

Diaquabis[2,5-bis(4-pyridyl)-1,3,4-thiadiazole]-
dithiocyanatocobalt(II) dihydrate

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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$

R factor = 0.040

wR factor = 0.102

Data-to-parameter ratio = 13.1

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

In the crystal structure of mononuclear $[\text{Co}(\text{SCN})_2(\text{L})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ [L is 2,5-bis(4-pyridyl)-1,3,4-thiadiazole, $\text{C}_{12}\text{H}_8\text{N}_4\text{S}$], the Co^{II} atom exists in an octahedral environment composed of two N atoms of the SCN^- groups and two aqua ligands, along with the two N atoms from two monodentate L ligands that are positioned *trans* to each other. Hydrogen-bonding interactions between the mononuclear units and uncoordinated water molecules result in a two-dimensional supramolecular network structure. The Co atom lies on a special position of $\bar{1}$ site symmetry.

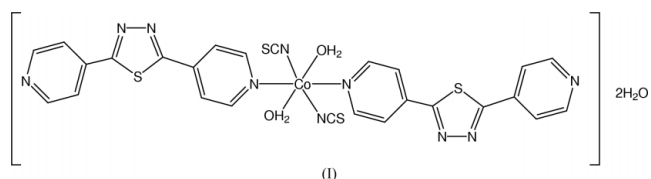
Received 19 January 2004

Accepted 28 January 2004

Online 7 February 2004

Comment

Self-assembly processes involving metal ions and organic ligands constitute a central theme of supramolecular chemistry and crystal engineering (Leininger *et al.*, 2000). Recently, we have initiated a research program of synthesizing coordination polymers or supramolecules based on a pyridyl-substituted oxadiazole system (Du & Zhao, 2003). The title Co^{II} compound, $[\text{Co}(\text{L})_2(\text{SCN})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, (I), represents a complex with the ligand 2,5-bis(4-pyridyl)-1,3,4-thiadiazole (L).



The Co^{II} atom is located on a crystallographic inversion center and is coordinated by two water molecules and two SCN^- groups, as well as two L ligands that are *trans* to each other, in a distorted octahedral geometry (Fig. 1). The SCN^- ligands form $\text{C13}-\text{N5}-\text{Co1}$ and $\text{N5}-\text{C13}-\text{S2}$ angles of $159.7(3)^\circ$ and $179.1(3)^\circ$, respectively. In the L ligand, the two pyridine rings are nearly coplanar with the five-membered ring [dihedral angles = $3.5(1)^\circ$ and $3.5(2)^\circ$]. The ligand uses

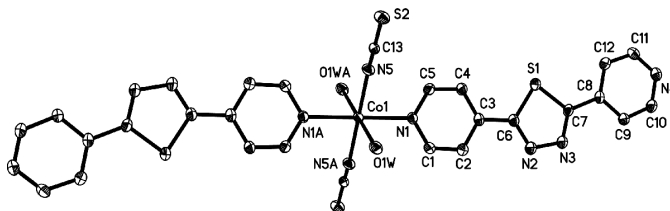


Figure 1

A view of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms and uncoordinated water molecules are not shown. The suffix A denotes atoms at symmetry position $(1-x, 1-y, 2-z)$.

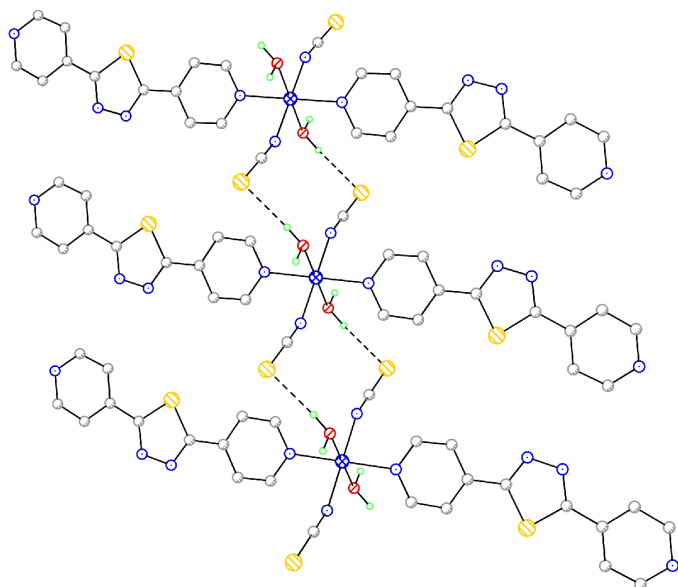


Figure 2
The linear chain structure. Hydrogen bonds are indicated by dashed lines.

only one of the pyridyl N atoms to coordinate to the Co atom; the other is engaged in hydrogen bonding with the uncoordinated water molecule.

