

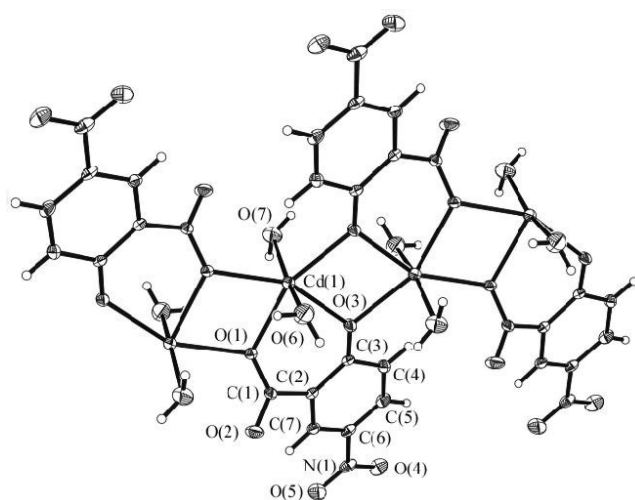
Crystal structure of diaqua(5-nitrosalicylate)cadmium(II), $\text{Cd}(\text{H}_2\text{O})_2(\text{C}_7\text{H}_7\text{NO}_7)$

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Abstract

$\text{C}_7\text{H}_7\text{CdNO}_7$, triclinic, $P\bar{1}$ (no. 2), $a = 7.0850(6)$ Å, $b = 7.5509(7)$ Å, $c = 10.713(1)$ Å, $\alpha = 104.696(1)^\circ$, $\beta = 99.354(1)^\circ$, $\gamma = 109.129(2)^\circ$, $V = 504.5$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.024$, $wR_{\text{ref}}(F^2) = 0.063$, $T = 298$ K.

Source of material

Crystals of diaqua(5-nitrosalicylate)cadmium(II) were formed during an experiment to synthesize the mixed-ligand cadmium complex. A solution of cadmium acetate dihydrate (27 mg, 0.1 mmol) in 5 mL of MeOH was added to a MeOH solution (3 mL) containing 3,5-dimethylpyrazole (19.2 mg, 0.2 mmol) and 5-nitrosalicylic acid (36.6 mg, 0.2 mmol), under continuous stirring. The solution was stirred for about 3 h at room temperature, a small amount of precipitate formed, then a few drops of concentrated ammonia was added till the precipitate dissolved completely. The clear solution was filtered into the test tube and after several days, colorless block crystals were obtained by slow evaporation of the ammonia solution at ambient temperature.

Experimental details

All H atoms attached to C atoms were fixed geometrically and treated as riding with $d(\text{C}—\text{H}) = 0.93$ Å with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. H atoms of water molecule were located in difference Fourier map and included in the subsequent refinement using restraints of $d(\text{O}—\text{H}) = 0.85(1)$ Å with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O})$. In the last stage of refinement, they were treated as riding on the O atom.

Discussion

Carboxylate complexes have been widely studied in recent years due to their interesting coordination chemistry allowing for unusual structural features and leading to various physical and chemical properties and practical applications in fields of dyes, extractants, drugs, pesticides and catalysts [1–4]. In recent years, the heavy element cadmium has received increased attention for its impact on plants and toxicity to humans as well as the luminescent properties of its complexes [5–6]. Up to date, many cadmium(II) carboxylates have been studied [7–8]. As an extension of our research on carboxylate coordination compounds [9–10], we here report the synthesis and crystal structure of the title compound.

The asymmetric unit of the title crystal structure consists of one Cd atom, one 5-nitrosalicylate dianion ligand, and two coordinated water molecules. The basic building blocks in the title compound are $[\text{CdO}_6]$. The Cd atoms are coordinated by four oxygen atoms of the 5-nitrosalicylate ligands (of which two are from the phenolates and the other two O atoms are from two carboxylates of two adjacent 5-nitrosalicylate ligands) and two water molecules to complete a distorted octahedral coordination. The phenol group and the carboxyl group of the 5-nitrosalicylic acid are both deprotonated which is verified by the distances $d(\text{C}—\text{O}) = 1.306(4)$, $1.233(4)$, and $1.281(4)$ Å, respectively. The phenolate O atom and one O atom of the carboxylate both act as bridging bidentate ligands. Because of this coordination mode, the compound displays a chain running along the a axis. In the chain, two Cd cations and two O atoms of the carboxylates made a parallelogram with a Cd–Cd separation of 3.675 Å. There were also parallelograms formed by two O atoms of the phenolates and two Cd atoms in which the Cd–Cd separation of 3.561 Å is slightly shorter. Such two kinds of parallelograms are arranged alternatively on the chains. The anions on the same side of the chain are parallel to each other, but the anions on different sides of the chain are antiparallel. Adjacent chains are joined together by $\text{O}—\text{H} \cdots \text{O}$, $\text{O} \cdots \pi$, and $\text{O}—\text{H} \cdots \pi$ associations to form a layer structure.

