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The crystal structure of aqua-bis(3-acetyl-2-oxo-2*H*-chromen-4-olato- $\kappa^2 O, O'$)zinc(II) monohydrate, $C_{22}H_{18}O_{10}Zn$

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Abstract

$C_{22}H_{18}O_{10}Zn$, triclinic, $P\bar{1}$ (no. 2), $a = 7.9616(3)$ Å, $b = 9.5386(3)$ Å, $c = 14.2569(4)$ Å, $\alpha = 81.713(3)^\circ$, $\beta = 82.724(3)^\circ$, $\gamma = 73.103(3)^\circ$, $V = 1021.03(6)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0223$, $wR_{ref}(F^2) = 0.0603$, $T = 295(2)$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The ligand was synthesized according to a previously published procedure [5]. To a hot solution of the ligand 3-acetyl-4-hydroxy-2*H*-chromen-2-one (non-systematic name: 3-acetyl-4-hydroxycoumarine) (1.8 g, 9 mmol) in ethanol (15 mL),

Table 1: Data collection and handling.

Crystal:	Plate, colorless
Size:	$0.46 \times 0.35 \times 0.09$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	1.26 mm^{-1}
Diffractometer, scan mode:	Gemini S, φ and ω -scans
$\theta_{\max}$, completeness:	26.4° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	20929, 4157, 0.022
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3901
$N(\text{param})_{\text{refined}}$:	312
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], PLATON [4], CrystalExplorer [16, 17]

0.85 g (4.5 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$ was added. The obtained mixture was refluxed for 30 minutes and afterwards cooled to room temperature. The solvent was allowed to slowly evaporate, and in this way appropriate colorless crystals of the title as the main product were obtained.

Experimental details

Coordinates of hydrogen atoms bonded to carbon atoms were introduced in idealized positions and refined using riding model. Their U_{iso} values are approximated as $U_{\text{iso}} = kU_{\text{eq}}$ of the parent atom ($k = 1.2$ for sp^2 and 1.5 for sp^3 hybridized carbon atoms). Coordinates of hydrogen atoms bonded to water oxygen atoms O5 and O6 were located in residual electron density map, and were refined with O–H and H–H distance restraints (0.86(2) Å and 1.30(2) Å, respectively). Their U_{iso} were set as $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the parent oxygen atom.

Comment

Coumarins are an important group of organic compounds. They are known to be excellent ligands for metal ions and have found significant uses in the synthesis of a number of complexes. Many of these products exhibit promising physiological activities including antimicrobial (specifically antitubercular and antifungal) [6–8] and antioxidant actions [9], or they were put forward as potential cancer chemotherapeutic agents [10, 11]. Likewise, they have a potential utilization as colorimetric chemosensors for metal cations [12].

