Crystal structure of *catena*-[(5-sulfosalicylato-κ^2O,O')-bis(μ_2-4-thiolatopyridinium-κ^2S:S)cadmium(II)] hydrate, $Cd(C_7H_4O_6S)(C_5H_5NS)_2 \cdot 2.5H_2O$

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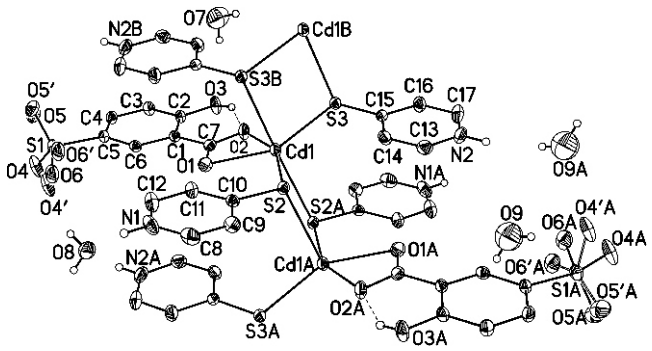

Abstract

$C_{17}H_{19}CdN_2O_{8.5}S_3$, triclinic, $P\bar{1}$ (no. 2), a = 7.3730(7) Å, b = 9.920(1) Å, c = 15.228(2) Å, α = 79.474(1)°, β = 89.189(1)°, γ = 81.344(1)°, V = 1082.4 Å^3, Z = 2, $R_{gt}(F)$ = 0.027, $wR_{ref}(F^2)$ = 0.077, T = 294 K.

Source of material

$Cd(CH_3COO)_2 \cdot 2H_2O$ (0.5 mmol, 0.133 g), 5-sulfosalicylic acid (H_3ssa, 0.5 mmol, 0.109 g) and pyridine-4-thiol (HSpy, 1.0 mmol, 0.111 g) were dissolved in 20 mL H_2O. Then the mixed solution was sealed in a 25 mL Teflon-lined reactor and kept under autogeneous pressure at 403 K for 5 days. After cooling to room temperature at a rate of 279 K/h, colourless needle-like crystals of the title compound suitable for X-ray diffraction were obtained and collected (yield 108 mg, 36 %, based on Cd).

Experimental details

We refined the O9 atom, but the residual values were not reduced by splitting it into two positions.

Discussion

In recent years, pyridine-4-thiol has aroused more and more attention in coordination chemistry, not only because it is a better bridging ligand in preparing structurally novel coordination compounds, but also because its compounds display potential application as anticancer [1], chemical switches [2], non-linear optical [3], or luminescence material [4,5].

The crystal structure of the title compound is comprised of $Cd(C_7H_4O_6S)(C_5H_5NS)_2$ complex and lattice water in a ratio 1 : 3. The Cd(II) center is six-coordinated in an elongated CdO_2S_4 octahedral configuration formed by two carboxylate O atoms (O1, O2) of one bidentate chelate 5-sulfosalicylate dianion (Hssa) and four S atoms (S2, S3, S2A, S3B) of four different 4-thiolatopyridinium (SpyH) (symmetry codes A: 1–x,–y,1–z; B: 2–x,–y, 1–z). The S2A, S3B atoms occupy the axial positions, while the O1, O2, S2, S3 atoms define the equatorial plane. The Cd(II) ion deviates from the equatorial least-squares plane O1/O2/S2/S3 by about 0.090 Å towards S2A. The N atoms of HSpy are protonated and thus forms SpyH ligands. Each SpyH ligand acts as a μ_2-bridging one, interlinking two adjacent Cd(II) ions. Thus a Cd_2S_2 parallelogram is formed between face-to-face arranged Cd(II) ions and SpyH ligands. The dihedral angle between the neighbouring parallelograms is 62.5°. Through the μ_2-bridging function of SpyH ligands a zigzag chain of the title complexes forms along [100]. The neighbouring Cd···Cd distances are 4.097 Å (Cd1···Cd1A) and 3.916 Å (Cd1A···Cd1B), respectively. The central Cd(II) ion is octahedrally coordinated. This is quite different from the two other Cd(II) compounds of SpyH [6], because the Cd(II) center ions of the latter adopt distorted tetrahedral coordination. In addition, the sulfo group of Hssa ligand displays positional disorder [occupancy 0.834(4):0.166(4)]. The partly deprotonated Hssa ligand forms intramolecular O–H···O hydrogen bonds. Together with the intermolecular O–H···O, O–H···S, N–H···O and N–H···S hydrogen bonding interactions among lattice water, Hssa dianion and SpyH ligands, the zigzag chain structure is stabilized and further interconnected to a three-dimensional supramolecular framework.

