

Heng-Shan Wang,<sup>a</sup> Ling Huang,<sup>a</sup>  
Zhen-Feng Chen,<sup>a\*</sup> Xian-Wen  
Wang,<sup>a</sup> Jian Zhou,<sup>a</sup> Shao-Ming  
Shi,<sup>a</sup> Hong Liang<sup>a</sup> and Kai-Bei  
Yu<sup>b</sup>

<sup>a</sup>College of Chemistry and Chemical  
Engineering, Guangxi Normal University,  
Guilin 541004, People's Republic of China, and

<sup>b</sup>Analysis and Test Center, Chinese Academy of  
Sciences, Chengdu 610041, People's Republic  
of China

Correspondence e-mail:  
chenzfgxnu@yahoo.com

#### Key indicators

Single-crystal X-ray study  
T = 296 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$   
R factor = 0.035  
wR factor = 0.092  
Data-to-parameter ratio = 13.0

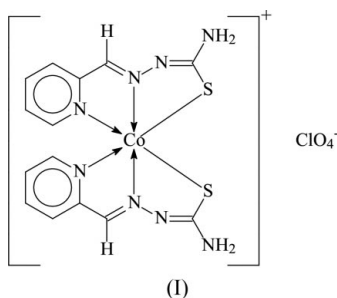
For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

## Bis(pyridine-2-carbaldehyde thiosemi- carbazonato)cobalt(III) perchlorate

In the crystal structure of the title complex,  $[\text{Co}(\text{C}_7\text{H}_7\text{-N}_4\text{S}_2)_2]\text{ClO}_4$ , which was synthesized solvothermally from cobalt diperchlorate and pyridine-2-carbaldehyde thiosemicarbazone, the two planar thiosemicarbazone ligands are aligned perpendicular to each other. The Co atom is octahedrally coordinated by the S, imino N and pyridinyl N atoms of each ligand. The cation interacts with the perchlorate counterion *via* hydrogen bonds.

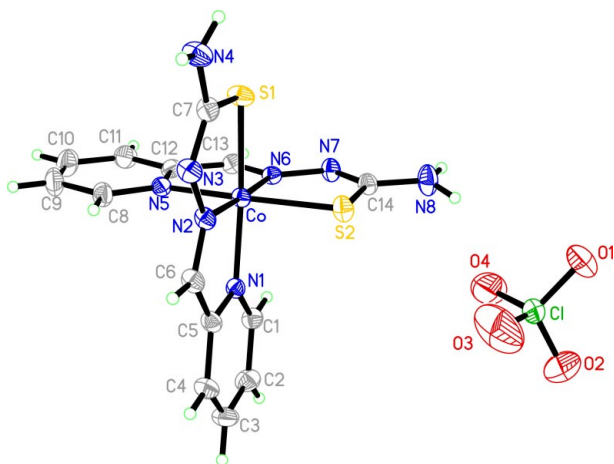
#### Comment

The Schiff base pyridine-2-carbaldehyde thiosemicarbazone and its metal complexes have been extensively investigated, because these compounds exhibit antibacterial, antitumour and antileukaemic activity *in vitro* and *in vivo* (Antholine & Taketa, 1982; Chattopadhyay *et al.*, 1997; García-Tojal *et al.*, 2001; Kovala-Demertzi *et al.*, 1999). Bamgboye & Bamgboye (1985) have reported cobalt(III) complexes of the type  $[\text{Co}(\text{L})_2]\text{X}$  (where X is Cl, SCN or  $\text{N}_3$ ). Their work is extended with the present  $\text{Co}^{\text{III}}$  perchlorate, (I) (Fig. 1).

