Crystal structure of *catena*-poly[diacquabis(4-formylpyridine-thiosemicarbazone-*N,S*)cadmium(II)] sulfate hydrate, [Cd(H₂O)₂(C₇H₈N₃S)₂][SO₄] · H₂O

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Abstract

$\text{C}_{56}\text{H}_{88}\text{Cd}_4\text{N}_{32}\text{O}_{28}\text{S}_{12}$, monoclinic, $C12/c1$ (no. 15),
 $a = 13.6879(6)$ Å, $b = 18.6173(8)$ Å, $c = 18.2470(7)$ Å,
 $\beta = 90.392(1)^\circ$, $V = 4649.8$ Å³, $Z = 2$, $R_g(F) = 0.050$,
 $wR_{\text{ref}}(F^2) = 0.159$, $T = 296$ K.

Source of material

4-Formylpyridine thiosemicarbazone (0.186 g, 1 mmol) was dissolved in ethanol (15 ml) and refluxed with $\text{CdSO}_4 \cdot \text{H}_2\text{O}$ (0.226 g, 1 mmol) dissolved in 10 ml of hot water. The product that separated out was collected, washed with ether and dried in vacuo. Single crystals of the title complex were obtained by vapour diffusion of diethyl ether into a DMF solution.

Experimental details

Hydrogen atoms were positioned geometrically and refined using a riding model, with $d(\text{C}—\text{H}) = 0.85 - 0.97 \text{ \AA}$ and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ [$1.5 U_{\text{eq}}(\text{C})$ for the methyl group]. The solvent molecule H_2O was found to be disordered over two sites with 0.50 occupancy.

Discussion

Heterocyclic thiosemicarbazones have attracted considerable interest in chemistry and in biology [1], since these compounds have remarkable coordination properties [2-5], antiviral [6], antibacterial [7], antimalarial [8], antifungal [9], and antitumoral activities [10]. The chemistry of copper complexes with these ligands is one of the interesting themes of current research due to their interesting structural [11], electrochemical [12], spectrophotometric [13], and magnetic properties [14] and also because of their relevance to the active sites of several metalloenzymes [15,16].

The crystal structure of the title complex is a chain polymer. The Cd(II) ion is coordinated by the four ligands, 4-formylpyridine thiosemicarbazone (L), and two aqua to form a distorted octahedral environment. The ligand L behaves as a bridging ligand through the N atom of the pyridyl ring and S atom of thiosemicarbazone moiety. Two N atoms and two O atoms comprise the equatorial plane with the Cd1—O1, Cd1—O2 and Cd1—N2 bond distances being 2.357(6) Å, 2.362(7) Å and 2.353(5) Å, respectively. The apical positions are occupied by two S atoms from two other ligands (L), the Cd2—S2 bond distance is 2.664(2) Å ($x+1/2, y-1/2, z; -x+3/2, -y-1/2, -z$), which are slightly longer than the corresponding values found in the reported complexes CdI₂(C₉H₁₁N₃OS)₂ with $d(\text{Cd}—\text{S})$ of 2.588(1) Å and 2.580 (1) Å [17] and C₁₄H₂₂CdCl₂N₁₀O₁₀S₂ $d(\text{Cd}—\text{S})$ of 2.573 (1) Å and 2.563 (1) Å [18]. The C6=N2 bond distance (1.277(8) Å) in the title complex is the same as those found in free ligand (1.279 Å) [19], but is shorter than that in the reported complex (1.293 Å) C₁₄H₂₂CdCl₂N₁₀O₁₀S₂ [18]. However, the C7=S1 bond distance 1.717(6) Å is longer than that observed in free ligand (1.677 Å) [19], but is the same within experimental error to that found in the reported complex (1.711 Å) [18]. The crystal packing of the complex is stabilized through strong intermolecular hydrogen bonds.

Table 1. Data collection and handling.

