Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Diaqua(pyridine-2,4,6-tricarboxylato-κ^3N,O^2,O^6)-[4-(4-pyridyl)pyridinium-κN^1]cobalt(II) dihydrate

Cheng-Zhi Xie,* Jian-Hua Qin, Jian-Ge Wang, Chang-Bin Li and Yong-Feng Li

Department of Chemistry, Luoyang Normal University, Luoyang 471022, People's Republic of China

Correspondence e-mail:
xcz03@mails.tsinghua.edu.cn

Received 10 January 2007
Accepted 10 January 2007

Key indicators

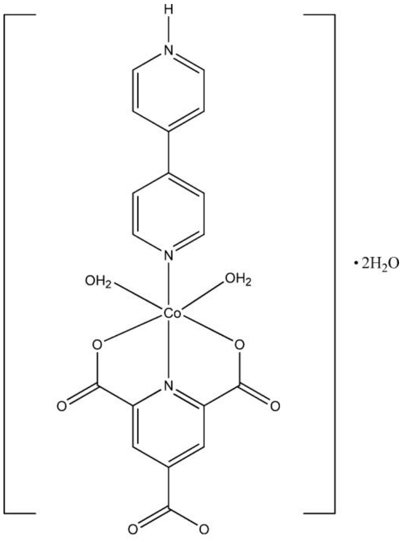
Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.002 Å
R factor = 0.028
wR factor = 0.076
Data-to-parameter ratio = 15.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title monomeric compound, $[Co(C_8H_2NO_6)(C_{10}H_9N_2)(H_2O)_2]\cdot 2H_2O$, the Co^{II} atom is in a distorted octahedral environment. Complex molecules are linked by extensive hydrogen bonds, forming a three-dimentional supramolecular structure.

Comment

Self-assembly processes involving metal ions and organic ligands and directed by either metal coordination or hydrogen bonds have received a great deal of attention over the past few decades in the fields of supramolecular chemistry and crystal engineering. Pyridine-2,4,6-tricarboxylic acid (ptcH$_3$) is an efficient ligand which acts as a multidentate ligand as well as a bridging linker in the chemical design of metal–organic molecular assemblies (Ghosh, El Fallah *et al.*, 2006; Ghosh, Savitha *et al.*, 2006; Ghosh & Bharadwaj, 2006, 2005*a*,*b*; Gao, Ding *et al.*, 2006; Gao, Yi *et al.*, 2006; Diao *et al.*, 2003). Weak intermolecular interactions, such as hydrogen bonding and π–π stacking, enable supramolecular assemblies by the creation of pyridine-2,4,6-tricarboxylate compounds (Ghosh & Bharadwaj, 2006, 2005*a*,*b*; Yigit *et al.*, 2006; Houser *et al.*, 2005). Taking advantage of the coordination ability of ptcH$_3$ with transition metals and introducing another organic ligand, namely 4,4′-bipyridine (4,4′-bpy), we synthesized a new mononuclear complex $[Co(ptc)(4,4'\text{-bpy})(H_2O)_2](H_2O)_2$, (I), with a three-dimensional supramolecular network structure.



(I)

The asymmetric unit of (I) comprises one mononuclear cobalt complex and two water molecules. The Co^{II} atom has a

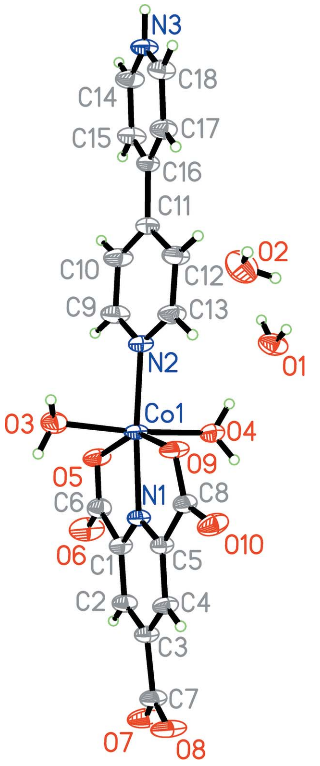


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids (small spheres for the H atoms) and the atom-numbering scheme.

