1—C6—O2 angle is $126.6(2)^\circ$. Intermolecular hydrogen bonds are formed between the uncoordinated carboxy O atoms and water molecules, resulting in a two-dimensional layer framework structure (Table 2). There are π - π stacking interactions between adjacent pyridine rings of $3.77(4)\text{ \AA}$. A supramolecular three-dimensional network structure is

constructed by intermolecular hydrogen bonds and π - π stacking interactions (Fig. 2).

Experimental

The title complex was prepared by the addition of cobalt diacetate trihydrate (20 mmol), pyridine (3 ml) and formic acid (1 ml) to an aqueous solution of benzene-1,4-dioxyacetic acid (20 mmol), and the pH was adjusted to 6 with 0.1 M sodium hydroxide. Pink crystals were separated from the filtered solution after several days. Analysis calculated for $C_{12}H_{16}CoN_2O_6$: C 41.99, H 4.70, N 8.16%; found: C 41.71, H 4.83, N 8.06%.

Crystal data



$M_r = 343.20$

Monoclinic, $C2/c$

$a = 16.564$ (6) Å

$b = 6.300$ (2) Å

$c = 14.597$ (6) Å

$\beta = 109.73$ (2)°

$V = 1433.7$ (9) Å³

$Z = 4$

$D_x = 1.590$ Mg m⁻³

Mo $K\alpha$ radiation

Cell parameters from 4837

reflections

$\theta = 3.2$ – 27.5°

$\mu = 1.23$ mm⁻¹

$T = 293$ (2) K

Prism, pink

$0.45 \times 0.36 \times 0.22$ mm

Data collection

Rigaku R-Axis RAPID
diffractometer

ω scans

Absorption correction: multi-scan
(*ABSCOR*; Higashi, 1995)

$T_{\min} = 0.602$, $T_{\max} = 0.766$

5339 measured reflections

1641 independent reflections

1488 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.042$

$\theta_{\max} = 27.5^\circ$

$h = -21 \rightarrow 21$

$k = -7 \rightarrow 8$

$l = -18 \rightarrow 18$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.128$

$S = 1.07$

1641 reflections

103 parameters

H atoms treated by a mixture of
independent and constrained
refinement

$w = 1/[\sigma^2(F_o^2) + (0.0875P)^2 + 0.7449P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.87$ e Å⁻³

$\Delta\rho_{\min} = -0.54$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Co1–N1	2.159 (2)	O1–C6	1.236 (3)
Co1–O1	2.081 (2)	O2–C6	1.253 (3)
Co1–O1W	2.143 (2)		
N1–Co1–N1 ⁱ	180	O1–Co1–O1W	93.30 (7)
O1–Co1–N1	92.37 (7)	O1W–Co1–N1	91.68 (7)
O1 ⁱ –Co1–N1	87.63 (7)	O1W ⁱ –Co1–N1	88.32 (7)
O1 ⁱ –Co1–O1	180	O1W ⁱ –Co1–O1W	180
O1 ⁱ –Co1–O1W	86.70 (7)	O1–C6–O2	126.6 (2)

Symmetry code: (i) $\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1W–H1W1 ⁱⁱ –O2 ⁱⁱⁱ	0.86 (3)	1.98 (3)	2.810 (3)	163 (3)
O1W–H1W2 ⁱⁱⁱ –O2 ⁱⁱⁱ	0.86 (3)	1.95 (3)	2.773 (3)	163 (3)

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

C-bound H atoms were placed in calculated positions [$C-H = 0.97$ Å (aliphatic) and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$] in the riding-model