Crystal:	yellow prism, size $0.08 \times 0.15 \times 0.20$ mm
Wavelength:	$\text{Mo } K_{\alpha}$ radiation ($0.71073 \text{ \AA}$)
μ :	12.62 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX CCD, φ/ω
$2\theta_{\text{max}}$:	52°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	28659, 4560
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}}), 3364$
$N(\text{param})_{\text{refined}}$:	306
Programs:	SHELXS-97 [20], SHELXL-97 [21], SHELXTL [22], ORTEP-III [23], PLATON [24]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U _{iso}
H(1)	8f		0.9082	0.2085	0.6279	0.048
H(2)	8f		0.8499	0.2025	0.5097	0.046
H(4)	8f		0.9256	0.4078	0.4826	0.051
H(5)	8f		0.9785	0.4102	0.6016	0.049
H(6)	8f		0.8350	0.3441	0.3799	0.049
H(8)	8f		0.9755	0.1145	0.1322	0.047
H(9)	8f		0.9220	0.2272	0.1622	0.050
H(11)	8f		0.8512	0.2562	-0.0503	0.043
H(12)	8f		0.9084	0.1439	-0.0740	0.040
H(13)	8f		0.8322	0.3403	0.1244	0.046
H(3)	8f		0.7750	0.2842	0.2856	0.052
H(4A)	8f		0.8021	0.1204	0.3491	0.066

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U _{iso}
H(4B)	8f		0.7476	0.0823	0.2898	0.066
H(7)	8f		0.7727	0.4466	0.0886	0.042
H(8B)	8f		0.8014	0.4213	-0.0874	0.058
H(8C)	8f		0.7486	0.4861	-0.1146	0.058
H(1A)	8f		1.0559	0.1662	0.7458	0.072
H(2A)	8f		1.0094	0.4574	0.7921	0.087
H(3B)	8f		1.0525	-0.0426	0.1413	0.057
H(3A)	8f		0.9517	-0.0497	0.1391	0.057
H(8A)	8f		0.5606	0.8701	0.2515	0.490
H(9A)	8f	0.50	0.9885	0.5488	0.8684	0.292
H(9C)	8f	0.50	0.9062	0.5439	0.8238	0.292

