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Crystal structure of diaqua-bis(3,3-dimethylacrylate- $\kappa^2 O, O'$)zinc(II), $C_{10}H_{18}ZnO_6$

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Abstract

$C_{10}H_{18}O_6Zn$, monoclinic, $P2/c$ (no. 13), $a = 11.0730(2)$ Å, $b = 5.52600(10)$ Å, $c = 10.8410(2)$ Å, $\beta = 100.350(1)^\circ$, $V = 652.56(2)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0318$, $wR_{ref}(F^2) = 0.0842$, $T = 293(2)$ 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 title complex was synthesized from a mixture of $ZnCl_2$ (0.123 g, 0.9 mmol), 3,3-dimethylacrylic acid (3-methylcrotonic acid) (0.09 g, 0.9 mmol), 1,3-diaminopropane (0.025 mL, 0.3 mmol), and ethanol (1.0 mL),

Table 1: Crystal collection and handling.

Crystal:	Rod, colorless
Size:	$0.10 \times 0.02 \times 0.01$ mm
Wavelength:	Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å)
μ :	1.894 mm^{-1}
Diffractometer, scan mode:	Bruker APEX, Φ and ω -scans
$2\theta_{\max}$, completeness:	28.32° , $>99\%$
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	7022, 1629, 0.0288
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 1473
$N(\text{param})_{\text{refined}}$:	88
Programs:	Bruker programs [1], SHELX [2, 3], Diamond [4]

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.500000	0.09597(5)	0.750000	0.01995(13)
O1	0.36077(15)	0.4042(2)	0.72855(13)	0.0240(3)
O2	0.41494(15)	0.2101(2)	0.57131(12)	0.0258(3)
C1	0.35581(19)	0.3818(3)	0.61192(18)	0.0220(4)
C2	0.2879(2)	0.5540(4)	0.52047(18)	0.0255(4)
H1	0.317491	0.575342	0.446189	0.031
C3	0.1888(2)	0.6820(4)	0.53298(18)	0.0258(4)
C4	0.1357(2)	0.8566(4)	0.4313(2)	0.0371(5)
H2A	0.181343	0.847633	0.364051	0.056
H2B	0.140303	1.018001	0.464543	0.056
H2C	0.051431	0.815677	0.400267	0.056
C5	0.1225(2)	0.6683(5)	0.6419(2)	0.0366(5)
H3A	0.152261	0.532212	0.693589	0.055
H3B	0.036102	0.649845	0.611502	0.055
H3C	0.136781	0.814256	0.690427	0.055
OW1	0.39298(16)	−0.1401(3)	0.82073(14)	0.0266(3)
H4A	0.401(3)	−0.156(5)	0.894(3)	0.045(8)
H4B	0.381(3)	−0.266(6)	0.794(3)	0.040(8)

which was sealed in a Pyrex tube and heated to 70 °C for 68 h, then cooled to room temperature at 20 °C/h. The solution pH values before and after the reaction were ~ 6 and ~ 5 , respectively. The solid products were recovered by vacuum filtration. Colorless rod crystals were obtained with unidentified colorless chunk. The product was stable in air. The yield of the compound was about 30% based on zinc. EDX analysis confirmed the presence of Zn.

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Experimental detail

All hydrogen atoms of 3,3-dimethylacrylate were placed in calculated positions and refined as riding model. The U_{iso} value of the methyl group was set to $1.5U_{\text{eq}}$ and the U_{iso} values of the other hydrogen atoms were set to $1.2U_{\text{eq}}$. The hydrogen atoms in water molecules were located in difference Fourier maps, and their positions and isotropic displacement parameters were refined.