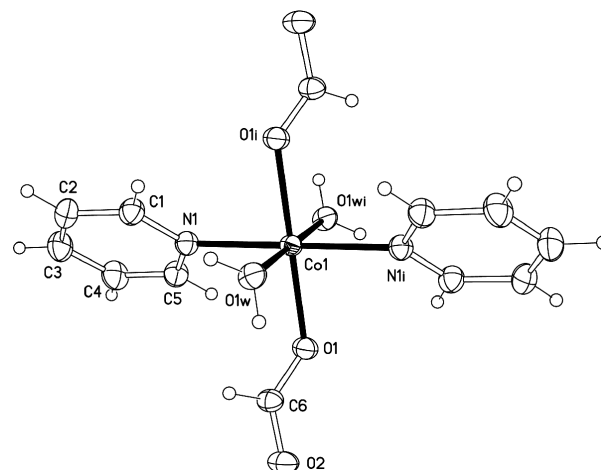


Figure 1

ORTEP II (Johnson, 1976) plot of (I), shown with 30% probability ellipsoids. [Symmetry code as in Table 1.]

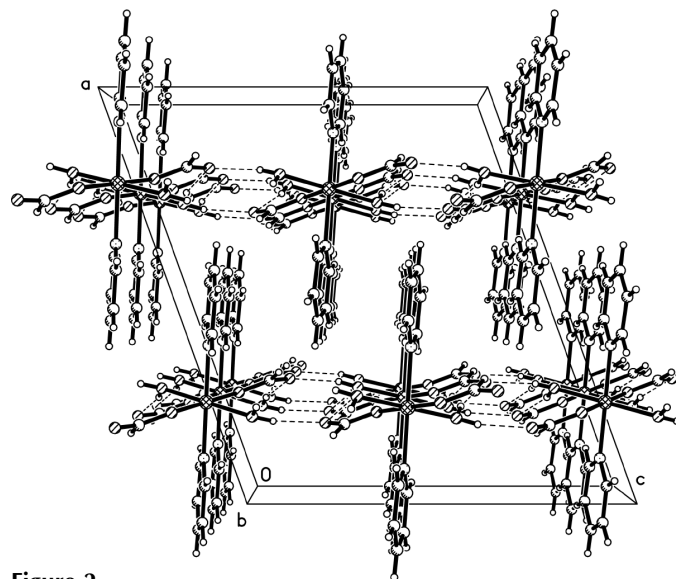


Figure 2

Packing diagram of (I).

approximation. Water H atoms were located in a difference Fourier map and refined using the riding-model approximation, with an O–H distance restraint of 0.85 (1) Å and $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(O)$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP II* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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References

- Coucovanis, D., Reynolds, R. A. & Dunham, W. R. (1995). *J. Am. Chem. Soc.* **117**, 7570–7571.
 Davies, J. E., Rivera, A. V. & Sheldrick, G. M. (1977). *Acta Cryst.* **B33**, 156–158.

- Groeneman, P. H., MacGillivray, L. R. & Atwood, J. L. (1999). *Inorg. Chem.* **38**, 208–209.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Lu, J., Yu, C., Niu, T.-Y., Paliwala, T., Crisci, G., Somosa, F. & Jacobson, A. J. (1998). *Inorg. Chem.* **37**, 4637–4640.
- Pan, L., Ching, N., Huang, X.-Y. & Li, J. (2000). *Inorg. Chem.* **39**, 5333–5340.
- Plater, M. J., Foreman, M. R. St J., Coronado, E., Gomez-Garcia, C. J. & Slawin, A. M. Z. (1999). *J. Chem. Soc. Dalton Trans.* pp. 4209–4216.
- Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Rigaku/MSO (2002). *CrystalStructure*. Rigaku/MSO, 9009 New Trails Drive, The Woodlands, TX 77381, USA.
- Sumner, C. E. (1988). *Inorg. Chem.* **27**, 1320–1327.
- Sumner, C. E. & Steinmetz, G. R. (1985). *J. Am. Chem. Soc.* **107**, 6124–6126.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Ye, B.-H., Chen, X.-M., Xue, F., Ji, L.-N. & Mak, T. C. W. (2000). *Inorg. Chim. Acta*, **299**, 1–8.