

Diazidobis(1,10-phenanthroline)cobalt(III) perchlorate

Xue-Yan Song, Xu-Da Wang,
Yun-He Xu and Li-Cun Li*Department of Chemistry, Nankai University,
Tianjin 300071, People's Republic of China

Correspondence e-mail: llicun@eyou.com

Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.009$ Å
 R factor = 0.047
 wR factor = 0.119
Data-to-parameter ratio = 9.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title cobalt(III) complex, $[\text{Co}(\text{N}_3)_2(\text{C}_{12}\text{H}_8\text{N}_2)_2]\text{ClO}_4$, has been synthesized and structurally characterized. The complex cations have distorted octahedral geometry, formed by two chelating 1,10-phenanthroline ligands and two azide ligands in a *cis* configuration. The cations and anions lie on twofold rotation axes. The ions are linked together into a linear one-dimensional chain by hydrogen bonding.

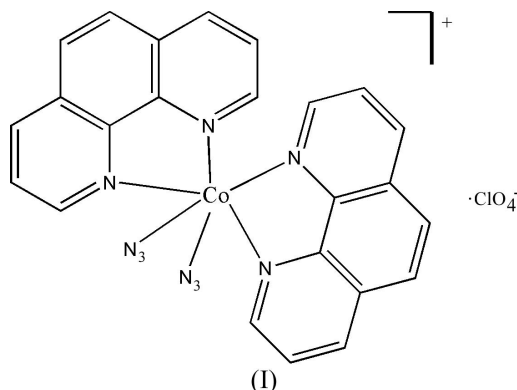
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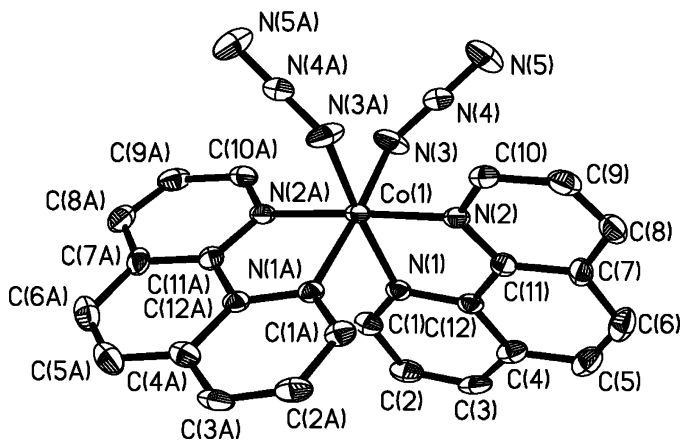
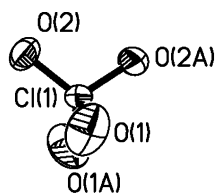
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Comment

Hydrogen-bonding interactions are of critical importance in biological systems, organic materials and coordination chemistry. Supramolecular architectures are of considerable contemporary interest by virtue of their potential applications in various fields. Recently, significant effort has been devoted to the crystal engineering of supramolecular architectures sustained by coordination, covalent bonding, hydrogen bonding or other intermolecular interactions, and their combination, owing to their fascinating structural diversity and potential application in the design of porous materials with novel inclusion or reactivity properties and in supramolecular devices such as sensors and indicators (Moulton & Zaworotko, 2001; Pan *et al.*, 2001; Ma *et al.*, 2001; Prior & Rosseinsky, 2001). In this report, a new complex, namely diazidobis(1,10-phenanthroline)cobalt(III) perchlorate, (I), has been synthesized, in which uncoordinated perchlorate anions are incorporated into a linear one-dimensional chain by hydrogen-bonding interactions.