Comment

Metal complexes containing carboxylate are one of the most important classes in coordination chemistry. Although limited in number, however, Zn(II) carboxylates have been studied due to their importance in supramolecular chemistry and in biological system [5–11]. In this study we report a new zinc(II) complex containing 3,3-dimethylacrylate. The crystal structure of the title compound simply comprises discrete zinc(II) complex moieties. The crystallographically unique Zn atom, located on a 2-fold axis, is coordinated by four oxygen atoms from two symmetry related 3,3-dimethylacrylate ligands [$d(\text{Zn}-\text{O}) = 2.0934(13) \text{ \AA}$ and $2.2810(14) \text{ \AA}$] in a κ^2, O, O' mode (see the figure). Two water molecules [$d(\text{Zn}-\text{O}) = 2.0051(15) \text{ \AA}$] in *cis*-configuration complete the distorted octahedral environment of Zn1. The bond valence sum (BVS) calculation for Zn gives a value of +2.00 indicating an oxidation state of +2 [12]. The crystal packing of the title compound is stabilized by the presence of hydrogen bonds between the coordinated water molecules and the carboxylate oxygen atoms [$d(\text{OH} \cdots \text{O}) = 1.9271(1) \text{ \AA}$ and $1.9538(1) \text{ \AA}$] in adjacent zinc(II) complex moieties, which results in the formation of layers on the *ac*-plane. The hydrogen bonded layers stack along the *a*-axis and interact through van der Waals forces between the methyl groups. The interlayer distance between the methyl groups is $>3.86 \text{ \AA}$.

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References

1. Bruker. SAINT, APEX2, Bruker Inc., Madison, WI, USA (2016).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
3. Hubschle, C. B.; Sheldrick, G. M.; Dittrich, B.: ShelXle: a Qt graphical user interface for SHELXL. *J. Appl. Crystallogr.* **44** (2011) 1281–1284.
4. Brandenburg, K.: DIAMOND. Visual crystal structure information system. Version 4.2.2. Crystal Impact, Bonn, Germany (2016).
5. Hafeez, S. T.; Ali, S.; Tahir, M. N.; Iqbal, M.; Munawar, K. S.: One-pot synthesis, structural elucidation, DNA binding and alkaline phosphatase inhibition studies of zinc(II) complexes with 4-nitrocinnamic acid and ethylenediamine. *J. Coord. Chem.* **67** (2014) 2479–2495.
6. Zelenák, V.; Sabo, M.; Massa, W.; Llewellyn, P.: Preparation, characterization and crystal structure of two zinc(II) benzoate complexes with pyridine-based ligands nicotinamide and methyl-3-pyridylcarbamate. *Inorg. Chim. Acta* **357** (2004) 2049–2059.
7. Cunneane, S. C.: Zinc: Clinical and Biochemical Significance, CRC Press, Boca Raton, FL (1988).
8. Burrows, A. D.; Chan, S.; Gee, W. J.; Mahon, M. F.; Richardson, C.; Sebestyen, V. M.; Turski, D.; Warren, M. R.: The impact of *N,N'*-ditopic ligand length and geometry on the structures of zinc-based mixed-linker metal–organic frameworks. *CrystEngComm* **19** (2017) 5549–5557.
9. Dybtsev, D. N.; Chun, H.; Kim, K.: Rigid and flexible: a highly porous metal-organic framework with unusual guest-dependent dynamic behavior. *Angew. Chem. Int. Ed.* **43** (2004) 5033–5036.
10. Chun, H.; Dybtsev, D. N.; Kim, H.; Kim, K.: Synthesis, X-ray crystal structures, and gas sorption properties of pillared square grid nets based on paddle-wheel motifs: implications for hydrogen storage in porous materials. *Chem. Eur. J.* **11** (2005) 3521–3529.
11. Chen, B.; Liang, C.; Yang, J.; Contreras, D. S.; Clancy, Y. L.; Lobkovsky, E. B.; Yaghi, O. M.; Dai, S.: A microporous metal-organic framework for gas-chromatographic separation of alkanes. *Angew. Chem. Int. Ed.* **45** (2006) 1390–1393.
12. Brese, N. E.; O'Keeffe, M.: Bond-valence parameters for solids. *Acta Crystallogr. B* **47** (1991) 192–197.