

Aquaoxalato(2,4,6-tri-2-pyridyl-1,3,5-triazine)cobalt(II) tetrahydrate

De-Yi Cheng, Wei Xu and
Yue-Qing Zheng*State Key Laboratory Base of Novel Functional
Materials and Preparation Science, Faculty of
Materials Science and Chemical Engineering,
Ningbo University, Ningbo, Zhejiang 315211,
People's Republic of ChinaCorrespondence e-mail:
zhengyueqing@nbu.edu.cn

Key indicators

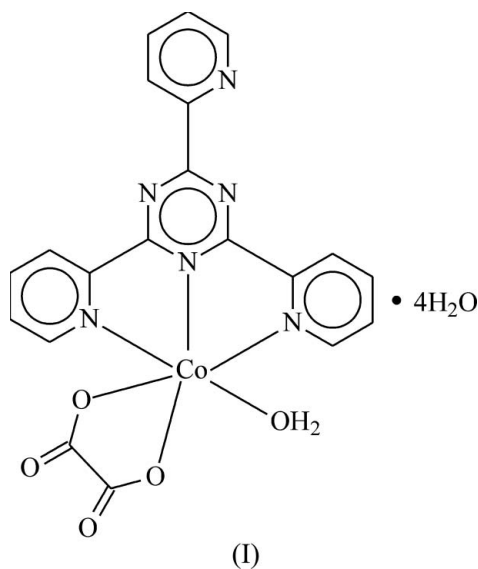
Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.040
 wR factor = 0.097
Data-to-parameter ratio = 15.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The asymmetric unit of the title compound consists of the complex molecule, $[\text{Co}(\text{C}_2\text{O}_4)(\text{C}_{18}\text{H}_{12}\text{N}_6)(\text{H}_2\text{O})]$, and four solvent water molecules. The complexes are assembled into one-dimensional double chains *via* hydrogen-bonding and weak $\pi-\pi$ interactions. These chains are further assembled through intermolecular $\pi-\pi$ stacking into two-dimensional layers. These are further aggregated to form a three-dimensional supramolecular structure *via* hydrogen bonding to chains of corner-sharing tetrameric and chair-like hexameric water clusters.

Received 19 August 2006
Accepted 7 September 2006

Comment

The ligand 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz) has been widely used as an analytical reagent for various metal ions for decades (Collins *et al.*, 1959; Byers *et al.*, 1996). It has attracted considerable interest as both a tridentate and a bidentate ligand, and is used as a spacer for designing novel complexes (Paul *et al.*, 1998; Chen *et al.*, 2001; Ghumaan *et al.*, 2006). Our interest in tptz transition metal complexes prompts us to report a new tptz complex, (I), obtained by self-assembly from Co^{II} , tptz and oxalate anions in aqueous methanolic solution.



The Co^{II} ion of (I) is in a six-coordinate distorted octahedral environment (Fig. 1, Table 1). The equatorial plane defined by atoms N1, N5, O1 and O5 is nearly perpendicular to the plane of tptz, with a dihedral angle of $87.16(6)^\circ$. One-dimensional chains of the complex molecules form along the a axis due to hydrogen-bonding interactions. These are coupled into double chains through weak $\text{C}-\text{H}\cdots\text{O}$ interactions between the

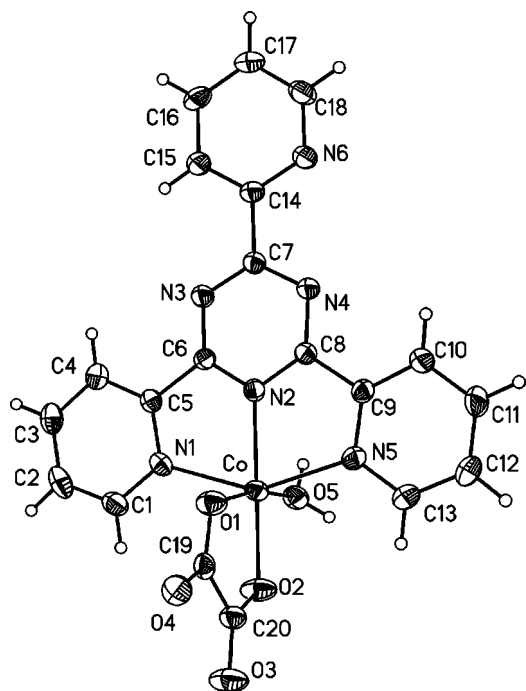


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 45% probability level. Solvent water molecules have been omitted.

