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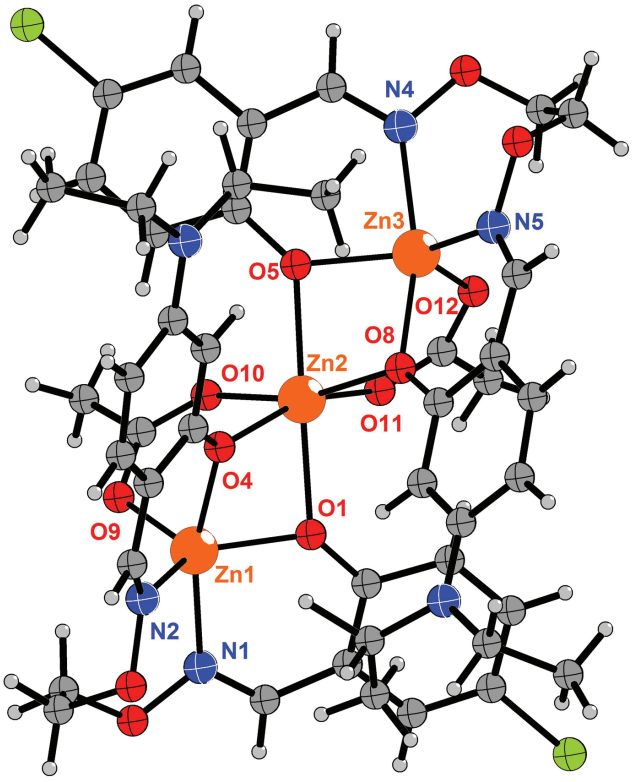
Synthesis and crystal structure of bis(μ_2-acetato-κ^2O:O')-bis{μ_2-4-chloro-2-(8-(4-(diethylamino)-2-oxidophenyl)-3,6-dioxa-2,7-diazaocta-1,7-dien-1-yl)phenolato-κ^6O:O,N,N',O':O'}trizinc(II), $C_{44}H_{49}Cl_2N_6O_{12}Zn_3$



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Abstract

$C_{44}H_{49}Cl_2N_6O_{12}Zn_3$, monoclinic, $P\bar{1}$ (no. 2), $a = 9.7387(8)$ Å, $b = 13.7034(12)$ Å, $c = 20.2498(16)$ Å, $\alpha = 72.539(8)°$, $\beta = 82.872(7)°$, $\gamma = 72.157(8)°$, $Z = 2$, $V = 2452.3(4)$ Å^3, $R_{gt}(F) = 0.0604$, $wR_{ref}(F^2) = 0.1392$, $T = 293(2)$ 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.

Table 1: Data collection and handling.

Crystal:	Clear light yellow block
Size:	0.20 × 0.15 × 0.12 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	1.63 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}	26.0°
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	16652, 9456, 0.119
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4735
$N(param)_{refined}$:	629
Programs:	CrysAlis^{PRO} [17], SHELX [18]

Source of material

A solution of zinc(II) acetate hydrate (3.32 mg, 0.015 mmol) in ethanol (3 mL) was added dropwise to a solution of H_2L 4-(diethylamino)-2-hydroxybenzaldehyde *O*-(2-(((5-chloro-2-hydroxybenzylidene)amino)oxy)ethyl) oxime (3.98 mg, 0.010 mmol) in acetonitrile (2 mL) at room temperature. The color of the mixing solution turned yellow immediately, the mixture was filtered and the filtrate was allowed to stand at room temperature for about two weeks. The solvent was partially evaporated and clear light colourless single crystals were obtained. Yield: 58%. Elemental analysis-anal. calcd. for $C_{44}H_{50}C_{l2}N_6O_{12}Zn_3$: C, 47.10%; H, 4.49%; N, 7.49%. Found: C, 47.05%; H, 4.46%; N, 7.36%.

Experimental details

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

Discussion

Salen-type compounds and their transition metal complexes have been investigated for many decades with a focus on modified ligand systems in the last years [1–4]. New research fields are the use of such complexes in a very wide and diversified subjects such as, optical and magnetic materials [5–10] and supramolecular architectures [11–16].