Table 1. Data collection and handling.

Crystal:	colorless needle, size 0.19 × 0.21 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	13.52 cm^{-1}
Diffractometer, scan mode:	Bruker APEX II CCD, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8292, 3988
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3674
$N(param)_{refined}$:	288
Programs:	SHELXS-97, SHELXL-97, SHELXTL [7]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
H(3)	2*i*		0.9459	0.4194	0.5612	0.077
H(1)	2*i*		0.4644	–0.3767	0.8963	0.065
H(2)	2*i*		0.7332	–0.1685	0.1406	0.062
H(3A)	2*i*		1.0185	0.6010	0.7150	0.046
H(4)	2*i*		0.9629	0.5387	0.8651	0.043
H(6)	2*i*		0.7306	0.2184	0.8159	0.037
H(8)	2*i*		0.3845	–0.4840	0.7906	0.062
H(9)	2*i*		0.4363	–0.3942	0.6444	0.051

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Table 2. Continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(11)	2*i*		0.6606	–0.0923	0.7273	0.048
H(12)	2*i*		0.6015	–0.1886	0.8719	0.064
H(13)	2*i*		0.6612	–0.2428	0.2814	0.057
H(14)	2*i*		0.7441	–0.1309	0.3898	0.048
H(16)	2*i*		0.9701	0.1282	0.1996	0.053
H(17)	2*i*		0.8861	0.0080	0.0961	0.064

Table 2. Continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(1W)	2*i*		1.3835	0.3622	0.5444	0.173
H(2W)	2*i*		1.2716	0.4714	0.5698	0.173
H(3W)	2*i*		0.4158	0.2656	0.9495	0.107
H(4W)	2*i*		0.2447	0.3416	0.9418	0.107
H(6W)	2*i*	0.50	0.3081	–0.0161	0.0263	0.246
H(5W)	2*i*	0.50	0.2133	0.0573	0.0838	0.246