The structure of (I) consists of cationic $[\text{Co}(\text{phen})_2(\text{N}_3)_2]^+$ units (phen is 1,10-phenanthroline) and non-coordinated perchlorate anions. The Co^{III} ion is hexacoordinate and possesses an MN_6 environment by virtue of two N atoms $[\text{N}3$ and $\text{N}3^i$; symmetry code: (i) $1 - x, 2 - y, z$] from two azide ions which occupy *cis* positions and four N atoms ($\text{N}1, \text{N}2, \text{N}1^i$


Figure 1

A displacement ellipsoid drawing of the title compound, with 30% probability ellipsoids. Symmetry code: (A) is $1 - x, 2 - y, -z$ for the cation and $1 - x, 1 - y, -z$ for the perchlorate anion.

and N2ⁱ) from two chelating phen groups. The average Co1–N(phen) bond length is 1.954 (5) Å, while the unique Co1–N(N₃) bond length is 1.924 (6) Å. Large deviations of bond angles from the value of 90° for an idealized octahedral geometry are found for N1–Co1–N2 [83.92 (2)°] and N3–Co1–N3ⁱ [92.1 (4)°]; the Co ion thus has a distorted octahedral coordination. The best equatorial plane is defined by atoms N1, N1ⁱ, N3 and N3ⁱ, with the largest deviation from the mean plane being 0.1024 Å for atom N3ⁱ; Co1 is located exactly in the plane. The apical positions are occupied by atoms N2 and N2ⁱ [Co1–N2 1.940 (4) and Co1–N2ⁱ 1.940 (4) Å].

Each perchlorate group acts as a bridging anion which is bound to two cations through hydrogen bonds, yielding a linear infinite chain structure. The hydrogen-bond length between a phen H atom and a perchlorate O atom is 2.53 (2) Å.

Experimental

A solution of 1,10-phenanthroline (0.2 mmol) in MeCN (10 ml) was added to a solution of Co(ClO₄)·6H₂O (0.4 mmol) in MeCN (10 ml). After stirring for 10 min, a solution of sodium azide (0.4 mmol) in water (10 ml) was added. The red–brown solution was filtered and the filtrate was allowed to stand undisturbed. Red–orange crystals of (I) were obtained after a week. The cobalt(II) was easily converted to cobalt(III) in the basic sodium azide solution.


Figure 2

The structure of the one-dimensional chain of the title compound. Dashed lines indicate hydrogen bonds.

Crystal data

[Co(N₃)₂(C₁₂H₈N₂)₂]ClO₄
 $M_r = 602.85$
 Orthorhombic, *Iba*2
 $a = 15.097$ (8) Å
 $b = 10.989$ (6) Å
 $c = 14.291$ (11) Å
 $V = 2371$ (2) Å³
 $Z = 4$
 $D_x = 1.689$ Mg m⁻³

Mo K α radiation
 Cell parameters from 933 reflections
 $\theta = 2.3$ – 23.5°
 $\mu = 0.89$ mm⁻¹
 $T = 293$ (2) K
 Block, red–orange
 0.20 × 0.18 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.638, T_{\max} = 0.870$
 5746 measured reflections

1640 independent reflections
 1317 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.048$
 $\theta_{\max} = 25.0^\circ$
 $h = -16 \rightarrow 17$
 $k = -13 \rightarrow 12$
 $l = -10 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.119$
 $S = 1.09$
 1640 reflections
 182 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0302P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.54$ e Å⁻³
 $\Delta\rho_{\min} = -0.58$ e Å⁻³
 Absolute structure: Flack (1983), with 553 Friedel pairs
 Flack parameter: 0.01 (4)

H atoms were located in difference Fourier maps and treated as riding, with C–H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART-NT (Bruker, 1998); cell refinement: SMART-NT; data reduction: SAINT-NT (Bruker, 1998); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL-NT (Bruker, 1998); software used to prepare material for publication: SHELXTL-NT.

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References

- Bruker (1998). SMART-NT, SAINT-NT and SHELXTL-NT. Versions 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Ma, B. Q., Gao, S., Sun, H. L. & Xu, G. X. (2001). *J. Chem. Soc. Dalton Trans.* pp. 130–133.
 Moulton, B. & Zaworotko, M. J. (2001). *Chem. Rev.* **101**, 1629–1658.
 Pan, L., Ching, N. & Huang, X. Y. (2001). *Chem. Eur. J.* **7**, 4431–4437.
 Prior, T. J. & Rosseinsky, M. J. (2001). *Chem. Commun.* pp. 1222–1223.
 Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
 Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.