The structure is built up by one $C_{44}H_{50}C_{l2}N_6O_{12}Zn_3$ complex. The assembly of three Zn(II) ions, two completely

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.66226(10)	1.10928(8)	0.36632(5)	0.0579(3)
Zn2	0.84169(9)	0.98703(7)	0.26781(4)	0.0463(3)
Zn3	0.96220(9)	0.87614(7)	0.15526(4)	0.0466(3)
Cl1	0.9101(3)	1.5470(2)	0.12327(15)	0.0979(9)
Cl2	0.9566(4)	0.3986(2)	0.44200(14)	0.1146(11)
O1	0.7683(6)	1.1516(4)	0.2780(3)	0.0583(15)
O2	0.6231(7)	1.2762(5)	0.4507(3)	0.088(2)
O3	0.3732(7)	1.2378(6)	0.4061(4)	0.103(2)
O4	0.6410(5)	1.0013(4)	0.3185(2)	0.0487(13)
O5	0.9202(5)	0.8247(4)	0.2558(2)	0.0512(14)
O6	1.1847(6)	0.6856(4)	0.1071(3)	0.0672(17)
O7	0.9190(6)	0.7997(4)	0.0363(3)	0.0661(17)
O8	0.7888(5)	1.0039(4)	0.1671(2)	0.0484(13)
O9	0.7917(5)	1.0044(4)	0.4401(3)	0.0581(15)
O10	0.9361(5)	0.9298(4)	0.3641(2)	0.0513(14)
O11	1.0329(5)	1.0161(4)	0.2275(3)	0.0502(14)
O12	1.1137(5)	0.9495(4)	0.1373(2)	0.0544(15)
N1	0.6740(8)	1.2490(5)	0.3881(4)	0.065(2)
N2	0.4497(8)	1.1399(6)	0.3889(4)	0.078(2)
N3	0.4570(9)	0.7425(7)	0.2752(4)	0.083(3)
N4	1.0913(6)	0.7171(5)	0.1612(3)	0.0515(17)
N5	0.8694(7)	0.8870(5)	0.0682(3)	0.0547(19)
N6	0.3801(9)	1.3050(7)	0.1172(5)	0.097(3)
C1	0.8052(9)	1.2390(7)	0.2460(4)	0.059(2)
C2	0.8590(8)	1.2554(6)	0.1772(4)	0.054(2)
H2	0.872506	1.201630	0.155779	0.064*
C3	0.8923(9)	1.3472(7)	0.1403(5)	0.069(3)
H3	0.928731	1.355002	0.094914	0.082*
C4	0.8714(9)	1.4274(7)	0.1709(5)	0.068(3)
C5	0.8223(9)	1.4152(7)	0.2375(5)	0.072(3)
H5	0.813445	1.469408	0.257779	0.087*
C6	0.7844(9)	1.3235(7)	0.2768(5)	0.064(2)
C7	0.7230(9)	1.3216(7)	0.3469(5)	0.065(3)
H7	0.719785	1.379371	0.362717	0.078*
C8	0.5501(13)	1.2049(9)	0.4925(5)	0.092(4)
H8A	0.554576	1.204123	0.540284	0.110*
H8B	0.601937	1.133967	0.488671	0.110*
C9	0.3978(12)	1.2260(9)	0.4777(5)	0.106(4)
H9A	0.362505	1.167871	0.507232	0.127*
H9B	0.341830	1.290715	0.489637	0.127*
C10	0.3600(10)	1.0952(9)	0.3766(5)	0.079(3)
H10	0.262836	1.124392	0.386552	0.095*
C11	0.3942(9)	1.0081(8)	0.3499(4)	0.067(3)
C12	0.5289(8)	0.9663(6)	0.3200(4)	0.052(2)
C13	0.5465(7)	0.8789(6)	0.2945(4)	0.052(2)
H13	0.634418	0.852244	0.273177	0.063*
C14	0.4367(9)	0.8295(7)	0.2998(4)	0.062(2)
C15	0.2993(9)	0.8747(8)	0.3289(4)	0.077(3)
H15	0.223090	0.845622	0.332732	0.093*
C16	0.2844(9)	0.9617(8)	0.3508(5)	0.080(3)
H16	0.193642	0.993194	0.367746	0.095*
C17	0.3503(12)	0.6813(10)	0.2897(7)	0.122(5)
H17A	0.368723	0.638066	0.257657	0.146*
H17B	0.254533	0.730801	0.281556	0.146*
C18	0.3536(16)	0.6089(12)	0.3636(8)	0.207(8)
H18A	0.295604	0.561930	0.367485	0.311*
H18B	0.316086	0.651691	0.395134	0.311*
H18C	0.451281	0.567590	0.374551	0.311*
C19	0.5850(10)	0.7027(8)	0.2374(6)	0.087(3)
H19A	0.597367	0.628174	0.241564	0.105*
H19B	0.667592	0.707118	0.257462	0.105*
C20	0.5811(13)	0.7633(9)	0.1624(6)	0.132(5)
H20A	0.669549	0.734389	0.139234	0.198*
H20B	0.569715	0.837028	0.157952	0.198*
H20C	0.501366	0.757222	0.141907	0.198*
C21	0.9332(8)	0.7275(7)	0.2972(4)	0.047(2)
C22	0.8666(8)	0.7126(6)	0.3630(4)	0.051(2)
H22	0.816223	0.772384	0.377753	0.061*
C23	0.8725(9)	0.6130(8)	0.4072(4)	0.070(3)
H23	0.824429	0.605910	0.450287	0.084*
C24	0.9513(10)	0.5235(7)	0.3863(4)	0.068(3)
C25	1.0189(9)	0.5344(7)	0.3236(5)	0.066(3)
H25	1.071187	0.473550	0.310478	0.079*
C26	1.0128(8)	0.6347(6)	0.2774(4)	0.051(2)
C27	1.0917(8)	0.6341(6)	0.2126(4)	0.051(2)
H27	1.147851	0.568362	0.207306	0.061*
C28	1.1778(9)	0.7719(7)	0.0491(4)	0.061(2)
H28A	1.268116	0.758657	0.022454	0.073*
H28B	1.167767	0.834758	0.064064	0.073*
C29	1.0583(10)	0.7946(7)	0.0036(4)	0.076(3)
H29A	1.052900	0.862154	−0.031032	0.091*
H29B	1.081982	0.739922	−0.020617	0.091*
C30	0.7522(10)	0.9568(7)	0.0402(4)	0.060(2)
H30	0.723331	0.948733	0.000562	0.072*
C31	0.6664(8)	1.0421(7)	0.0640(4)	0.051(2)
C32	0.6827(8)	1.0661(6)	0.1253(4)	0.0430(18)
C33	0.5839(7)	1.1530(6)	0.1418(4)	0.055(2)
H33	0.592182	1.165545	0.183593	0.066*
C34	0.4744(8)	1.2214(7)	0.0998(4)	0.060(2)
C35	0.4586(8)	1.1997(7)	0.0368(4)	0.057(2)
H35	0.386737	1.245033	0.006405	0.069*
C36	0.5511(9)	1.1116(7)	0.0225(4)	0.054(2)
H36	0.537389	1.095969	−0.017446	0.064*
C37	0.2673(13)	1.3796(11)	0.0714(7)	0.123(5)
H37A	0.190712	1.416414	0.098335	0.148*
H37B	0.226712	1.340519	0.050081	0.148*
C38	0.3223(17)	1.4591(11)	0.0166(8)	0.180(7)
H38A	0.378711	1.488223	0.037012	0.270*
H38B	0.242521	1.515370	−0.006309	0.270*
H38C	0.381419	1.425188	−0.016424	0.270*
C41	0.9036(8)	0.9387(6)	0.4239(4)	0.0435(19)
C42	1.0001(8)	0.8685(6)	0.4809(4)	0.065(2)
H42A	0.949275	0.824586	0.514441	0.098*
H42B	1.030367	0.911474	0.502697	0.098*
H42C	1.083184	0.824015	0.462714	0.098*
C43	1.1174(8)	1.0033(6)	0.1782(4)	0.0461(19)
C44	1.2339(8)	1.0602(6)	0.1622(4)	0.054(2)
H44A	1.228446	1.097156	0.196302	0.081*
H44B	1.220149	1.110523	0.117124	0.081*
H44C	1.326966	1.008928	0.162927	0.081*
C39	0.365(3)	1.312(2)	0.1880(8)	0.090(8)