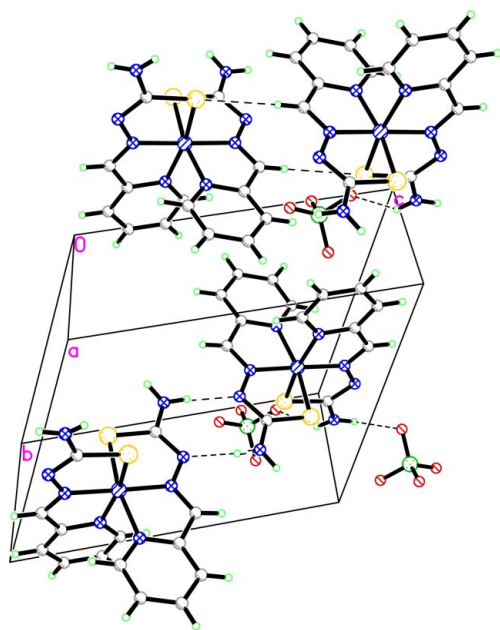


The two thiosemicarbazone ligands in (I) are planar and the coordinating atoms of each ligand occupy a meridional plane, binding to the metal atom through the S, imino N and pyridyl N atoms. The  $\text{Co}/\text{N}1/\text{C}5/\text{C}6/\text{N}2/\text{N}3/\text{C}7/\text{S}1$  and  $\text{Co}/\text{N}5/\text{C}12/\text{C}13/\text{N}6/\text{N}7/\text{C}14/\text{S}2$  planes are nearly perpendicular to each other [dihedral angle  $88.96(3)^\circ$ ]. The perchlorate counterion in (I) is not involved in coordination, as was observed in the SCN analogue (García-Tojal *et al.*, 2001). The pyridine-2-carbaldehyde thiosemicarbazone ligands possess an *E* configuration with respect to the C–N azomethine double bond.

The Co–S and Co–N bond distances in (I) compare well with the values found for  $[\text{Co}(\text{L})_2](\text{SCN})$  (García-Tojal *et al.*, 2001) and  $[\text{Co}(\text{L})_2](\text{SCN})\cdot\text{H}_2\text{O}$  (Chattopadhyay *et al.*, 1997). The bond dimensions of the deprotonated ligand in (I) are not significantly different from those of the free ligand (Byushkin *et al.*, 1987), except that the C–S bonds [ $\text{C}7-\text{S}1$  1.733(3) and  $\text{C}14-\text{S}2$  1.736(3) Å] are longer than that found in the parent ligand [ $\text{C}7-\text{S}1$  1.698(3) Å].



**Figure 1**  
A view of the cation and anion of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.



**Figure 2**  
The packing in (I).

Intermolecular hydrogen bonds (Table 2) lead to the formation of a two-dimensional network in the structure of (I) (Fig. 2).

## Experimental

The ligand was prepared using the method described by Chattopadhyay & Ghosh (1989). A single crystal of (I) suitable for X-ray crystallographic analysis was obtained by solvothermal reaction of  $\text{Co}(\text{ClO}_4) \cdot 6\text{H}_2\text{O}$  with the ligand. Cobalt perchlorate hexahydrate (0.1 mmol), the ligand (0.2 mmol), methanol (0.5 ml) and ethanol (0.5 ml) were placed in a 20 ml Pyrex tube. The tube was cooled with liquid  $\text{N}_2$  and the air inside it was evacuated. It was then sealed and heated at 343 K for 1 d to yield (I).

## Crystal data

$[\text{Co}(\text{C}_7\text{H}_7\text{N}_4\text{S}_2)_2]\text{ClO}_4$   
 $M_r = 516.83$   
 Triclinic,  $P\bar{1}$   
 $a = 8.568$  (1) Å  
 $b = 10.352$  (1) Å  
 $c = 12.440$  (2) Å  
 $\alpha = 103.73$  (1)°  
 $\beta = 102.42$  (1)°  
 $\gamma = 100.16$  (1)°  
 $V = 1016.3$  (3) Å<sup>3</sup>

$Z = 2$   
 $D_x = 1.689$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 30 reflections  
 $\theta = 3.6\text{--}14.4$ °  
 $\mu = 1.22$  mm<sup>-1</sup>  
 $T = 296$  (2) K  
 Block, red  
 $0.30 \times 0.26 \times 0.20$  mm