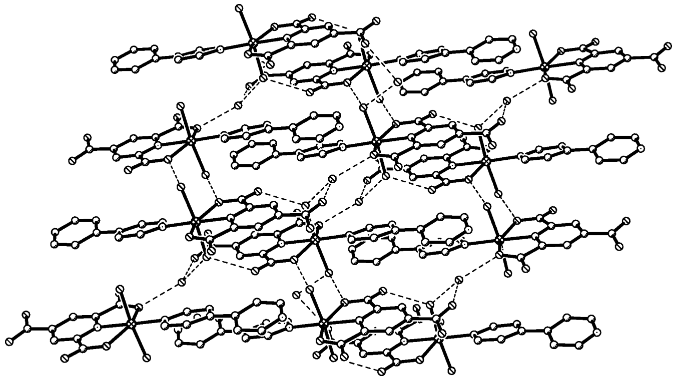


Figure 2
Perspective view of the three-dimensional network of (I), showing hydrogen bonds as dashed lines. H atoms have been omitted for clarity.

distorted octahedral geometry (Fig. 1) with equatorial coordination from N and two carboxylate O atoms of the ptc^{3-} ligand and one N atom of the 4,4′-bipyridine (4,4′-bpy) group. The two axial sites are occupied by water molecules. The uncoordinated N atom of the 4,4′-bpy is protonated. The two pyridyl rings are twisted from each other, with a dihedral angle of 18.3 **(su?)**°. All carboxyl groups of ptcH$_3$ are deprotonated, in agreement with the IR data in which no strong absorption peaks were observed around 1700 cm^{-1} for –COOH. The Co—N and Co—O distances are listed in Table 1.

The molecules are further connected by intricate N—H···O and O—H···O hydrogen-bonding interactions (Table 2), forming an overall three-dimensional structure (Fig. 2).

Experimental

The ligand ptcH$_3$ was prepared as described by Syper *et al.* (1980). Complex (I) was synthesized hydrothermally under autogenous pressure. A mixture of cobalt(II) perchlorate hexahydrate (73 mg, 0.2 mmol), ptcH$_3$ (42 mg, 0.2 mmol), 4,4′-bpy (32 mg, 0.2 mmol) and H$_2$O (8 ml) was sealed in a stainless steel reactor with a Teflon liner, which was heated to 433 K for 2 d. After slow cooling to room temperature at a rate of 2 K h^{-1}, orange block-shaped crystals of (I) were obtained by filtration; these were washed with distilled water and finally dried in air (50% yield).

Crystal data

$[Co(C_8H_2NO_6)(C_{10}H_9N_2)(H_2O)_2]\cdot 2H_2O$
M_r = 496.29
Triclinic, $P\bar{1}$
a = 8.6711 (9) Å
b = 10.7727 (12) Å
c = 11.5702 (13) Å
α = 95.8040 (10)°
β = 96.6040 (10)°
γ = 110.5470 (10)°
V = 993.62 (19) Å^3
Z = 2
D_x = 1.659 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.93 mm^{-1}
T = 291 (2) K
Block, orange
0.39 × 0.29 × 0.21 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.715, T_{max} = 0.832
8834 measured reflections
4478 independent reflections
3980 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 27.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.076
S = 1.05
4478 reflections
293 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0382P)^2 + 0.3303P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—N1	2.0386 (12)	O5—C6	1.2793 (19)
Co1—O4	2.0617 (12)	O6—C6	1.229 (2)
Co1—N2	2.1028 (13)	O7—C7	1.248 (2)
Co1—O3	2.1111 (12)	O8—C7	1.256 (2)
Co1—O5	2.1427 (12)	O9—C8	1.2738 (18)
Co1—O9	2.2150 (12)	O10—C8	1.2376 (19)
N1—Co1—O4	89.39 (5)	N2—Co1—O5	107.51 (5)
N1—Co1—N2	174.55 (5)	O3—Co1—O5	88.32 (5)
O4—Co1—N2	87.45 (5)	N1—Co1—O9	75.42 (5)
N1—Co1—O3	96.00 (5)	O4—Co1—O9	93.25 (5)
O4—Co1—O3	174.20 (4)	N2—Co1—O9	100.31 (5)
N2—Co1—O3	87.34 (5)	O3—Co1—O9	90.19 (5)
N1—Co1—O5	76.96 (5)	O5—Co1—O9	152.03 (4)
O4—Co1—O5	90.82 (5)		