Table 2 (continued)

	x	*y*	*z*	U_{iso}*/U_{eq}
H39A	0.262550	1.339108	0.198572	0.108*
H39B	0.397672	1.240477	0.218296	0.108*
C40	0.438(3)	1.3775(19)	0.2062(15)	0.133(10)
H40A	0.539964	1.352789	0.196137	0.200*
H40B	0.422270	1.372345	0.254711	0.200*
H40C	0.401530	1.450462	0.179785	0.200*
C39′	0.427(3)	1.355(2)	0.1678(12)	0.104(9)
H39C	0.529580	1.328493	0.175734	0.125*
H39D	0.396234	1.432182	0.153593	0.125*
C40′	0.337(3)	1.307(2)	0.2287(11)	0.110(8)
H40D	0.236039	1.342874	0.220918	0.166*
H40E	0.362298	1.315493	0.270483	0.166*
H40F	0.354418	1.232430	0.233144	0.166*

deprotonated $(L)^{2-}$ units, two acetate ions result in an unsymmetrical trinuclear Zn(II) complex. The coordination sphere of penta-coordinated terminal Zn2 or Zn3 atoms is completed by N_2O_2 donor atoms (O3, O8, N4 and N14 or O9, O15, N19 and N25) and one oxygen atom (O13 or O17) of the acetate ion, adopting a trigonal bipyramidal geometry with axial donor atoms (O8 and N14 or O9 and N25). The coordination sphere of the hexa-coordinated central Zn1 atom is completed by four phenolato oxygen atoms (O3, O8, O9 and O15) and two oxygen atoms (O10 and O11) of the two acetate ions, to form a octahedral coordination geometry. The two acetate ligands bridge the three Zn metal centers in typicall κ^2O:O'-mode (*cf.* the figure).

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