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Key indicators

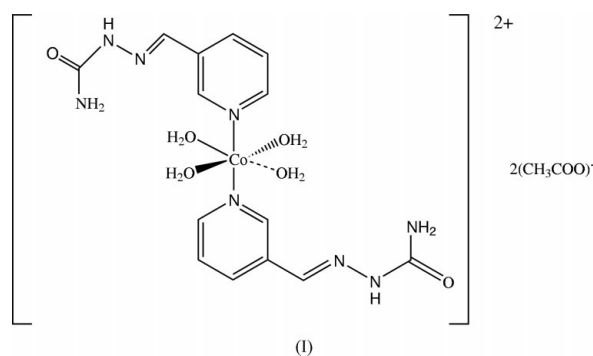
Single-crystal X-ray study
T = 193 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.028
wR factor = 0.068
Data-to-parameter ratio = 13.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Bis{3-[(*E*)-2-(aminocarbonyl)hydrazono-
methyl]pyridine- κ N}tetraaquacobalt(II)
diacetate

The Co atom in the title complex, $[\text{Co}(\text{H-Pysc})_2(\text{H}_2\text{O})_4](\text{CH}_3\text{COO})_2$ {where H-Pysc is 3-[2-(aminocarbonyl)hydrazonomethyl]pyridine, $\text{C}_{14}\text{H}_{16}\text{N}_8\text{O}_2$ }, occupies an inversion centre and is octahedrally coordinated by four aqua ligands and two molecules of the neutral Schiff base derived from the condensation of pyridine-3-carbaldehyde and semicarbazone (H-Pysc); the Schiff base molecules act as monodentate ligands, coordinating the metal through the pyridyl N, with the amide O and imine N atoms remaining uncoordinated. The crystal packing is stabilized by intermolecular hydrogen bonds involving the cations and acetate counter-ions.

Received 5 May 2004
Accepted 11 May 2004
Online 22 May 2004

Comment

Metal complexes of Schiff bases synthesized by the condensation of pyridine-2-carbaldehyde and thiosemicarbazone, semicarbazone and other amines (Chen *et al.*, 2003; Javier & Teofilo, 1999; Singh *et al.*, 2002; Wang *et al.*, 2004) have received attention owing to their antimicrobial, cytotoxic and antioxidant activities (Reddy *et al.*, 2000; Tarafder *et al.*, 2001). For complexes of the analogous ligand pyridine-2-carbaldehyde semicarbazone, the cobalt(II) (Zhou, Chen, Tan *et al.*, 2004) and nickel(II) (Zhou, Chen, Wang *et al.*, 2004) complexes have been crystallographically characterized. As part of a continuing study, we have synthesized pyridine-3-carbaldehyde semicarbazone (H-Pysc) and its cobalt(II) complex, (I).



The structure of (I) (Fig. 1) consists of discrete $[\text{Co}(\text{H-Pysc})_2(\text{H}_2\text{O})_4]^{2+}$ cations and acetate counter-ions. Atom Co1, lying on an inversion centre, has a slightly distorted octahedral coordination formed by two monodentate H-Pysc and four aqua ligands (Table 1). The two neutral semicarbazone ligands are planar and only utilize their pyridyl N atoms for metal coordination. The amide O and imine N atoms are non-coordinating, which is different from the analogous ligand

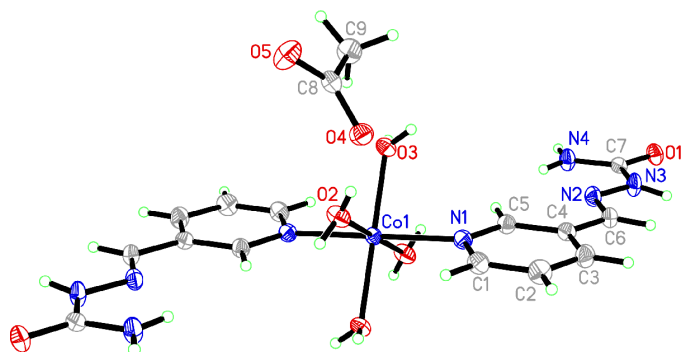


Figure 1

The structure of (I), showing 50% probability displacement ellipsoids and the atom-labelling scheme. H atoms are represented by small spheres of arbitrary radius.

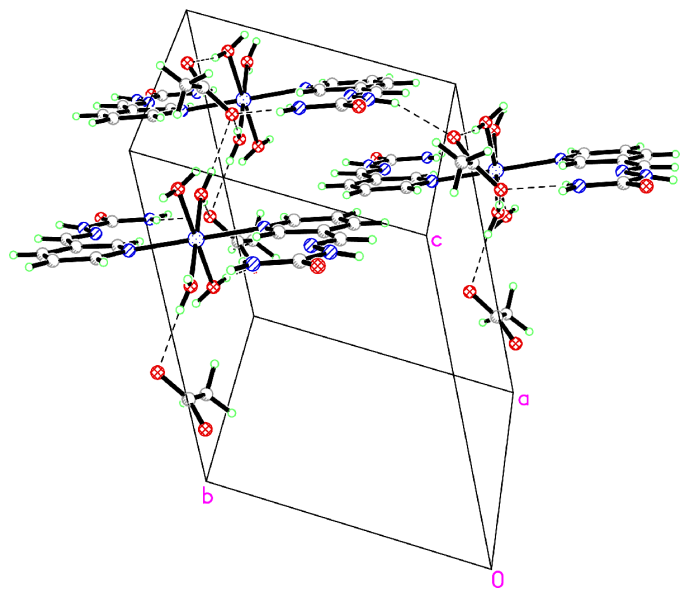


Figure 2

Packing diagram of (I), with hydrogen bonds indicated by dashed lines.

pyridine-2-carbaldehyde semicarbazone in its cobalt(II) (Zhou, Chen, Tan *et al.*, 2004) and nickel(II) (Zhou, Chen, Wang *et al.*, 2004) complexes. The H-Pysc ligand exhibits an E configuration with respect to the azomethine double bond.

