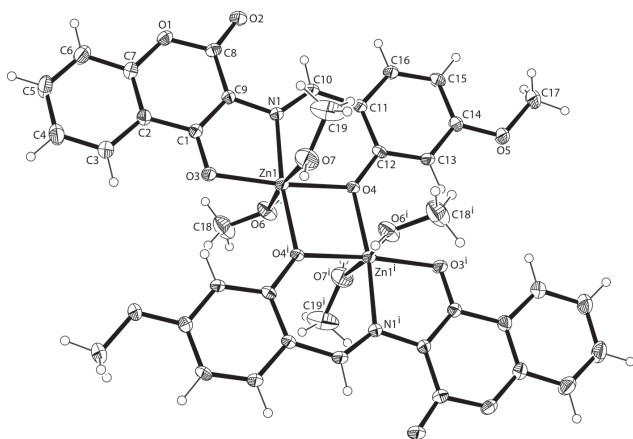


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Crystal structure of tetrakis(methanol- κO)-bis $\{\mu_2$ -3-((4-methoxy-2-oxidobenzylidene)amino)-2-oxo-2H-chromen-4-olate- $\kappa^4 O, N; O': O'\}$ dizinc(II), $C_{38}H_{38}Zn_2N_2O_{14}$



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Abstract

$C_{38}H_{38}Zn_2N_2O_{14}$, monoclinic, $P2_1/n$ (no. 14), $a = 9.6906(6)$ Å, $b = 7.9055(5)$ Å, $c = 24.0501(18)$ Å, $\beta = 99.878(7)^\circ$, $Z = 2$, $V = 1815.1(2)$ Å³, $R_{gt}(F) = 0.0474$, $wR_{ref}(F^2) = 0.1143$, $T = 293$ 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 materials

The ligand was synthesized according to a method reported previously [3–5]. To an ethanol solution (5 mL) of 2-hydroxy-4-methoxybenzaldehyde (152.2 mg, 1 mmol) was added an ethanol solution (5 mL) of 3-amino-4-hydroxy-2H-chromen-2-one (177.2 mg, 1 mmol). The solution was stirred under reflux conditions at 434 K for 6 h. After cooling to room temperature, the precipitate was filtered and washed with ethanol and

Table 1: Data collection and handling.

Crystal:	Clear light Yellow, block
Size:	0.33 × 0.21 × 0.20 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	9.5 cm ^{−1}
Diffractometer, scan mode:	Bruker SMART, φ and ω -scans
$2\theta_{max}$, completeness:	26°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	7013, 3565, 0.038
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 2853
$N(param)_{refined}$:	262
Programs:	Bruker programs [1], SHELX [2]

hexane. The product was dried under vacuum (yield 71.8%, m.p. 460–461 K). Anal. Calcd. for $C_{17}H_{13}NO_5$ (%): C, 65.59; H, 4.21; N, 4.50. Found (%): C, 66.47; H, 4.13; N, 4.85.

A solution of zinc(II) acetate dihydrate (3.00 mg, 0.014 mmol) in methanol (5 mL) was added dropwise to a mixed solution composed by triethylamine (0.5 mL) and dichloromethane (5 mL) of 4-hydroxy-3-[(2-hydroxy-4-methoxy-benzylidene)-amino]-benzopyran-2-one (4.40 mg, 0.014 mmol) at room temperature. The color of the mixing solution turns to yellow immediately, and the mixture was filtered and the filtrate was allowed to stand at room temperature for about 2 weeks and we obtained yellow block crystals. Elemental analysis-Anal. calcd. for $C_{38}H_{38}Zn_2N_2O_{14}$ (%): C, 52.01; H, 4.36; N, 3.19. Found (%): C, 52.53; H, 4.22; N, 3.46.

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

Comment

Coumarin derivatives have been found to exhibit anti-biotic, antibacterial, antifungal, anticoagulating and plant regulating activities. Schiff base (contain $-C=N-$ group) as a class of ligands are known to coordinate with metal ions through the azomethine nitrogen atom [6, 7]. And they can form all kinds of stable metal complexes [8, 9], which have interesting structures and wide use in biochemistry [10, 11]. Furthermore, they may have magnetic properties [12, 13], photophysical properties [14, 15], and used in the

