

Bis(methyl 2-pyridylmethylidenehydrazine-carbodithioato)cobalt(III) perchlorate

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Received 2 August 2006
Accepted 8 September 2006

The brown cobalt(III) complex of the designed ligand bis(methyl 2-pyridylmethylidenehydrazinecarbodithioate) (HNNS), [Co(NNS)₂]ClO₄ or [Co(C₈H₈N₃S₂)₂]ClO₄, has been synthesized and characterized using single-crystal X-ray diffraction, elemental analysis and mass spectroscopic techniques. X-ray crystallography of the title compound has shown unambiguously that the crystallographic asymmetric unit consists of a [Co(NNS)₂]⁺ cation and one ClO₄⁻ anion. The two NNS⁻ ligands coordinate orthogonally to the central Co^{III} ion with a *mer* configuration.

Key indicators

Single-crystal X-ray study
T = 298 K
 Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
 Disorder in solvent or counterion
R factor = 0.048
wR factor = 0.126
 Data-to-parameter ratio = 17.3

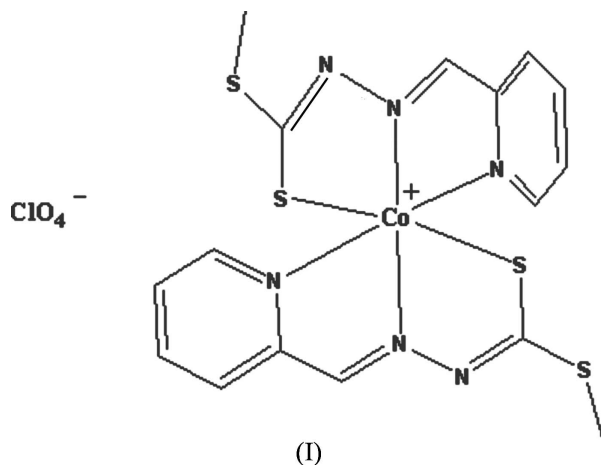
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Comment

The microbial enzyme nitrile hydratase (NHase) catalyzes the conversion of nitriles to amides and consists of an α,β -heterodimer containing either a low-spin Co^{III} or a Fe^{III} ion at its active site (Kobayashi & Shimizu, 1999). Although most of the reported model complexes of the Co^{III} site in Co-NHase contain thiolate sulfur donors, only a subset of them also include carboxamide nitrogen in their ligand sets (Noveron *et al.*, 1999). Kovacs and coworkers have consistently utilized Schiff base ligands with imine nitrogen donors to model the biological Co^{III} site (Shearer *et al.*, 2001). To date, many studies have been undertaken to investigate symmetrical and unsymmetrical Schiff bases formed from *N*-heterocyclic carboxaldehydes, thiosemicarbazides and alkyl hydrazinecarbodithioates, as well as their transition metal complexes. However, there have been only a few reports of the crystal structures of complexes containing the unsymmetrical Schiff base resulting from the condensation of 2-pyridine-carbaldehyde and methyl hydrazinecarbodithioate (Su *et al.*, 1999; Akbar Ali *et al.*, 2005). Recently, we have synthesized the Co^{III} complex of the S-containing Schiff base ligand methyl 2-pyridylmethylidenehydrazinecarbodithioate (NNS⁻) (see scheme) in order to check the reactivity of the imine N atom in such model complexes. In this paper, we report the crystal structure of the title cobalt complex containing NNS⁻, [Co(NNS)₂]ClO₄, (I).

Fig. 1 shows the molecular structure of complex (I), together with the atom-numbering scheme. In complex (I), the Co^{III} ion has a distorted octahedral coordination environment and a pair of monodeprotonated ligands (NNS⁻) coordinate to the Co^{III} ion through the thiolate S (S1 and S3), the pyridyl (tertiary) ring N (N1 and N4) and the azomethine N (N2 and N5) atoms. The crystallographic asymmetric unit in the complex consists of a [Co(NNS)₂]⁺ cation and one ClO₄⁻ anion, which is disordered. Two molecules of the tridentate methyl-2-pyridylmethylidenehydrazinecarbodithioate ligand coordinate to the Co^{III} ion to form four five-membered chelate

rings (Co1/N1/C3/C4/N2, Co1/S1/C5/N4/N3, Co1/N4/C13/C14/N5 and Co1/N5/N6/C15/S3).



The geometry about the Co^{III} ion in (I) compares well with those reported for other similar structures (West *et al.*, 1999). The shortening of the Co–N distance involving the azomethine N atoms relative to that of the pyridyl ring N atoms may be attributed to the fact that the azomethine N is a stronger base than the pyridyl N. The two azomethine N atoms (N2 and N5) are *trans* to each other, while the pyridyl ring N atoms (N1 and N4) and the thiolate S atoms (S1 and S3) are in the *cis* positions.