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd(1)	2*i*		0.74405(3)	0.05794(2)	0.52931(1)	0.0367(1)	0.0411(1)	0.0281(1)	–0.0157(1)	0.00562(9)	–0.01231(9)
S(1)	2*i*		0.8097(1)	0.3219(1)	0.97161(5)	0.0442(5)	0.0574(5)	0.0241(4)	–0.0094(4)	0.0037(3)	–0.0027(3)
S(2)	2*i*		0.5910(1)	–0.16612(8)	0.55617(5)	0.0344(4)	0.0383(4)	0.0241(3)	–0.0139(3)	0.0003(3)	–0.0013(3)
S(3)	2*i*		0.9342(1)	0.10583(8)	0.38601(5)	0.0322(4)	0.0363(4)	0.0270(4)	–0.0091(3)	0.0024(3)	–0.0058(3)
O(1)	2*i*		0.6945(3)	0.1409(2)	0.6667(2)	0.044(1)	0.039(1)	0.046(1)	–0.013(1)	0.001(1)	–0.016(1)
O(2)	2*i*		0.8299(3)	0.2690(3)	0.5601(2)	0.061(2)	0.053(1)	0.030(1)	–0.016(1)	0.002(1)	–0.017(1)
O(3)	2*i*		0.9610(4)	0.4809(3)	0.5886(2)	0.083(2)	0.051(1)	0.027(1)	–0.030(1)	0.013(1)	–0.007(1)
O(4)	2*i*	0.834(4)	0.7194(5)	0.4489(3)	1.0024(2)	0.113(3)	0.060(2)	0.039(2)	–0.009(2)	0.031(2)	–0.017(2)
O(5)	2*i*	0.834	0.9870(4)	0.2739(4)	1.0142(2)	0.054(2)	0.128(4)	0.038(2)	–0.010(2)	–0.012(1)	0.017(2)
O(6)	2*i*	0.834	0.6891(4)	0.2196(3)	0.9839(2)	0.076(3)	0.075(2)	0.036(2)	–0.032(2)	0.005(2)	–0.000(2)
O(4')	2*i*	0.166	0.6324(4)	0.3848(3)	0.9838(2)	0.113(3)	0.060(2)	0.039(2)	–0.009(2)	0.031(2)	–0.017(2)
O(6')	2*i*	0.166	0.7898(5)	0.1587(3)	0.9723(2)	0.076(3)	0.075(2)	0.036(2)	–0.032(2)	0.005(2)	–0.000(2)
O(5')	2*i*	0.166	0.9590(4)	0.3302(4)	1.0085(2)	0.054(2)	0.128(4)	0.038(2)	–0.010(2)	–0.012(1)	0.017(2)
N(1)	2*i*		0.4868(5)	–0.3426(3)	0.8418(2)	0.066(2)	0.054(2)	0.034(2)	–0.001(2)	0.017(1)	0.008(1)
N(2)	2*i*		0.7659(4)	–0.1255(3)	0.1805(2)	0.050(2)	0.064(2)	0.044(2)	–0.002(2)	–0.014(1)	–0.025(2)
C(1)	2*i*		0.8254(4)	0.3289(3)	0.7043(2)	0.030(1)	0.030(1)	0.028(1)	–0.003(1)	0.001(1)	–0.007(1)
C(2)	2*i*		0.9160(4)	0.4441(3)	0.6747(2)	0.039(2)	0.034(2)	0.025(1)	–0.007(1)	0.003(1)	–0.004(1)
C(3)	2*i*		0.9632(5)	0.5229(3)	0.7352(2)	0.049(2)	0.035(2)	0.034(2)	–0.017(1)	0.005(1)	–0.008(1)
C(4)	2*i*		0.9288(4)	0.4865(3)	0.8249(2)	0.042(2)	0.039(2)	0.031(2)	–0.010(1)	–0.000(1)	–0.012(1)
C(5)	2*i*		0.8425(4)	0.3708(3)	0.8553(2)	0.035(2)	0.039(2)	0.025(1)	–0.005(1)	0.002(1)	–0.007(1)
C(6)	2*i*		0.7901(4)	0.2942(3)	0.7954(2)	0.029(1)	0.030(1)	0.031(2)	–0.006(1)	0.003(1)	–0.002(1)
C(7)	2*i*		0.7777(4)	0.2411(3)	0.6408(2)	0.031(2)	0.034(2)	0.036(2)	–0.001(1)	–0.003(1)	–0.011(1)
C(8)	2*i*		0.4393(5)	–0.4043(4)	0.7767(3)	0.051(2)	0.044(2)	0.053(2)	–0.011(2)	0.011(2)	0.010(2)
C(9)	2*i*		0.4707(5)	–0.3512(3)	0.6896(2)	0.047(2)	0.037(2)	0.042(2)	–0.014(1)	0.002(2)	0.001(1)
C(10)	2*i*		0.5549(4)	–0.2316(3)	0.6683(2)	0.027(1)	0.031(1)	0.028(1)	–0.002(1)	0.003(1)	0.001(1)
C(11)	2*i*		0.6040(5)	–0.1713(3)	0.7388(2)	0.051(2)	0.038(2)	0.030(2)	–0.006(1)	0.003(1)	–0.004(1)
C(12)	2*i*		0.5687(6)	–0.2286(4)	0.8249(2)	0.073(3)	0.053(2)	0.031(2)	–0.002(2)	0.005(2)	–0.008(2)
C(13)	2*i*		0.7241(5)	–0.1675(4)	0.2659(3)	0.040(2)	0.053(2)	0.056(2)	–0.011(2)	0.004(2)	–0.021(2)
C(14)	2*i*		0.7733(4)	–0.1006(3)	0.3306(2)	0.042(2)	0.046(2)	0.036(2)	–0.014(2)	0.011(1)	–0.013(1)
C(15)	2*i*		0.8680(4)	0.0139(3)	0.3083(2)	0.027(1)	0.038(2)	0.027(1)	–0.001(1)	–0.000(1)	–0.005(1)
C(16)	2*i*		0.9081(5)	0.0530(4)	0.2177(2)	0.052(2)	0.051(2)	0.029(2)	–0.011(2)	0.001(1)	–0.004(1)
C(17)	2*i*		0.8572(6)	–0.0182(4)	0.1558(2)	0.068(2)	0.063(2)	0.029(2)	–0.008(2)	–0.006(2)	–0.009(2)
O(7)	2*i*		1.3750(6)	0.4244(5)	0.5767(3)	0.114(3)	0.098(3)	0.140(4)	–0.003(2)	–0.021(3)	–0.048(3)
O(8)	2*i*		0.3336(4)	0.3092(3)	0.9131(2)	0.066(2)	0.087(2)	0.071(2)	–0.014(2)	–0.003(2)	–0.037(2)
O(9)	2*i*	0.50	0.307(2)	0.046(1)	0.0563(8)	0.165(4)	0.163(4)	0.164(4)	–0.026(1)	0.001(1)	–0.030(1)

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