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Synthesis and crystal structure of bis(μ_2 -acetato- $\kappa^2 O:O'$)-bis(μ_2 -1-(8-(2-oxidophenyl)-3,6-dioxa-2,7-diazaocta-1,7-dien-1-yl)naphthalen-2-olato- $\kappa^6 O:O,N,N',O':O'$)trizinc(II), $C_{44}H_{38}Zn_3N_4O_{12}$

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.20 × 0.20 × 0.20 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.5 mm ⁻¹
Diffractometer, scan mode:	Bruker SMART, φ and ω -scans
$\theta_{\max}$, completeness:	50°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	28278, 7220, 0.055
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4975
$N(\text{param})_{\text{refined}}$:	582
Programs:	Bruker programs [1], SHELX [2]

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.0000	0.55777(9)	0.2500	0.0350(4)
Zn2	0.19058(5)	0.54874(7)	0.26763(5)	0.0404(3)
O1	0.1077(3)	0.6531(4)	0.2863(3)	0.0367(13)
O2	0.3745(3)	0.5945(4)	0.3520(3)	0.0560(17)
O3	0.3491(4)	0.4232(5)	0.2622(4)	0.070(2)
O4	0.1024(3)	0.4596(4)	0.2850(3)	0.0432(14)
O5	0.1583(3)	0.5779(4)	0.1619(3)	0.0506(16)
O6	0.0160(3)	0.5655(4)	0.1459(3)	0.0404(14)
N1	0.2887(4)	0.6336(5)	0.3286(4)	0.0476(19)
N2	0.2708(4)	0.4244(5)	0.2805(4)	0.050(2)
C1	0.1219(5)	0.7234(6)	0.3330(4)	0.0358(19)
C2	0.0512(5)	0.7729(6)	0.3447(4)	0.040(2)
H2	−0.0045	0.7531	0.3188	0.049*
C3	0.0606(5)	0.8487(6)	0.3924(4)	0.042(2)
H3	0.0118	0.8797	0.3972	0.051*
C4	0.1437(5)	0.8802(6)	0.4341(4)	0.043(2)
C5	0.1507(6)	0.9552(7)	0.4821(6)	0.072(3)
H5	0.1004	0.9837	0.4860	0.087*
C6	0.2306(7)	0.9906(7)	0.5255(5)	0.067(3)
H6	0.2347	1.0407	0.5587	0.080*
C7	0.3057(7)	0.9457(7)	0.5161(6)	0.073(3)
H7	0.3605	0.9672	0.5430	0.087*
C8	0.2972(6)	0.8694(7)	0.4666(6)	0.066(3)
H8	0.3471	0.8411	0.4615	0.080*
C9	0.2161(5)	0.8336(6)	0.4242(4)	0.042(2)
C10	0.2065(5)	0.7543(6)	0.3746(4)	0.038(2)
C11	0.2815(5)	0.7040(6)	0.3719(4)	0.044(2)
H11	0.3331	0.7240	0.4057	0.053*
C12	0.4081(5)	0.5827(7)	0.2905(5)	0.062(3)

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Abstract

$C_{44}H_{38}Zn_3N_4O_{12}$, monoclinic, $C2/c$ (no. 15), $a = 16.2076(17)$ Å, $b = 13.9361(19)$ Å, $c = 19.029(3)$ Å, $\beta = 107.635(14)^\circ$, $V = 4096.1(10)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0760$, $wR_{\text{ref}}(F^2) = 0.1768$, $T = 173$ 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.

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Table 3: (continued)

Atom	x	y	z	U _{iso} */U _{eq}
H12A	0.4684	0.5639	0.3097	0.074*
H12B	0.4065	0.6447	0.2669	0.074*
C13	0.3630(6)	0.5116(8)	0.2325(6)	0.068(3)
H13A	0.3077	0.5379	0.2038	0.081*
H13B	0.3975	0.5014	0.1995	0.081*
C14	0.2589(6)	0.3438(7)	0.3081(5)	0.065(3)
H14	0.3005	0.2966	0.3120	0.079*
C15	0.1861(5)	0.3202(6)	0.3337(5)	0.051(2)
C16	0.1915(6)	0.2338(7)	0.3711(6)	0.082(4)
H16	0.2400	0.1952	0.3773	0.098*
C17	0.1276(7)	0.2039(7)	0.3991(6)	0.074(3)
H17	0.1344	0.1481	0.4271	0.088*
C18	0.0525(6)	0.2577(7)	0.3854(5)	0.061(3)
H18	0.0072	0.2361	0.4017	0.073*
C19	0.0449(6)	0.3440(6)	0.3473(5)	0.048(2)
H19	−0.0058	0.3796	0.3386	0.058*
C20	0.1116(5)	0.3786(6)	0.3216(4)	0.041(2)
C21	0.0789(5)	0.5836(6)	0.1235(4)	0.040(2)
C22	0.0607(5)	0.6181(7)	0.0470(5)	0.063(3)
H22A	0.0312	0.5688	0.0134	0.094*
H22B	0.1142	0.6335	0.0376	0.094*
H22C	0.0249	0.6743	0.0400	0.094*