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C(1)	8f		0.9112(5)	0.2491(3)	0.5984(3)	0.051(4)	0.035(3)	0.033(3)	0.002(3)	-0.006(3)	0.000(2)
C(2)	8f		0.8768(4)	0.2451(3)	0.5272(3)	0.045(4)	0.042(3)	0.029(3)	0.000(3)	-0.002(3)	-0.003(2)
C(3)	8f		0.8825(4)	0.3043(3)	0.4822(3)	0.035(3)	0.043(3)	0.028(3)	0.006(2)	-0.004(2)	-0.002(2)
C(4)	8f		0.9211(5)	0.3667(3)	0.5113(3)	0.049(4)	0.038(3)	0.039(3)	0.006(3)	-0.003(3)	0.004(3)
C(5)	8f		0.9530(5)	0.3677(3)	0.5828(3)	0.050(4)	0.041(3)	0.032(3)	-0.002(3)	-0.008(3)	-0.003(3)
C(6)	8f		0.8441(5)	0.3018(3)	0.4063(3)	0.048(4)	0.043(3)	0.030(3)	0.009(3)	-0.008(3)	0.003(3)
C(7)	8f		0.7486(5)	0.1826(3)	0.2784(3)	0.054(4)	0.043(3)	0.025(3)	0.015(3)	-0.003(3)	-0.003(2)
C(8)	8f		0.9508(5)	0.1437(3)	0.0951(3)	0.048(4)	0.031(3)	0.039(3)	0.009(3)	-0.004(3)	0.005(2)
C(9)	8f		0.9186(5)	0.2114(3)	0.1139(3)	0.054(4)	0.037(3)	0.033(3)	0.008(3)	-0.003(3)	-0.001(3)
C(10)	8f		0.8807(4)	0.2556(3)	0.0588(3)	0.032(3)	0.033(3)	0.036(3)	0.009(2)	0.002(2)	-0.002(2)
C(11)	8f		0.8769(4)	0.2285(3)	-0.0124(3)	0.040(3)	0.033(3)	0.034(3)	0.004(2)	-0.006(3)	0.003(2)
C(12)	8f		0.9111(4)	0.1610(3)	-0.0261(3)	0.035(3)	0.036(3)	0.030(3)	0.004(2)	-0.002(2)	-0.001(2)
C(13)	8f		0.8421(5)	0.3269(3)	0.0759(3)	0.045(4)	0.035(3)	0.036(3)	0.011(3)	0.004(3)	-0.006(3)
C(14)	8f		0.7473(4)	0.4773(3)	-0.0112(3)	0.034(3)	0.026(3)	0.034(3)	0.002(2)	-0.001(2)	0.000(2)
Cd(1)	4e	0	0.31224(3)	¾	0.0655(5)	0.0359(4)	0.0266(3)	0	-0.0131(3)	0	0
Cd(2)	4a	0	0	0	0.0385(4)	0.0242(3)	0.0341(3)	0.0079(2)	-0.0009(3)	-0.0002(2)	0
N(1)	8f		0.9489(4)	0.3104(3)	0.6266(3)	0.045(3)	0.042(3)	0.027(2)	0.004(2)	-0.002(2)	0.001(2)
N(2)	8f		0.8235(4)	0.2413(3)	0.3771(2)	0.047(3)	0.043(3)	0.025(2)	0.007(2)	-0.008(2)	-0.001(2)
N(3)	8f		0.7808(4)	0.2441(3)	0.3085(3)	0.062(4)	0.038(3)	0.029(3)	0.013(2)	-0.011(2)	0.001(2)
N(4)	8f		0.7683(5)	0.1216(3)	0.3092(3)	0.082(4)	0.043(3)	0.040(3)	0.015(3)	-0.027(3)	-0.001(2)
N(5)	8f		0.9489(4)	0.1175(2)	0.0269(3)	0.040(3)	0.027(2)	0.042(3)	0.010(2)	-0.005(2)	-0.002(2)
N(6)	8f		0.8222(3)	0.3705(2)	0.0242(3)	0.036(3)	0.029(2)	0.040(3)	0.013(2)	0.003(2)	-0.003(2)
N(7)	8f		0.7791(4)	0.4345(2)	0.0434(3)	0.046(3)	0.029(2)	0.031(2)	0.012(2)	0.002(2)	-0.004(2)
N(8)	8f		0.7681(4)	0.4595(3)	-0.0788(3)	0.071(4)	0.047(3)	0.027(3)	0.017(3)	0.006(3)	0.001(2)
O(1)	4e	0	0.1856(3)	¾	0.070(5)	0.038(4)	0.071(5)	0	-0.017(4)	0	0
O(2)	4e	0	0.4391(4)	¾	0.101(2)	0.043(1)	0.073(2)	0	-0.014(2)	0	0
O(3)	8f		0.9995(3)	-0.0231(2)	0.1272(2)	0.048(3)	0.055(3)	0.041(2)	0.005(2)	-0.001(2)	0.015(2)
O(4)	8f		0.7362(7)	0.9967(3)	0.2232(4)	0.189(8)	0.050(4)	0.093(5)	-0.009(4)	-0.061(5)	0.011(3)
O(5)	8f		0.8165(4)	0.9411(3)	0.3240(2)	0.068(3)	0.105(4)	0.033(3)	-0.036(3)	-0.009(2)	0.007(3)
O(6)	8f		0.6943(4)	0.8778(3)	0.2548(3)	0.084(4)	0.065(3)	0.061(3)	-0.024(3)	-0.011(3)	-0.003(3)
O(7)	8f		0.8480(5)	0.9021(4)	0.2021(3)	0.119(6)	0.123(6)	0.053(4)	-0.028(5)	0.033(4)	-0.019(4)
O(8)	4e	½	0.850(2)	¼	0.16(2)	0.35(4)	0.71(7)	0	-0.04(3)	0	0
O(9)	8f	0.50(2)	0.968(2)	0.544(1)	0.825(2)	0.21(2)	0.24(3)	0.28(3)	0.16(2)	-0.12(2)	-0.13(2)
S(1)	8f		0.6829(1)	0.18993(9)	0.19825(8)	0.068(1)	0.056(1)	0.0246(7)	0.0214(8)	-0.0117(7)	-0.0068(7)
S(2)	8f		0.6808(1)	0.55206(7)	0.01071(8)	0.0402(8)	0.0266(7)	0.0390(8)	0.0058(6)	-0.0040(6)	-0.0016(6)
S(3)	8f		0.7746(1)	0.93101(8)	0.25232(8)	0.069(1)	0.0346(8)	0.0232(7)	-0.0094(7)	-0.0019(7)	0.0009(6)

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