Table 1. Data collection and handling.

Crystal:	colorless block, size $0.28 \times 0.37 \times 0.44$ mm
Wavelength:	Mo K_{α} radiation (0.71073 Å)
μ :	21.85 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{\text{max}}$:	50.02°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	2629, 1756
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1645
$N(\text{param})_{\text{refined}}$:	145
Programs:	SHELXS-97, SHELXL-97, SHELXTL [11]

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

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(6C)	2i	0.2609	0.3207	0.6807	0.061
H(6D)	2i	0.2004	0.4688	0.7425	0.061
H(7C)	2i	0.4372	0.8080	0.3753	0.058
H(7D)	2i	0.2422	0.6613	0.3128	0.058

Table 2. Continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(4)	2i	0.4888	0.1248	0.2152	0.034
H(5)	2i	0.3018	−0.1483	0.0287	0.036
H(7)	2i	−0.2243	−0.1773	0.1330	0.028

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

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Cd(1)	2i	0.27715(4)	0.55400(4)	0.51697(2)	0.0214(2)	0.0210(2)	0.0294(2)	0.0074(1)	0.0080(1)	0.0054(1)
N(1)	2i	−0.0979(6)	−0.3566(5)	−0.0550(3)	0.051(2)	0.022(2)	0.022(2)	0.015(2)	0.003(2)	0.003(1)
O(1)	2i	−0.0488(4)	0.3059(4)	0.4044(3)	0.021(1)	0.017(1)	0.039(1)	0.005(1)	0.010(1)	0.001(1)
O(2)	2i	−0.2383(5)	−0.0087(4)	0.3721(3)	0.041(2)	0.022(1)	0.062(2)	0.004(1)	0.033(2)	0.005(1)
O(3)	2i	0.3606(4)	0.3048(4)	0.3960(2)	0.019(1)	0.023(1)	0.028(1)	0.006(1)	0.004(1)	−0.002(1)
O(4)	2i	−0.0028(5)	−0.4212(4)	−0.1299(3)	0.065(2)	0.037(2)	0.028(1)	0.022(2)	0.016(1)	−0.002(1)
O(5)	2i	−0.2868(5)	−0.4332(5)	−0.0760(3)	0.042(2)	0.037(2)	0.041(2)	0.005(1)	−0.003(1)	−0.007(1)
O(6)	2i	0.2798(5)	0.4422(5)	0.6958(3)	0.056(2)	0.050(2)	0.060(2)	0.024(2)	0.029(2)	0.026(2)
O(7)	2i	0.3205(5)	0.7478(5)	0.3870(3)	0.047(2)	0.045(2)	0.049(2)	0.009(2)	0.015(2)	0.016(2)
C(1)	2i	−0.0948(5)	0.1192(5)	0.3539(3)	0.018(2)	0.020(2)	0.025(2)	0.005(1)	0.003(1)	0.002(1)
C(2)	2i	0.0288(5)	0.0533(5)	0.2634(3)	0.025(2)	0.016(2)	0.022(2)	0.009(1)	0.006(1)	0.006(1)
C(3)	2i	0.2477(5)	0.1503(5)	0.2904(3)	0.023(2)	0.014(2)	0.023(2)	0.007(1)	0.006(1)	0.005(1)
C(4)	2i	0.3455(6)	0.0667(5)	0.1988(4)	0.024(2)	0.026(2)	0.034(2)	0.010(2)	0.012(2)	0.006(2)
C(5)	2i	0.2346(6)	−0.0970(6)	0.0873(4)	0.040(2)	0.027(2)	0.027(2)	0.018(2)	0.016(2)	0.004(2)
C(6)	2i	0.0218(6)	−0.1847(5)	0.0630(3)	0.038(2)	0.017(2)	0.020(2)	0.013(2)	0.006(2)	0.003(1)
C(7)	2i	−0.0814(5)	−0.1137(5)	0.1501(3)	0.025(2)	0.018(2)	0.026(2)	0.007(1)	0.004(1)	0.006(1)

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