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Bis{1-[(*E*)-2-pyridinylmethylidene]semicarbazide}cobalt(II) diperchlorate monohydrate

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Key indicators

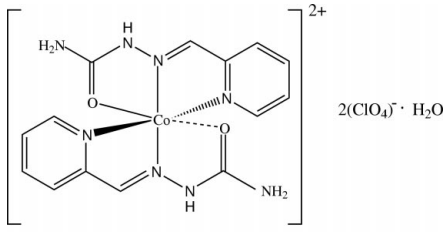
Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.005 Å
R factor = 0.051
wR factor = 0.105
Data-to-parameter ratio = 15.4

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

The Co atom in the title complex, $[Co(C_7H_8N_4O)_2](ClO_4)_2\cdot H_2O$, is octahedrally coordinated by two molecules of the neutral Schiff bases derived from the condensation of pyridine-2-carbaldehyde and semicarbazone; the Schiff base molecules act as meridional tridentate ligands, coordinating the metal through the amido O atom, imine N and pyridyl N atoms. The ligands are perpendicular to each other [dihedral angle = 87.27 (5)°]. The crystal packing is stabilized by intermolecular hydrogen bonds involving the cations, perchlorate counter-ions and water molecules.

Comment

The metal complexes of the Schiff bases that are synthesized from the condensation of pyridine-2-carbaldehyde and thiosemicarbazone, semicarbazone and other amines (Chen *et al.*, 2003; García-Tojal *et al.*, 2001; Kasuga *et al.*, 2001) are of practical applications owing to their antimicrobial, cytotoxic, antioxidant (Reddy, *et al.*, 1999; Tarafder *et al.*, 2001) and optical (Kwiat *et al.*, 1999) properties. A number of the complexes have been crystallographically authenticated (Alistair *et al.*, 1987; Kovala-Demertzi *et al.*, 1999; Wang *et al.*, 2004). For the complexes of the analogous ligand, pyridine-2-carbaldehyde semicarbazone, only limited spectroscopic measurements have been reported (Iskander *et al.*, 1979; Liang *et al.*, 2002).



(I)

The structure of the title compound, (I), consists of discrete $[Co(C_7H_8N_4O)_2]^{2+}$ cations, perchlorate counter-ions and water molecules. The two neutral semicarbazone ligands are planar, and each set of the coordinating amido O, imino N and pyridyl N atoms occupies a meridional plane of the octahedron around the Co atom. The Co1/N1/C5/C6/N2/N3/C7/O1 and Co1/N5/C12/C13/N6/N7/O2 planes are nearly perpendicular to each other [dihedral angle 87.27 (5)°]. The perchlorate counter-ion is not involved in coordination, a feature that is also observed in bis(pyridine-2-carbaldehyde thiosemicarbazonate)cobalt(III) perchlorate (Wang *et al.*, 2004). The pyridine-2-carbaldehyde semicarbazone ligands possess an *E* configuration with respect to the azomethine double bond.

The Co—N and Co—O coordination distances are comparable with those reported for other cobalt(II)

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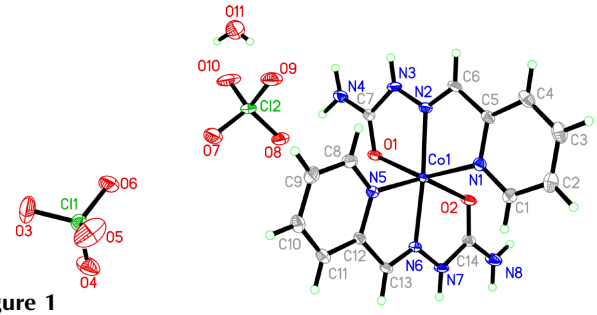

Figure 1
The asymmetric unit of compound (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme.

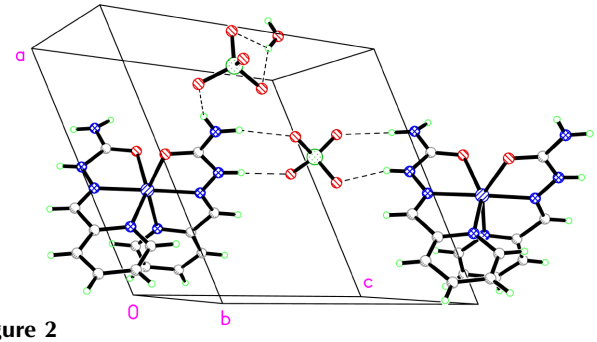

Figure 2
Partial packing diagram of compound (I). H bonds are indicated by dashed lines.

complexes with 2,6-diacetylpyridine bis(semicarbazone) (Carcelli *et al.*, 1999; Palenik & Wester, 1978). The carbonyl O atoms that are involved in bonding [C7—O1 = 1.245 (3) Å and C14—O2 = 1.253 (3) Å] do not show significant lengthening [*cf.* C—O = 1.237 (4) Å reported by Liang *et al.* (2002)]. The distortions from ideal octahedral coordination of the cobalt are seen in the chelate bite angles, which are less than 90°. The supramolecular architecture is stabilized by an extensive two-dimensional network (Fig. 2, Table 2) of hydrogen bonds (O—H···O and N—H···O) involving the cations, counter-ions and water molecules.

Experimental

The Schiff base of pyridine-2-carbaldehyde semicarbazone was prepared according to Gong *et al.* (1994). Single crystals of the title complex suitable for X-ray crystallographic analysis were obtained by solvothermal treatment of $Co(ClO_4)_2·6H_2O$ (0.2 mmol) and the Schiff base (0.4 mmol), methanol (1.5 ml) and CH_2Cl_2 (0.5 ml). The reagents were placed in a thick Pyrex tube (*ca* 20 cm long). The tube was cooled with liquid N_2 and the air evacuated. The sealed tube was heated at 343 K for 2 d to yield orange–red plate crystals in about 65% yield.

