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(5-Carboxy-1*H*-pyrazole-3-carboxylato-κ^2N^2,O^3)bis(1,10-phenanthroline-κ^2N,N')-cobalt(III) perchlorate 2.5-hydrate

Hui-Dong Xie, Cheng-Zhi Xie, Xiao-Qing Wang,* Guang-Qiu Shen and De-Zhong Shen

Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China

Correspondence e-mail:
xqwang@tsinghua.edu.cn

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Key indicators

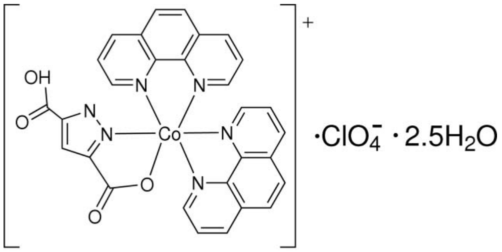
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.005 Å
Disorder in solvent or counterion
R factor = 0.044
wR factor = 0.129
Data-to-parameter ratio = 14.1

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

In the title mononuclear complex, $[Co(C_5H_2N_2O_4)(C_{12}H_8N_2)_2]ClO_4\cdot2.5H_2O$, the Co^{III} atom is in a slightly distorted octahedral environment, coordinated by four N atoms from two *N*,*N*′-bidentate phenanthroline ligands, and one O and one N atom of the 5-carboxy-1*H*-pyrazole-3-carboxylate ligand. The molecules are linked into a three-dimensional framework by O—H···O hydrogen bonds and π–π interactions.

Comment

Rigid ligands are most commonly used for the rational construction of various molecular architectures. The 5-carboxy-1*H*-pyrazole-3-carboxylate ligand is asymmetric and has six potential coordination sites which can link together metal centers through a number of bridging modes (King *et al.*, 2004). A variety of complexes containing this ligand have been reported (Bentiss *et al.*, 2004; Frisch *et al.*, 2005; King *et al.*, 2004, 2003; Li *et al.*, 2005; Pan, Ching *et al.*, 2001; Pan, Frydel *et al.*, 2001). We report here the structure of a mononuclear cobalt(III) complex with 5-carboxy-1H-pyrazole-3-carboxylate and phenanthroline ligands.



(I)

The Co^{III} atom has a distorted octahedral coordination geometry (Fig. 1 and Table 1), in which the 5-carboxy-1*H*-pyrazole-3-carboxylate group and phenanthroline ligands act in chelating modes. Four nitrogen atoms (N1–N4) from two phenanthroline ligands, a pyrazole N atom and a carboxylate O atom are coordinated to the Co^{III} atom to form an isolated complex cation. The Co—N bond length involving the 5-carboxy-1*H*-pyrazole-3-carboxylate ligand is shorter than those involving the phenanthroline ligands. One of the pyrazole N atoms (N5) and the coordinated carboxylate group are deprotonated, while the other carboxylic acid group is protonated but non-coordinated.

The molecules are connected by O—H···O hydrogen-bonding interactions (Table 2), forming a three-dimensional supramolecular network. The molecular packing is further stabilized by π-π interactions between the C16–C19/C23/C24

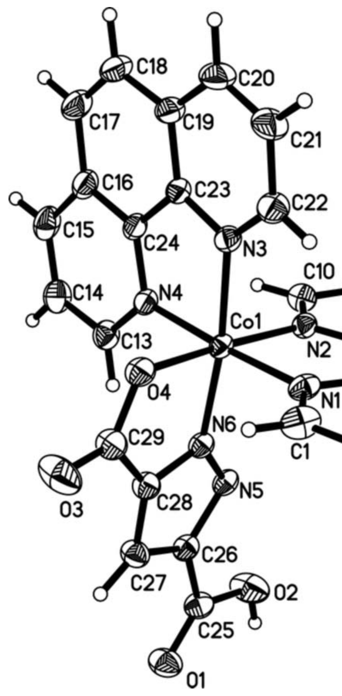


Figure 1
The structure the cation of (I), showing 30% probability displacement ellipsoids (small spheres for H atoms) and the atom-numbering scheme. The anion and the water molecules have been omitted for clarity.

benzene rings of the phenanthroline ligands at (x, y, z) and ($-x$, $1 - y$, $1 - z$), the centroid–centroid separation being 3.546 (2) Å.