## Data collection

Siemens *P4* diffractometer  
 $\omega$  scans  
 Absorption correction: empirical  
 via  $\psi$  scan (North *et al.*, 1968)  
 $T_{\min} = 0.690$ ,  $T_{\max} = 0.783$   
 4144 measured reflections  
 3735 independent reflections  
 2937 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.015$   
 $\theta_{\text{max}} = 25.5$ °  
 $h = 0 \rightarrow 10$   
 $k = -11 \rightarrow 11$   
 $l = -15 \rightarrow 14$   
 3 standard reflections  
 every 97 reflections  
 intensity decay: 3.5%

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.035$   
 $wR(F^2) = 0.092$   
 $S = 1.05$   
 3735 reflections  
 288 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.77$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.53$  e Å<sup>-3</sup>  
 Extinction correction: *SHELXL97*  
 (Sheldrick, 1997)  
 Extinction coefficient: 0.0029 (9)

**Table 1**

Selected geometric parameters (Å, °).

Co—N1	1.957 (2)	Co—N6	1.883 (2)
Co—N2	1.887 (2)	Co—S1	2.2176 (10)
Co—N5	1.966 (2)	Co—S2	2.2239 (10)
N1—Co—N2	82.90 (10)	N2—Co—S1	85.81 (8)
N1—Co—N5	90.29 (10)	N2—Co—S2	95.66 (8)
N1—Co—N6	99.41 (10)	N5—Co—N6	82.91 (10)
N1—Co—S1	168.68 (7)	N5—Co—S1	91.64 (7)
N1—Co—S2	89.46 (7)	N5—Co—S2	168.23 (7)
N2—Co—N5	95.99 (10)	N6—Co—S1	91.89 (7)
N2—Co—N6	177.43 (10)	N6—Co—S2	85.52 (8)

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
N4—H4B <sup>i</sup> ···N3 <sup>i</sup>	0.86 (1)	2.11 (1)	2.959 (4)	171 (4)
N4—H4A···O4 <sup>ii</sup>	0.86 (1)	2.24 (2)	3.024 (5)	151 (3)
N8—H8A···O1 <sup>iii</sup>	0.86 (1)	2.17 (1)	3.021 (4)	175 (3)
C1—H1···N7 <sup>iv</sup>	0.93	2.55	3.460 (4)	166
C6—H6···S2 <sup>v</sup>	0.93	2.89	3.679 (3)	144

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

H atoms bound to C atoms were positioned geometrically and refined as riding [ $\text{C—H} = 0.93$  Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ]. H atoms bound to N atoms were located in a difference map and refined, subject to a distance restraint of 0.86 (1) Å.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1994); software used to prepare material for publication: *SHELXTL*.

The authors thank the Youth Science Foundation of Guangxi, the Natural Science Foundation of Guangxi Autonomous Region, the Project of the One-Hundred Persons Plan of the Guangxi Universities, and the Teaching and Research Award Program for Outstanding Young Teachers in Higher Education Institutions of the Chinese Ministry of Education.

## References

- Antholine, W. & Taketa, F. (1982). *J. Inorg. Biochem.* **16**, 145–149.
- Bamgboye, T. T. & Bamgboye, O. A. (1985). *Inorg. Chim. Acta*, **105**, 223–226.
- Byushkin, V. N., Chumakov, Y. M., Samus, N. M. & Baka, I. O. (1987). *Zh. Strukt. Khim.* **28**, 140–141.
- Chattopadhyay, S. K., Banerjee, T., Rouchoudhury, P., Mak, T. C. W. & Ghosh, S. (1997). *Transition Met. Chem.* **22**, 216–219.
- Chattopadhyay, S. K. & Ghosh, S. (1989). *Inorg. Chim. Acta*, **163**, 245–253.
- García-Tojal, J., García-Orad, G., Díaz, A. A., Serra, J. L., Urtiaga, M. K., Arriortua, M. I. & Rojo, T. (2001). *J. Inorg. Biochem.* **84**, 271–248.
- Kovala-Demertzi, D., Miller, J. R., Kourkoumelis, N., Hadjikakou, S. K. & Demertzi, M. A. (1999). *Polyhedron*, **18**, 1005–1013.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Siemens (1994). *XSCANS* (Version 2.10b) and *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.