Acta Cryst. (2007). E**63**, m498–m500 Xie *et al.* • $[Co(C_8H_2NO_6)(C_{10}H_9N_2)(H_2O)_2]\cdot 2H_2O$ **m499**

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O7^{i}	0.88 (3)	2.47 (3)	3.1036 (19)	129 (2)
N3—H3···O8^{i}	0.88 (3)	1.86 (3)	2.7309 (18)	172 (2)
O4—H8*W*···O1	0.83	1.85	2.6666 (17)	172.9
O1—H2*W*···O8^{ii}	0.84	2.02	2.8223 (17)	161.2
O2—H4*W*···O7^{iii}	0.83	1.93	2.7290 (18)	160.2
O1—H1*W*···O5^{iv}	0.84	1.91	2.7311 (16)	165.2
O2—H3*W*···O7^{ii}	0.84	2.05	2.875 (2)	166.0
O3—H5*W*···O9^{v}	0.82	1.95	2.7555 (16)	167.7
O3—H6*W*···O2^{v}	0.82	1.97	2.7981 (19)	176.7
O4—H7*W*···O10^{ii}	0.83	1.87	2.7043 (16)	178.5

Symmetry codes: (i) $x-2, y-1, z-1$; (ii) $-x+2, -y+2, -z+1$; (iii) $x-1, y, z-1$; (iv) $-x+1, -y+1, -z+1$; (v) $-x+1, -y+2, -z+1$.

The H atom attached to N3 was refined freely with an isotropic displacement parameter. The water H atoms were located in a difference map and their positions fixed. All other H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

This work was supported by the Natural Science Foundation of Henan province (No. 0311021200).

References

Bruker (1997). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Diao, Y.-X., Tian, Y., Zhan, S.-H., Zhang, W.-X., Jiao, X.-L. & Chen, D.-R. (2003). *Chin. Chem. Lett.* **14**, 740–743.

Gao, H.-L., Ding, B., Yi, L., Cheng, P., Liao, D.-Z., Yan, S.-P. & Jiang, Z.-H. (2006). *Inorg. Chem. Commun.* **8**, 151–154.

Gao, H.-L., Yi, L., Ding, B., Wang, H.-S., Cheng, P., Liao, D.-Z. & Yan, S.-P. (2006). *Inorg. Chem.* **45**, 481–483.

Ghosh, S. K. & Bharadwaj, P. K. (2005*a*). *Eur. J. Inorg. Chem.* pp. 4886–4889.

Ghosh, S. K. & Bharadwaj, P. K. (2005*b*). *J. Chem. Sci.* **117**, 23–26.

Ghosh, S. K. & Bharadwaj, P. K. (2006). *Inorg. Chim. Acta*, **359**, 1685–1689.

Ghosh, S. K., El Fallah, M. S., Ribas, J. & Bharadwaj, P. K. (2006). *Inorg. Chim. Acta*, **359**, 468–474.

Ghosh, S. K., Savitha, G. & Bharadwaj, P. K. (2006). *Cryst. Growth Des.* **6**, 63–69.

Houser, R. P. & Cheng, D. (2005). *Acta Cryst.* E**61**, m1649–m1651.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997*a*). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (1997*b*). *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.

Syper, L., Kloc, K. & Mlochowski, J. (1980). *Tetrahedron*, **36**, 123–129.

Yigit, M. V., Biyikli, K., Moulton, B. & MacDonald, J. C. (2006). *Inorg. Chim. Acta*, **6**, 63–69.

m500 Xie *et al.* • $[Co(C_8H_2NO_6)(C_{10}H_9N_2)(H_2O)_2]\cdot 2H_2O$ *Acta Cryst.* (2007). E**63**, m498–m500