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

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Zn1	0.39341(4)	0.10872(6)	0.525675(17)	0.04040(17)
O1	−0.0488(2)	0.4116(3)	0.57414(10)	0.0378(6)
O2	−0.1022(2)	0.2989(3)	0.49031(10)	0.0405(6)
O3	0.3550(2)	0.2433(3)	0.59301(10)	0.0421(6)
O4	0.4016(2)	−0.0388(3)	0.45665(9)	0.0302(5)
O5	0.2802(3)	−0.2579(3)	0.27440(10)	0.0464(7)
O6	0.3326(3)	−0.1402(4)	0.56647(11)	0.0509(7)
H6	0.271(3)	−0.209(3)	0.5491(8)	0.076*
O7	0.4601(3)	0.3285(4)	0.47869(13)	0.0607(8)
H7	0.538(2)	0.382(4)	0.4863(15)	0.091*
N1	0.1833(3)	0.1571(3)	0.49796(11)	0.0272(6)
C1	0.2271(3)	0.2917(4)	0.58657(13)	0.0295(7)
C2	0.1795(4)	0.3873(4)	0.63125(13)	0.0309(7)
C3	0.2653(4)	0.4235(4)	0.68308(14)	0.0391(9)
H3	0.3576	0.3858	0.6898	0.047*
C4	0.2142(5)	0.5141(5)	0.72391(16)	0.0492(10)
H4	0.2716	0.5366	0.7582	0.059*
C5	0.0773(5)	0.5718(5)	0.71400(17)	0.0514(11)
H5	0.0433	0.6339	0.7416	0.062*
C6	−0.0084(4)	0.5381(5)	0.66372(17)	0.0480(10)
H6A	−0.1003	0.5772	0.6570	0.058*
C7	0.0430(4)	0.4453(4)	0.62303(14)	0.0334(8)
C8	−0.0102(3)	0.3162(4)	0.53107(14)	0.0290(7)
C9	0.1292(3)	0.2544(4)	0.53833(13)	0.0275(7)
C10	0.1128(3)	0.1064(4)	0.45094(14)	0.0312(7)
H10	0.0185	0.1357	0.4434	0.037*
C11	0.1655(3)	0.0081(4)	0.40855(13)	0.0275(7)
C12	0.3024(3)	−0.0600(4)	0.41142(12)	0.0250(7)
C13	0.3320(3)	−0.1492(4)	0.36523(13)	0.0284(7)
H13	0.4211	−0.1945	0.3668	0.034*
C14	0.2340(4)	−0.1729(4)	0.31713(13)	0.0316(7)
C15	0.0992(4)	−0.1103(4)	0.31372(14)	0.0373(8)
H15	0.0319	−0.1273	0.2817	0.045*
C16	0.0688(4)	−0.0227(5)	0.35922(14)	0.0364(8)
H16	−0.0216	0.0190	0.3573	0.044*
C17	0.1883(4)	−0.2626(5)	0.22137(15)	0.0507(11)
H17A	0.2359	−0.3125	0.1936	0.076*
H17B	0.1600	−0.1496	0.2101	0.076*
H17C	0.1072	−0.3289	0.2248	0.076*
C18	0.3295(6)	−0.1604(7)	0.62426(18)	0.0738(15)
H18A	0.2415	−0.1206	0.6323	0.111*
H18B	0.4044	−0.0965	0.6459	0.111*
H18C	0.3407	−0.2779	0.6341	0.111*
C19	0.3768(6)	0.4115(6)	0.4331(2)	0.0863(18)
H19A	0.3244	0.3294	0.4087	0.129*
H19B	0.4359	0.4744	0.4123	0.129*
H19C	0.3134	0.4874	0.4471	0.129*

fields of molecular recognition [16, 17], and supramolecular architectures [18].

The X-ray structural study reveals that the title complex is dinuclear (*cf.* the figure). Thus the title complex Zn(II) consists of two tridentate deprotonated ligands, and four coordinated

methanol molecules. Each Zn(II) is hexa-coordinated by one nitrogen atoms and three oxygen atoms of deprotonated ligands defining the N₂O₂ basal plane, plus two oxygen atoms from the methanol molecules occupying the apical positions. Thus, the coordination geometry of the Zn(II) center can be described as a slightly distorted octahedron.

In the crystal structure there are two intermolecular (O6—H6···O2 and O7—H7···O7) hydrogen bonds, which link the title complex molecules into an infinite chain-like supramolecular structure. This linkage is further stabilized by two C—H···π and π···π stacking interactions with the centroid-centroid distances of 3.916(2)–4.003(2) Å to form a 3D network.