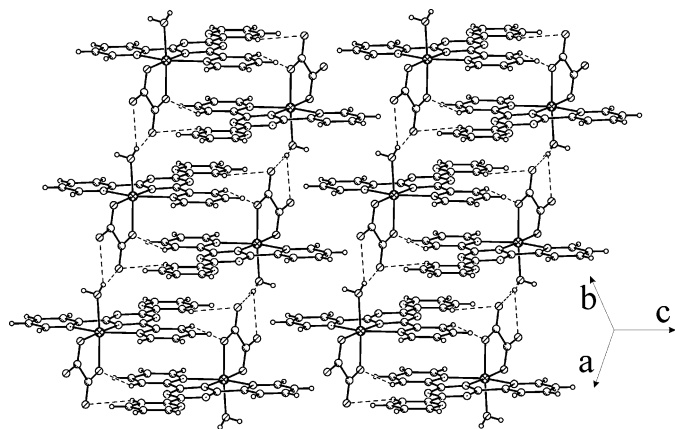


Figure 2
A view of the one-dimensional double chains formed by the $[\text{Co}(\text{H}_2\text{O})(\text{tptz})(\text{C}_2\text{O}_4)]$ molecules of (I) via hydrogen bonding (dashed lines) and π - π stacking interactions between two neighbouring chains.

oxalate anions and the tptz ligands (Table 2), and through intermolecular π - π stacking interactions with interplanar distances in the range 3.332–3.337 Å. A distance of 3.463 Å between the pyridine rings of two neighbouring double chains indicates further π - π stacking, which generates a two-dimensional layer structure along [100] (Fig. 2).

The uncoordinated water molecules appear both between these layers and outside them and are hydrogen bonded to one another. The O6 and O9 water molecules form rhombic tetrameric $(\text{H}_2\text{O})_4$ clusters, while the O7, O8 and O9 water molecules bind to give hexameric chair-like $(\text{H}_2\text{O})_6$ clusters.

These clusters are corner-shared by the one-dimensional chains that extend in the [100] direction. These form hydrogen bonds to the two-dimensional layers of complex molecules to achieve a three-dimensional supramolecular structure (Fig. 3).

Experimental

A 0.5 M NaOH solution (4.0 ml) was added dropwise to an aqueous solution (5.0 ml) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.238 g, 1.0 mmol) to produce a blue-green precipitate. This was centrifuged and washed with doubly distilled water until no Cl^- was observed in the supernatant liquid. The fresh precipitate was treated with a mixed solution of oxalic acid (0.126 g, 1.0 mmol) and tptz (0.314 g, 1.0 mmol) in $\text{MeOH-H}_2\text{O}$ (20 ml; 1:1 v/v) with continuous stirring. Slow evaporation of the final rose-coloured solution (pH = 2.96) at room temperature for several days afforded red platelet crystals of (I) suitable for single-crystal X-ray diffraction (yield 19.3%, based on $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$).

Crystal data

$[\text{Co}(\text{C}_2\text{O}_4)(\text{C}_{18}\text{H}_{12}\text{N}_6)(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$	$V = 1174.7(4) \text{ \AA}^3$
$M_r = 549.37$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.553 \text{ Mg m}^{-3}$
$a = 7.8902(16) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 11.730(2) \text{ \AA}$	$\mu = 0.79 \text{ mm}^{-1}$
$c = 13.988(3) \text{ \AA}$	$T = 298(2) \text{ K}$
$\alpha = 98.10(3)^\circ$	Platelet, red
$\beta = 102.80(3)^\circ$	$0.26 \times 0.21 \times 0.09 \text{ mm}$
$\gamma = 107.37(3)^\circ$	