Experimental

A mixture of $Co(ClO_4)_2{\cdot}6H_2O$ (0.4 mmol, 146 mg), phenanthroline (0.4 mmol, 79.3 mg), potassium 5-carboxy-1*H*-pyrazole-3-carboxylate (0.5 mmol, 97 mg) and H_2O (18.0 ml) in a 1:1:1.25:2500 molar ratio was sealed in a 25 ml stainless steel reactor with a Teflon liner; the mixture was heated to 433 K, kept at 433 K for 72 h, and then cooled to room temperature. After 2 days, orange block-shaped crystals of the title complex were collected by filtration (yield 70%). IR spectra analysis: strong characteristic bands corresponding to two carboxylic acid groups in the 5-carboxy-1H-pyrazole-3-carboxylate ligand were observed at 1689 and 1637 cm^{-1} for asymmetric stretching, and at 1490 and 1430cm^{-1} for symmetric stretching; the vibration frequencies of the phenanthroline ligand were shifted after coordination; the peak at 1605 cm^{-1} corresponding to ν(C=N) shifts to 1585 cm^{-1} upon coordination, while the phenanthroline ν(C=C) frequency of 1500 cm^{-1} was shifted to about 1521 cm^{-1} (Yang *et al.*, 2003). No N5-bound H atom was found as the infrared spectrum did not show a strong N—H absorption peak near 3490 cm^{-1}.

Crystal data

$[Co(C_5H_2N_2O_4)(C_{12}H_8N_2)_2]$-$ClO_4{\cdot}2.5H_2O$
$M_r = 717.91$
Monoclinic, $C2/c$
$a = 33.905$ (7) Å
$b = 9.6566$ (19) Å
$c = 23.237$ (5) Å
$\beta = 129.50$ (3)°
$V = 5870$ (2) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.75$ mm^{-1}
$T = 295$ (2) K
0.25 × 0.20 × 0.16 mm

Data collection

Rigaku R-AXIS RAPID IP area-detector diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.802$, $T_{max} = 0.866$
27567 measured reflections
6717 independent reflections
5351 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.129$
$S = 1.01$
6717 reflections
475 parameters
94 restraints
H-atom parameters constrained
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.51$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Co1—N6	1.887 (2)	O3—C29	1.222 (3)
Co1—O4	1.8968 (18)	O4—C29	1.302 (3)
Co1—N2	1.938 (2)	N5—N6	1.333 (3)
Co1—N1	1.942 (2)	N5—C26	1.363 (3)
Co1—N4	1.943 (2)	N6—C28	1.347 (3)
Co1—N3	1.954 (2)	C26—C27	1.388 (4)
O1—C25	1.210 (3)	C27—C28	1.375 (3)
O2—C25	1.315 (3)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W1···O3^i	0.85	1.91	2.756 (5)	175
O1W—H1W2···O8	0.85	2.28	3.121 (11)	173
O2—H2O···O1W	0.85	1.77	2.591 (5)	161
O2W—H2W1···O1	0.85	2.07	2.874 (4)	157
O3W—H3W1···O3	0.85	2.38	3.187 (8)	159

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

C-Bound H atoms were placed in geometrically idealized positions and were refined isotropically in the riding-model approximation, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. O-bound H atoms were initially located in difference Fourier maps and were refined isotropically in the riding-model approximation with O—H = 0.85 Å and $U_{iso}(H) = 1.5U_{eq}(O)$. The perchlorate ion is disordered over two positions with occupancies of 0.729 (10) and 0.271 (10). The Cl—O and O···O distances in each disordered component were restrained to be equal.

Data collection: *RAPID-AUTO* (Rigaku, 2004); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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