An intermolecular $O1W-H1WA \cdots S2(x-1, y, z)$ hydrogen bond connects the coordinated water molecule to the thiocyanate group, thus forming a chain (Fig. 2). Additionally, the coordinated water molecule forms an $O1W-H1WB \cdots O2W$ hydrogen bond with the uncoordinated water molecule, which is also linked to an adjacent complex molecule through an $O2W-H2WB \cdots N4(2-x, 1-y, 1-z)$ hydrogen bond, furnishing a layer structure (Fig. 3 and Table 2).

Experimental

A solution of NH_4SCN (24 mg, 0.3 mmol) in H_2O (15 ml) was added to a $CH_3OH/CHCl_3$ solution (20 ml) of $Co(ClO_4)_2 \cdot 6H_2O$ (36 mg, 0.1 mmol) and 2,5-bis(4-pyridyl)-1,3,4-thiadiazole (50 mg, 0.2 mmol). After *ca* 30 min of heating under reflux, a red solid formed. The solid was redissolved by the addition of more water (20 ml). The filtered solution was set aside and red crystals separated after one week, in 65% yield. Analysis, calculated for $C_{26}H_{24}CoN_{10}O_4S_4$: C 42.91, H 3.32, N 19.25%; found: C 42.88, H 3.09, N 19.44%.

Crystal data

$[Co(SCN)_2(C_{12}H_8N_4S)_2 \cdot (H_2O)_2] \cdot 2H_2O$	$Z = 1$
$M_r = 727.76$	$D_x = 1.572 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.0566(5) \text{ \AA}$	Cell parameters from 674 reflections
$b = 8.3022(6) \text{ \AA}$	$\theta = 2.3\text{--}24.2^\circ$
$c = 14.8495(10) \text{ \AA}$	$\mu = 0.88 \text{ mm}^{-1}$
$\alpha = 104.593(2)^\circ$	$T = 293(2) \text{ K}$
$\beta = 93.149(1)^\circ$	Block, red
$\gamma = 112.148(1)^\circ$	$0.38 \times 0.32 \times 0.22 \text{ mm}$
$V = 768.79(9) \text{ \AA}^3$	

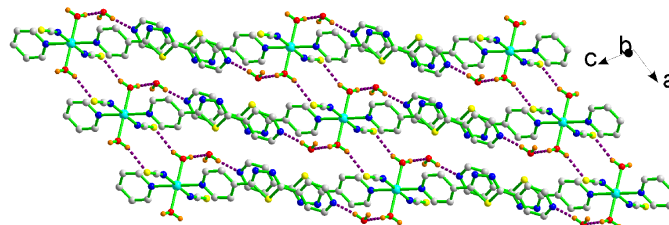


Figure 3
The layered supramolecular structure. Hydrogen-bonding interactions are indicated by purple dashed lines.

Data collection

Bruker SMART CCD area-detector diffractometer	2695 independent reflections
φ and ω scans	2126 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 1996)	$R_{int} = 0.050$
$T_{min} = 0.731, T_{max} = 0.830$	$\theta_{max} = 25.0^\circ$
4193 measured reflections	$h = -7 \rightarrow 8$
	$k = -9 \rightarrow 9$
	$l = -17 \rightarrow 14$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.040$	$w = 1/[\sigma^2(F_o^2) + (0.0535P)^2]$
$wR(F^2) = 0.102$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} < 0.001$
2695 reflections	$\Delta\rho_{max} = 0.46 \text{ e \AA}^{-3}$
205 parameters	$\Delta\rho_{min} = -0.28 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

Co1—N1	2.174 (2)	Co1—O1W	2.118 (2)
Co1—N5	2.067 (2)		
N1 ⁱ —Co1—N1	180	N5—Co1—N5 ⁱ	180
N1—Co1—N5	88.71 (10)	N5—Co1—O1W	91.13 (10)
N1—Co1—N5 ⁱ	91.29 (10)	N5—Co1—O1W ⁱ	88.87 (10)
N1—Co1—O1W	86.49 (8)	O1W—Co1—O1W ⁱ	180
N1—Co1—O1W ⁱ	93.51 (9)		

Symmetry code: (i) $1-x, 1-y, 2-z$.

Table 2

Hydrogen-bonding geometry ($\text{\AA}, ^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O1W-H1WA \cdots S2^{ii}$	0.86	2.472	3.304 (3)	162
$O1W-H1WB \cdots O2W$	0.87	1.900	2.766 (3)	174
$O2W-H2WB \cdots N4^{iii}$	0.88	1.966	2.836 (4)	173

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

H atoms were placed geometrically ($C-H = 0.93 \text{ \AA}$ and $O-H = 0.86\text{--}0.88 \text{ \AA}$) and included in the final refinement in the riding-model approximation, with displacement parameters set to $1.2U_{eq}(C)$ for C-bound H atoms and $1.5U_{eq}(O)$ for O-bound H atoms.

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: *XP* in

SHELXTL (Bruker, 1998); software used to prepare material for publication: *SHELXL97*.

The authors gratefully acknowledge financial support from the Natural Science Foundation of Tianjin (grant No. 033609711) and the Starting Funding of Tianjin Normal University (to MD).

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