The two tridentate ligands (NNS[−]) in compound (I) are practically planar and orthogonal to each other; the dihedral angle between the two ligands is 92.87 (3)°. In addition, in each ligand three individual rings, namely the pyridine and the two five-membered chelate rings, are individually almost planar, with small dihedral angles between them. The largest dihedral angle of 9.3 (1)° is between the pyridyl ring N1/C1–C5 and the chelate ring Co1/S1/C7/N3/N2.

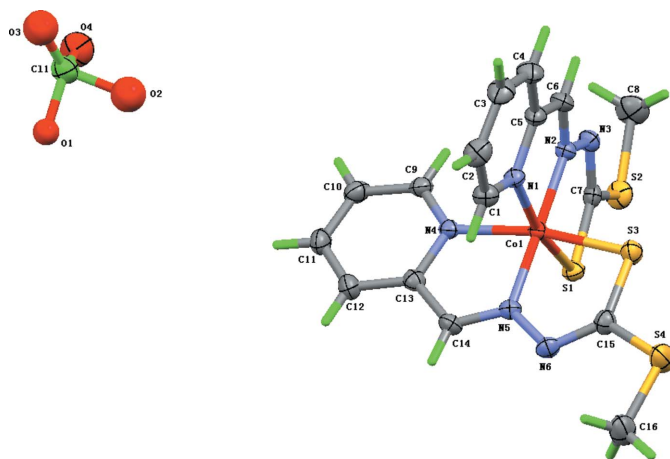


Figure 1
The asymmetric unit of compound (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Only one disorder component is shown.

Experimental

A solution of Co(ClO₄)₂ (134 mg, 0.50 mmol) in C₂H₅OH (20 ml) was slowly added to a solution of HNNS (210 mg, 1.00 mmol) in C₂H₅OH (10 ml) and the mixture was refluxed for 1 h in a water bath. On slow evaporation of the resulting dark-brown solution, the desired Co^{III} complex was obtained. The reddish brown solids were filtered off, washed with cold ethanol and dried over anhydrous CaCl₂ (yield 78%). Brown crystals of (I) were formed, suitable for X-ray diffraction. The assigned structure was substantiated by elemental analysis and MS data. Elemental analysis, calculated for C₁₆H₁₆ClCoN₆O₄S₄: C 33.04, H 2.01, N 14.02%; found: C 32.95, H 2.10, N 13.93%. FAB–MS *m/z* (%): 480(*M*⁺ + 1, 68), 479 (*M*⁺, 100).

Crystal data

[Co(C₈H₈N₃S₂)₂]ClO₄
M_r = 578.97
 Monoclinic, *P*₂₁/*c*
a = 10.783 (2) Å
b = 12.049 (2) Å
c = 17.613 (3) Å
 β = 93.249 (4)°
V = 2284.8 (7) Å³

Z = 4
D_x = 1.683 Mg m^{−3}
 Mo Kα radiation
 μ = 1.27 mm^{−1}
T = 298 (2) K
 Block, brown
 0.26 × 0.22 × 0.20 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
*T*_{min} = 0.734, *T*_{max} = 0.785

12549 measured reflections
 4990 independent reflections
 3204 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.034
 θ_{max} = 27.1°

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.048
wR(*F*²) = 0.126
S = 1.04
 4990 reflections
 289 parameters
 H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0535*P*)² + 2.4373*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δσ)_{max} = 0.005
 Δρ_{max} = 0.67 e Å^{−3}
 Δρ_{min} = −0.45 e Å^{−3}

Table 1

Selected geometric parameters (Å, °).

Co1–N2	1.884 (3)	Co1–N4	1.977 (3)
Co1–N5	1.888 (3)	Co1–S3	2.2294 (12)
Co1–N1	1.967 (3)	Co1–S1	2.2403 (11)
N2–Co1–N5	176.69 (13)	N1–Co1–S3	88.69 (10)
N2–Co1–N1	81.93 (13)	N4–Co1–S3	168.11 (9)
N5–Co1–N1	94.90 (13)	N2–Co1–S1	85.42 (10)
N2–Co1–N4	98.25 (13)	N5–Co1–S1	97.75 (10)
N5–Co1–N4	82.76 (13)	N1–Co1–S1	167.33 (9)
N1–Co1–N4	92.49 (12)	N4–Co1–S1	89.97 (9)
N2–Co1–S3	93.64 (10)	S3–Co1–S1	91.46 (5)
N5–Co1–S3	85.34 (10)		

Atoms O1, O2 and O3 of the ClO₄[−] anion were disordered over two positions, each with an occupancy factor of 0.5. All H atoms were placed in idealized positions, with C–H = 0.93–0.96 Å and constrained to ride on their parent atoms, with *U*_{iso}(H) = 1.2 or 1.5*U*_{eq}(C).

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

The authors are grateful for funding from the National Natural Science Foundation of China and the Natural Science Foundation of Guangdong Province.

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