Data collection

Rigaku R-Axis RAPID	11557 measured reflections
diffractometer	5312 independent reflections
ω scans	3985 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{\text{int}} = 0.034$
(ABSCOR; Higashi, 1995)	$\theta_{\text{max}} = 27.5^\circ$
$T_{\text{min}} = 0.761, T_{\text{max}} = 0.930$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0381P)^2 + 0.6021P]$
$R[F^2 > 2\sigma(F^2)] = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.097$	$(\Delta/\sigma)_{\text{max}} = 0.008$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.36 \text{ e \AA}^{-3}$
5312 reflections	$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$
355 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Co—O1	2.0750 (19)	Co—N1	2.247 (2)
Co—O2	2.0127 (19)	Co—N2	2.060 (2)
Co—O5	2.087 (2)	Co—N5	2.215 (2)
O2—Co—O1	80.15 (7)	O2—Co—N5	104.28 (9)
O1—Co—O5	169.28 (7)	O5—Co—N1	90.83 (8)
O2—Co—O5	89.29 (8)	N2—Co—O5	93.56 (8)
O1—Co—N1	90.46 (8)	O5—Co—N5	90.49 (8)
N2—Co—O1	97.04 (8)	N2—Co—N1	74.25 (8)
O1—Co—N5	93.92 (8)	N5—Co—N1	148.73 (8)
O2—Co—N1	106.98 (9)	N2—Co—N5	74.49 (8)
O2—Co—N2	176.89 (8)		

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O5—H5A...O4 ⁱ	0.83 (3)	1.94 (3)	2.754 (3)	165 (3)
O5—H5A...O3 ⁱ	0.83 (3)	2.56 (3)	3.069 (3)	121 (3)
O5—H5B...O7	0.82 (2)	1.93 (3)	2.749 (3)	172 (3)
O6—H6A...N6 ⁱⁱ	0.85 (4)	2.24 (4)	3.058 (4)	161 (3)
O6—H6B...O3	0.84 (4)	1.88 (4)	2.718 (3)	176 (3)
O7—H7A...O8 ⁱⁱⁱ	0.85 (4)	2.00 (3)	2.835 (4)	169 (4)
O7—H7B...O9 ^{iv}	0.82 (4)	2.05 (4)	2.859 (4)	168 (4)
O8—H8A...O9 ^v	0.86 (4)	1.98 (4)	2.833 (5)	171 (5)
O8—H8B...N6	0.85 (3)	2.27 (4)	3.060 (4)	154 (5)
O8—H8B...N4	0.85 (3)	2.69 (5)	3.375 (4)	139 (5)
O9—H9A...O6 ^{vi}	0.84 (4)	2.01 (5)	2.780 (5)	152 (5)
O9—H9B...O6 ^{vii}	0.86 (2)	2.00 (3)	2.841 (4)	166 (4)
C15—H15A...O4 ^{viii}	0.93	2.57	3.277 (3)	133
C4—H4A...O1 ^{viii}	0.93	2.55	3.395 (3)	151

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

All H atoms bound to C were positioned geometrically and refined as riding, with C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. H atoms attached to O were located in a difference Fourier map and refined isotropically, with O—H distances restrained to 0.85 (2) Å and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

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: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

This project was supported by the Expert Project of Key Basic Research of the Ministry of Science and Technology of China (grant No. 2003CCA00800), the Zhejiang Provincial Natural Science Foundation (grant No. Z203067) and the Ningbo Municipal Natural Science Foundation (grant No. 2006 A610061).

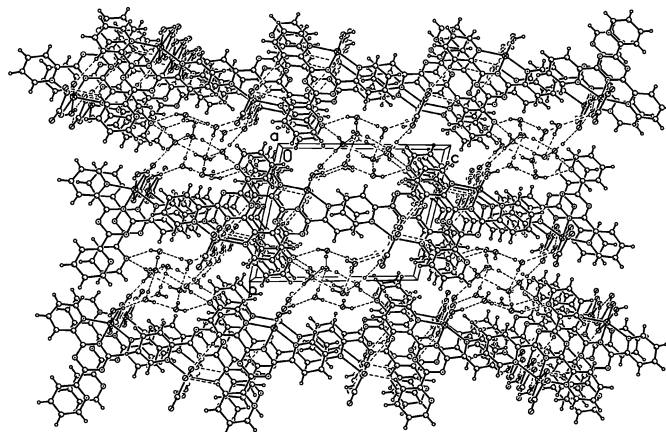


Figure 3
The packing of (I), showing the supramolecular layers stabilized by hydrogen-bonding interactions (dashed lines) between the water clusters and the chains of complex molecules.

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