Crystal data

$[Co(C_7H_8N_4O)_2](ClO_4)_2·H_2O$
M_r = 604.19
Triclinic, $P\overline{1}$
a = 9.984 (3) Å
b = 11.082 (4) Å
c = 12.196 (5) Å
α = 112.954 (4)°
β = 110.050 (4)°
γ = 94.017 (3)°
V = 1134.4 (7) Å^3
Z = 2
D_x = 1.769 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4571 reflections
θ = 3.3–27.5°
μ = 1.07 mm^{-1}
T = 193 (2) K
Plate, orange–red
0.31 × 0.30 × 0.09 mm

Data collection

Rigaku Mercury diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
T_{min} = 0.733, T_{max} = 0.910
12785 measured reflections
5106 independent reflections
4358 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
θ_{max} = 27.5°
$h = -11 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.105
S = 1.14
5106 reflections
331 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0346P)^2 + 1.3252P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—N1	2.120 (2)	Co1—O1	2.145 (2)
Co1—N2	2.051 (2)	Co1—O2	2.136 (2)
Co1—N5	2.158 (2)	C7—O1	1.245 (3)
Co1—N6	2.043 (2)	C14—O2	1.253 (3)
N1—Co1—N2	76.26 (10)	N2—Co1—O1	74.83 (9)
N1—Co1—N5	93.98 (9)	N2—Co1—O2	108.96 (9)
N1—Co1—N6	106.22 (9)	N5—Co1—O1	95.03 (9)
N2—Co1—N5	100.11 (9)	N5—Co1—O2	150.82 (8)
N2—Co1—N6	175.45 (10)	N6—Co1—O1	102.90 (9)
N5—Co1—N6	76.04 (9)	N6—Co1—O2	75.01 (9)
N1—Co1—O1	150.79 (8)	O1—Co1—O2	94.87 (9)
N1—Co1—O2	90.59 (9)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1w—H1w2···O4^{i}	0.848 (10)	2.221 (19)	3.052 (5)	166 (6)
N3—H3b···O10^{ii}	0.88	1.96	2.808 (3)	161
N4—H4b···O3^{iii}	0.88	2.50	3.353 (5)	165
N4—H4b···O4^{iii}	0.88	2.61	3.283 (4)	134
N4—H4c···O9^{ii}	0.88	2.21	3.063 (4)	165
N7—H7a···O8^{i}	0.88	2.06	2.899 (3)	159
N8—H8b···O4^{i}	0.88	2.30	3.102 (4)	151
N8—H8b···O5^{iv}	0.88	2.65	3.104 (5)	113
N8—H8c···O7^{i}	0.88	2.20	3.062 (4)	165

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

H atoms on C and N atoms were positioned geometrically and were allowed to ride on their parent atoms, with C—H distances of 0.93 Å and N—H distances of 0.86 Å, and U_{iso}(H) = 1.2U_{eq}(C) or 1.2U_{eq}(N). Water H atoms were located in a difference map and refined, subject to an O—H restraint of 0.85 (1) Å.

Data collection: *CrystalClear* (Rigaku, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1994); software used to prepare material for publication: *SHELXTL*.

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References

Alistair, G. B., Bögge, H. & Müller, A. (1987). *J. Chem. Soc. Dalton Trans.* pp. 493–499.
Carcelli, M., Lanelli, S. & Pelagatti, G. (1999). *Inorg. Chim. Acta*, **292**, 121–126.
Chen, Z.-F., Tang, Y.-Z., Shi, S.-M., Wang X.-W., Liang, H. & Yu, K.-B. (2003). *Acta Cryst.* E**59**, m1461–m1463.
García-Tojal, J., García-Orad, A., Díaz, A. A., Serra, J. L., Urtiaga, M. K., Arriortua, M. I. & Rojo, T. (2001). *J. Inorg. Biochem.* **84**, 271–278.
Gong, Y.-Q., Chen, C.-G. & Huan, X.-F. (1994). *Synth. React. Inorg. Met. Org. Chem.* **24**, 877–889.
Iskander, M. F., El-Sayed, L. & Zaki, K. I. (1979). Transition *Met. Chem.* **4**, 225–230.
Jacobson, R. (1998). Private communication to Rigaku Corporation, Tokyo, Japan.
Kasuga, N. C., Sekino, K., Koumo, C., Shimada, N. & Nomiya, K. (2001). *J. Inorg. Biochem.* **84**, 55–56.
Kovala-Demertzi, D., Miller, J. R., Kourkoumelis, N., Hadjikakou, S. K. & Demertzis, M. A. (1999). *Polyhedron*, **18**, 1005–1013.
Kwiat, K. E., Klein, M. & Romanowski, G. (1999). *Inorg. Chim. Acta*, **293**, 115–122.
Liang, H., Chen, X.-B., Hu, R.-X. & Chen, Z.-F. (2002). *Acta Chim. Sin.* **60**, 939–946.
Palenik, G. J. & Wester, D. W. (1978). *Inorg. Chem.* **17**, 864–870.
Reddy, K. H., Reddy, P. S. & Babu, P. R. (1999). *J. Inorg. Biochem.* **77**, 169–176.
Rigaku (1999). *CrystalClear Software User's Guide*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2000). *Crystal Structure*. Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Siemens (1994). *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Tarafder, M. T. H., Kasbollah, A. & Crouse, K. (2001). *Polyhedron*, **20**, 2363–2370.
Wang, H.-S., Huang, L., Chen, Z.-F., Wang, X.-W., Zhou, J., Shi, S.-M., Liang, H. & Yu, K.-B. (2004). *Acta Cryst.* E**60**, m354–m356.