The Co—N and Co—O distances are comparable with those reported for other cobalt(II) complexes with pyridine-2-carbaldehyde semicarbazone (Zhou, Chen, Tan *et al.*, 2004) and 2,6-diacetylpyridine bis(semicarbazone) (Carcelli *et al.*, 1999). The distances and angles for H-Pysc are within their normal ranges, in contrast to those of the Schiff base derived from picolinaldehyde N-oxide and semicarbazone (Liang *et al.*, 2002). The packing is stabilized by an extensive three-dimensional network (Fig. 2 and Table 2) of hydrogen bonds (O—H...O and N—H...O) involving the aqua ligands, H-Pysc and uncoordinated acetate counter-ions.

Experimental

The Schiff base ligand pyridine-3-carbaldehyde semicarbazone (H-Pysc) was synthesized by the condensation of semicarbazide with pyridine-3-carbaldehyde in a 1:1 molar ratio in methanol at 333 K for

1 h. $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.2 mmol) and H-Pysc (0.4 mmol) were placed in a thick Pyrex tube (*ca* 20 cm long). After addition of ethanol (1.5 ml) and water (0.5 ml), the tube was cooled with liquid N_2 , evacuated under vacuum and sealed with a torch. The tube was heated at 348 K for 2 d to yield gold block-shaped crystals of (I), in about 53% yield.

Crystal data

$[\text{Co}(\text{C}_{14}\text{H}_{16}\text{N}_8\text{O}_2)_2(\text{H}_2\text{O})_4]^-$
 $(\text{C}_2\text{H}_3\text{O}_2)_2$
 $M_r = 577.43$
 Triclinic, $P\bar{1}$
 $a = 7.8694$ (13) Å
 $b = 8.8660$ (13) Å
 $c = 10.2643$ (11) Å
 $\alpha = 65.788$ (11)°
 $\beta = 69.511$ (12)°
 $\gamma = 81.816$ (14)°
 $V = 611.83$ (15) Å³

$Z = 1$

$D_x = 1.567$ Mg m⁻³

Mo $K\alpha$ radiation

Cell parameters from 3096 reflections

$\theta = 3.7$ – 27.5 °

$\mu = 0.77$ mm⁻¹

$T = 193$ (2) K

Block, gold

$0.60 \times 0.37 \times 0.20$ mm

Data collection

Rigaku Mercury CCD diffractometer
 ω scans
 Absorption correction: multi-scan (Jacobson, 1998)
 $T_{\min} = 0.655$, $T_{\max} = 0.861$
 6754 measured reflections

2723 independent reflections
 2622 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$
 $\theta_{\max} = 27.5$ °
 $h = -10 \rightarrow 9$
 $k = -10 \rightarrow 11$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.069$
 $S = 1.08$
 2723 reflections
 198 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0279P)^2 + 0.3346P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.29$ e Å⁻³
 $\Delta\rho_{\min} = -0.37$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Co1—O2	2.0895 (11)	Co1—N1	2.1647 (13)
Co1—O3	2.1039 (11)		
O2—Co1—O2 ⁱ	180	O3—Co1—N1 ⁱ	91.34 (5)
O2—Co1—O3	91.17 (5)	O2—Co1—N1	89.50 (5)
O2 ⁱ —Co1—O3	88.83 (5)	O3—Co1—N1	88.66 (5)
O3—Co1—O3 ⁱ	180	N1—Co1—N1 ⁱ	180
O2—Co1—N1 ⁱ	90.50 (5)		

Symmetry code: (i) $1 - x, -y, 1 - z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O2—H2C...O4	0.79 (2)	2.02 (2)	2.7839 (16)	164 (2)
O2—H2B...O4 ⁱⁱ	0.86 (3)	1.79 (3)	2.6524 (16)	179 (2)
O3—H3D...O5 ⁱⁱⁱ	0.86 (3)	1.79 (3)	2.6438 (16)	171 (2)
O3—H3C...O1 ^{iv}	0.79 (3)	2.00 (3)	2.7846 (16)	172 (2)
N3—H3B...O5 ^v	0.83 (2)	2.19 (2)	2.9462 (18)	151.6 (19)
N4—H4B...O1 ^{vi}	0.89 (2)	2.02 (2)	2.9075 (18)	175.5 (18)
N4—H4A...O4 ⁱⁱⁱ	0.84 (2)	2.35 (2)	3.0893 (18)	147.3 (18)

Symmetry codes: (ii) $-x, -y, 1 - z$; (iii) $1 + x, y, z$; (iv) $2 - x, 1 - y, -z$; (v) $1 + x, 1 + y, z$; (vi) $3 - x, 1 - y, -z$.

H atoms bound to C atoms were positioned geometrically and included in the refinement in the riding-model approximation [$C-H = 0.93 \text{ \AA}$ and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}$]. Water H atoms were located in difference maps and refined, subject to an O–H distance restraint of $0.85(1) \text{ \AA}$. H atoms bound to N atoms were located in a difference map and refined isotropically, subject to an N–H distance restraint of $0.86(1) \text{ \AA}$.

Data collection: *CrystalClear* (Rigaku, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2000); 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, and the Project of One Hundred Persons Plan of Guangxi Universities of the People's Republic of China, as well as the Teaching and Research Award Program for Outstanding Young Teachers in Higher Education Institutions of the Chinese Ministry of Education.

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