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References

1. Bruker: APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA (2009).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
3. Xu, L.; Li, N.; Zhao, L.: Crystal structure of 4-chloro-4',6'-dichloro-2,2'-[propane-1,3-diyl]bis(dinitrobenzylidene) diphenol, C₁₇H₁₄Cl₃N₂O₄. *Z. Kristallogr. NCS* **231** (2016) 967–968.
4. Zhao, L.; Wang, F.; An, Q. Q.; Zhao, J. X.: Crystal structure of (E)-1-(4-(((E)-3,5-dichloro-2-hydroxybenzylidene)amino)phenyl)ethan-1-one O-ethyl oxime, C₁₇H₁₆Cl₂N₂O₂. *Z. Kristallogr. NCS* **231** (2016) 1045–1046.
5. Sun, Y. X.; Liu, G. H.; Wang, J.; Liu, S. H.; Wang, H.: Crystal structure of bis(3-ethoxy-4-hydroxybenzaldehyde)O,O'-(butane-1,4-diyl)dioxime, C₂₂H₂₈N₂O₆. *Z. Kristallogr. NCS* **227** (2012) 123–124.
6. Dong, W. K.; Zhu, L. C.; Dong, Y. J.; Ma, J. C.; Zhang, Y.: Mono, di and heptanuclear metal(II) complexes based on symmetric and asymmetric tetradentate Salamo-type ligands: syntheses, structures and spectroscopic properties. *Polyhedron* **117** (2016) 148–154.
7. Sun, Y. X.; Zhao, Y. Y.; Li, C. Y.; Yu, B.; Guo, J. Q.; Li, J.: Supramolecular cobalt(II) and copper(II) complexes with Schiff base ligand: syntheses, characterizations and crystal structures. *Chin. J. Inorg. Chem.* **32** (2016) 913–920.
8. Wang, P.; Zhao, L.: Synthesis, structure and spectroscopic properties of the trinuclear cobalt(II) and nickel(II) complexes based on 2-hydroxynaphthaldehyde and bis(aminoxoyl)alkane. *Spectrochim. Acta A* **135** (2015) 342–350.
9. Dong, W. K.; Duan, J. G.; Guan, Y. H.; Shi, J. Y.; Zhao, C. Y.: Synthesis, crystal structure and spectroscopic behaviors of Co(II) and Cu(II) complexes with Salen-type bisoxime ligands. *Inorg. Chim. Acta* **362** (2009) 1129–1134.
10. Wu, H. L.; Yuan, J. K.; Bai, Y.; Jia, F.; Liu, B.; Kou, F.; Kong, J.: Synthesis, structure, DNA-binding properties, and antioxidant

- activity of copper(II) and cobalt(II) complexes with bis(*N*-allylbenzimidazol-2-ylmethyl)benzylamine. *Trans. Met. Chem.* **36** (2011) 819–827.
11. Wu, H. L.; Bai, Y. C.; Zhang, Y. H.; Li, Z.; Wu, M. C.; Chen, C. Y.; Zhang, J. W.: Synthesis, crystal structure, antioxidation and DNA-binding properties of a dinuclear copper(II) complex with bis(*N*-salicylidene)-3-oxapentane-1,5-diamine. *J. Coord. Chem.* **67** (2014) 3054–3066.
 12. Song, X. Q.; Liu, P. P.; Liu, Y. A.; Zhou, J. J.; Wang, X. L.: Two dodecanuclear heterometallic $[Zn_6Ln_6]$ clusters constructed by a multidentate salicylamide salen-like ligand: Synthesis, structure, luminescence and magnetic properties. *Dalton Trans.* **45** (2016) 8154–8163.
 13. Dong, W. K.; Ma, J. C.; Dong, Y. J.; Zhu, L. C.; Zhang, Y.: Di- and tetranuclear heterometallic 3d-4f cobalt(II)-lanthanide(III) complexes derived from a hexadentate bisoxime: syntheses, structures and magnetic properties. *Polyhedron* **115** (2016) 228–235.
 14. Wang, L.; Ma, J. C.; Dong, W. K.; Zhu, L. C.; Zhang, Y.: A novel self-assembled nickel(II)-cerium(III) heterotetranuclear dimer constructed from N_2O_2 -type bisoxime and terephthalic acid: synthesis, structure, and photophysical properties. *Z. Anorg. Allg. Chem.* **642** (2016) 834–839.
 15. Dong, W. K.; Ma, J. C.; Zhu, L. C.; Sun, Y. X.; Sunday, F. A.; Zhang, Y.: A series of heteromultinuclear zinc(II)-lanthanide(III) complexes based on 3-MeOsalamo: syntheses, structural characterizations, and luminescent properties. *Cryst. Growth Des.* **14** (2016) 6903–6914.
 16. Dong, W. K.; Li, X. L.; Wang, L.; Zhang, Y.; Ding, Y. J.: A new application of Salamo-type bisoximes: As a relay-sensor for Zn^{2+}/Cu^{2+} and its novel complexes for successive sensing of H^+/OH^- . *Sens. Actuators B* **229** (2016) 370–378.
 17. Dong, W. K.; Sunday, F. A.; Zhang, Y.; Sun, Y. X.; Dong, X. Y.: A reversible “turn-on” fluorescent sensor for selective detection of Zn^{2+} . *Sens. Actuators B* **238** (2017) 723–734.
 18. Dong, W. K.; Sun, Y. X.; Zhao, C. Y.; Dong, X. Y.; Xu, L.: Synthesis, structure and properties of supramolecular Mn(II), Co(II), Ni(II) and Zn(II) complexes containing Salen-type bisoxime ligands. *Polyhedron* **29** (2010) 2087–2097.