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U_{iso}^*/U_{eq}
Zn1	0.64578(2)	0.45085(2)	0.31876(2)	0.03222(7)
O1A	0.63360(15)	0.63037(12)	0.38425(8)	0.0383(3)
O2A	0.69653(15)	0.33663(11)	0.44329(7)	0.0351(2)
O3A	0.91778(15)	0.41036(11)	0.66749(8)	0.0355(2)
O4A	0.86649(15)	0.64478(12)	0.62606(8)	0.0379(3)
O5	0.88543(16)	0.41142(14)	0.24433(9)	0.0412(3)
H51	0.885(3)	0.484(2)	0.2075(14)	0.062*
H52	0.963(3)	0.394(2)	0.2786(14)	0.062*
O6	0.8258(2)	0.6787(2)	0.13113(11)	0.0631(4)
H61	0.721(2)	0.697(3)	0.1523(18)	0.095*
H62	0.828(4)	0.679(3)	0.0752(12)	0.095*
O1B	0.54969(16)	0.29418(12)	0.28331(8)	0.0408(3)
O2B	0.49580(17)	0.58689(12)	0.22434(9)	0.0436(3)
O3B	0.22826(17)	0.52896(13)	0.01383(8)	0.0436(3)
O4B	0.2517(2)	0.29949(14)	0.06270(10)	0.0570(4)
C1A	0.84626(19)	0.53114(16)	0.60594(11)	0.0284(3)
C2A	0.76168(18)	0.51316(15)	0.52628(10)	0.0268(3)
C3A	0.75927(18)	0.36873(16)	0.51207(10)	0.0261(3)
C4A	0.83525(19)	0.24585(16)	0.58178(10)	0.0277(3)
C5A	0.8381(2)	0.10082(17)	0.57375(11)	0.0353(3)
H5A	0.783221	0.081383	0.525214	0.042*
C6A	0.9214(3)	−0.01307(18)	0.63698(13)	0.0438(4)
H6A	0.922986	−0.109284	0.631047	0.053*
C7A	1.0034(3)	0.01503(19)	0.70989(13)	0.0487(4)
H7A	1.061444	−0.062836	0.751797	0.058*
C8A	0.9993(3)	0.15703(19)	0.72055(12)	0.0440(4)
H8A	1.051910	0.176358	0.770056	0.053*
C9A	0.9152(2)	0.27041(16)	0.65606(11)	0.0301(3)
C10A	0.68387(19)	0.64137(16)	0.46167(11)	0.0290(3)
C11A	0.6554(2)	0.79602(17)	0.48405(12)	0.0396(4)
H11A	0.767134	0.816615	0.481088	0.059*
H11B	0.596719	0.806339	0.546828	0.059*
H11C	0.584082	0.864031	0.438566	0.059*
C1B	0.2877(2)	0.40832(18)	0.07839(11)	0.0363(3)
C2B	0.38591(19)	0.42133(16)	0.15440(10)	0.0294(3)
C3B	0.4114(2)	0.56015(17)	0.16212(11)	0.0307(3)
C4B	0.3360(2)	0.68528(17)	0.09369(11)	0.0316(3)
C5B	0.3493(2)	0.82744(18)	0.09750(13)	0.0420(4)
H5B	0.405406	0.844835	0.146260	0.050*
C6B	0.2813(3)	0.94102(19)	0.03072(14)	0.0480(4)
H6B	0.291807	1.034792	0.033830	0.058*
C7B	0.1960(3)	0.9157(2)	−0.04217(14)	0.0489(4)
H7B	0.150559	0.992899	−0.087929	0.059*
C8B	0.1785(3)	0.7779(2)	−0.04703(13)	0.0461(4)
H8B	0.120541	0.761230	−0.095233	0.055*
C9B	0.2488(2)	0.66443(17)	0.02127(11)	0.0345(3)
C10B	0.4564(2)	0.29226(17)	0.21940(11)	0.0323(3)
C11B	0.4232(3)	0.14676(19)	0.21550(14)	0.0488(5)
H11D	0.298512	0.158792	0.220803	0.073*
H11E	0.474722	0.077847	0.267085	0.073*
H11F	0.475076	0.110278	0.156102	0.073*

Asymmetric part of the unit cell consists of the [Zn(C₁₁H₇O₄)₂H₂O] complex and a water molecule. The structure of [Zn(C₁₁H₇O₄)₂H₂O] approximately conforms to C₂ point-group symmetry (excluding hydrogen atoms), with a twofold axis coinciding with the Zn1—O5 bond direction.

The coordination environment of Zn(II) can be best described as slightly deformed square pyramidal, since traverse along Berry pseudorotation coordinate ($D_{3h} \rightarrow C_{2v} \rightarrow C_{4v}$) is 97%, as calculated by Holmes' method [13]. The basal plane of square pyramid is occupied by two bidentately coordinated coumarin ligands, while the apical site is occupied by a coordinated water molecule. The organic ligands are coordinated in a monoanionic form, through O3A of deprotonated hydroxyl group and O4A of acetyl group. Bond lengths Zn1—O3A, Zn1—O3B and Zn1—O3A, Zn1—O4B (1.9673(10), 1.9811(11), 2.0384(11), and 2.0135(11) Å, respectively) are slightly shorter than chemically equivalent bonds found in structurally related octahedral Zn(II) complexes with coumarin derivatives [14, 15]. This may be explained by the lower coordination number of Zn(II) in the title complex. Bond lengths within six-membered metallocycles are consistent with electron delocalization through O3A—C4A—C3A—C9A—O4A and O3B—C4B—C3B—C9B—O4B fragments.

Catenation of structural units is achieved by hydrogen bonding along [101]. Each coordinated water molecule O5 (i) is hydrogen bonded to neighboring complex molecule (ii) and the non-coordinated water molecule (i) [symmetry operations: (i) x, y, z ; (ii) $-x+2, -y+1, -z$]. Furthermore, the non-coordinated water molecule (i) is hydrogen bonded to an adjacent complex (iii) [symmetry operation: (iii) $-x+1, -y+1, -z$]. Pairwise interaction energies, calculated using CE-B3LYP model energies via *CrystalExplorer17* [16, 17], indicate that these interactions are dominantly electrostatic in nature, with interaction energies $-165, -72$ and -32 kJ mol^{−1}, respectively. Interestingly, calculations reveal that interactions dominated by dispersion contributions are not negligible, amounting -66 kJ mol^{−1} between intra-chain pair [Zn(C₁₁H₇O₄)₂H₂O] (i) ... [Zn(C₁₁H₇O₄)₂H₂O] (iii) and -104 kJ mol^{−1} between inter-chain pair [Zn(C₁₁H₇O₄)₂H₂O] (i) ... [Zn(C₁₁H₇O₄)₂H₂O] (iv) [symmetry operation: (iv) $-x+1, -y+1, -z+1$].

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