Source of material

Synthesis of the ligand H₂L: A solution of salicylaldehyde (305.3 mg, 2.5 mmol) in ethanol (50 mL) was added to a solution of 1,2-bis(aminoxy)ethane (460.5 mg, 5 mmol) in ethanol (100 mL) and the mixture was heated at 323–328 K for 6 h. The solution was concentrated *in vacuo* and the residue was purified by column chromatography (SiO₂, chloroform/ethyl acetate 30:1) to afford a yellow oily product of 2-[O-(1-ethyloxyamide)]oxime-phenol. Yield 69.8%. Elemental analysis – Anal. Calcd. for C₉H₁₂N₂O₃: C, 55.09%; H, 6.16%; N, 14.28%. Found: C, 55.33%; H, 6.03%; N, 14.02%. Then, a solution of 2-[O-(1-ethyloxyamide)]oxime-phenol (294.3 mg, 1.5 mmol) in ethanol (10 mL) was added to a solution of 2-hydroxy-1-naphthaldehyde (258.3 mg, 1.5 mmol) in ethanol (20 mL) and the mixture was heated at 333 K for 2 h. After cooling to room temperature, white precipitates were collected. Yield 71.3%, m.p. 402–403 K. Elemental analysis – Anal. Calcd. for C₂₀H₁₈N₂O₄: C, 68.56%; H, 5.18%; N, 8.00%. Found: C, 68.83%; H, 4.98%; N, 7.83%.

Synthesis of the Zn(II) complex An ethanol solution (3.0 mL) of zinc(II) acetate tetrahydrate (7.7 mg, 0.03 mmol) was added to a acetonitrile solution (2.0 mL) of H₂L (700.7 mg, 0.02 mmol) at room temperature, the color of the mixing solution turned light yellow immediately. After the mixture was stirred for 10 min and then the mixture was filtered. The resulting filtrate as left undisturbed for about two weeks to form clear light yellow block-like crystals. Yield:

63.3%. Elemental analysis – Anal. Calcd. for C₄₄H₃₈Zn₃N₄O₁₂: C, 56.55%; H, 4.00%; N, 6.18%; Zn, 14.43%. Found: C, 56.73%; H, 4.21%; N, 6.01%; Zn, 14.22%.

Experimental details

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

Discussion

Some salen-type ligands (R-CCH=N-C(CH₂)₂-CN=CH-CR) and their transition metal complexes have been extensively investigated for several decades [4–7], which can be used in electrochemical and biological fields [9], magnetisms, luminescent materials and supramolecular architectures [10–13]. It is important to introduce suitable functional groups into the organic ligands in order to improve or tune the properties of these metal complexes. When an *O*-alkyl oxime moiety (–CCH=N–CO–C(CH₂)_n–CO–CN=CH–C) instead of the imine moiety is used, the larger electronegativity of the oxygen atoms is expected to affect the electronic properties of the Salamo-type ligands, which leads to much more stable complexes [14].

The title compound is only built up by the C₄₄H₃₈Zn₃N₄O₁₂ molecules, in which all bond lengths are within the normal ranges (*cf.* the figure). Because of the centrosymmetric trinuclear structure of the title Zn(II) complex, the two terminal Zn(II) atoms (Zn2 and Zn2') are both in the *cis*-N₂O₂ coordination of the deprotonated (L)^{2−} units. The carboxylate oxygen (O5) atom from the bridging acetato ligand coordinates to Zn2 in axial positions. The coordination sphere of the central Zn1 atom is completed by four phenoxo oxygen (O1, O1', O4 and O4') atoms from two (L)^{2−} moieties and two acetato oxygen (O6 and O6') atoms. All of the six oxygen atoms coordinate to Zn1 constituting an octahedral geometry [15, 16].

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