Crystal structure of [3,7,11,19,23,27-hexaaza-33,34-dihydroxy-15,31-dimethyl-tricyclo-tetratriaconta-1(32),13,15,17(34),29(33),30-hexaene]dizinc(II) dichloride — methanol (1:1), $[Zn_2(C_{30}H_{48}N_6O_2)]Cl_2 \cdot CH_3OH$

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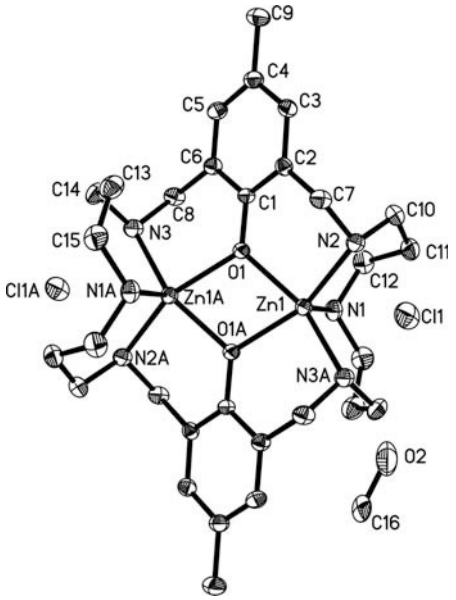

Abstract

$C_{31}H_{52}Cl_2N_6O_3Zn_2$, triclinic, $P\bar{1}$ (no. 2), a = 8.577(1) Å, b = 10.5889(9) Å, c = 11.791(1) Å, α = 63.61(1)°, β = 75.13(1)°, γ = 84.045(8)°, V = 927.0 Å^3, Z = 1, $R_{gt}(F)$ = 0.049, $wR_{ref}(F^2)$ = 0.150, T = 293 K.

Source of material

The macrocyclic ligand, 3,7,11,19,23,27-hexaaza-33,34-dihydroxy-15,31-dimethyl-tricyclo-tetratriaconta-1(32),13,15,17(34),29(33),30-hexaene (HDTH, H_2L), was prepared by the reported procedure [1]. A mixture of H_2L (0.054 g, 0.1 mmol) and $ZnCl_2$ (0.027 g, 0.2 mmol) in methanol (20 ml) was stirred for 10 min. The resulting solution was filtered. Colorless single crystals were obtained by slow evaporation of the filtrate at room temperature (yield 61%).

Experimental details

All H atoms on C atoms were generated geometrically and refined as riding atoms with d(C—H) = 0.93 Å and U_{iso}(H) = 1.2 U_{eq}(C). The imino H atoms were located from difference Fourier map and their positions and U_{iso} values were freely refined. The hydroxyl H atom was located from difference Fourier map and refined with d(O—H) distance restraint 0.85(2) Å. The C16···H1B distance was restrained to 2.30(2) Å to avoid the short C···H contact. The refinement of occupancies for C16 and O2 could not be converged, so the occupancies for C16 and O2 were fixed.

Discussion

In recent years, the design and synthesis of crown ether derivatives have been a fascinating area of research, owing to their significance in biological transport systems and selective molecular recognition [2,3].

The crystal structure of the title compound contains a centrosymmetric dinuclear zinc complex. Each of the two Zn(II) ions has a distorted square pyramidal environment. It is bridged by two phenolate groups, three nitrogen donors on one side of the macrocycle. These two Zn atoms are bridged by two phenolate O atoms, generating a four-membered Zn_2O_2 ring, with a Zn···Zn distance of 2.467(3) Å. The Zn—O and Zn—N distances are similar to the reported values [4]. The two chloride ions are situated symmetrically outside the macrocyclic cavity.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.20 × 0.24 × 0.36 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	14.76 cm^{-1}
Diffractometer, scan mode:	Oxford Diffraction Gemini R Ultra, ω
$2\theta_{max}$:	59.36°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10123, 4604
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3137
$N(param)_{refined}$:	226
Programs:	SHELXS-97 [5], SHELXL-97 [6]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
H(3)	2*i*		0.5875	0.1921	0.8431	0.041
H(5)	2*i*		0.1253	0.1024	0.9037	0.043
H(7A)	2*i*		0.7892	0.1581	0.6814	0.043
H(7B)	2*i*		0.7521	0.0302	0.6587	0.043
H(8A)	2*i*		0.0328	0.0228	0.7758	0.045
H(8B)	2*i*		0.1314	0.0856	0.6304	0.045
H(9A)	2*i*		0.2173	0.2595	0.9955	0.077
H(9B)	2*i*		0.3988	0.2431	1.0027	0.077
H(9C)	2*i*		0.2798	0.1139	1.0857	0.077
H(10A)	2*i*		0.6262	0.3711	0.5507	0.056
H(10B)	2*i*		0.8072	0.4102	0.4780	0.056
H(11A)	2*i*		0.7440	0.4528	0.2840	0.060

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Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(11B)	2*i*		0.6557	0.5548	0.3430	0.060
H(12A)	2*i*		0.4264	0.3814	0.4360	0.060
H(12B)	2*i*		0.4498	0.4980	0.2922	0.060
H(13A)	2*i*		0.1166	–0.3178	0.8786	0.057
H(13B)	2*i*		0.1010	–0.1981	0.9243	0.057
H(14A)	2*i*		0.3930	–0.1799	0.8556	0.065
H(14B)	2*i*		0.3189	–0.3089	0.9860	0.065
H(15A)	2*i*	0.50	0.5237	–0.3942	0.8792	0.062
H(15B)	2*i*	0.50	0.3660	–0.4493	0.8718	0.062
H(16A)	2*i*	0.50	1.1792	0.5143	0.1439	0.081
H(16B)	2*i*		1.0167	0.5882	0.1143	0.081
H(16C)	2*i*		1.0146	0.4471	0.2402	0.081
H(1A)	2*i*		0.422(5)	0.266(4)	0.322(4)	0.03(1)
H(2A)	2*i*		0.837(4)	0.224(4)	0.467(3)	0.021(9)
H(3A)	2*i*		0.080(5)	–0.142(4)	0.707(4)	0.03(1)
H(1B)	2*i*	0.50	1.09(1)	0.603(7)	0.325(5)	0.06(3)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2*i*		0.4272(4)	0.0794(4)	0.6837(3)	0.029(2)	0.030(2)	0.025(2)	0.001(1)	–0.005(1)	–0.015(1)
C(2)	2*i*		0.5479(4)	0.1229(3)	0.7190(3)	0.029(2)	0.028(2)	0.033(2)	0.001(1)	–0.008(1)	–0.014(1)
C(3)	2*i*		0.5067(4)	0.1611(4)	0.8215(3)	0.036(2)	0.037(2)	0.034(2)	–0.001(2)	–0.012(2)	–0.017(2)
C(4)	2*i*		0.3482(5)	0.1546(4)	0.8927(4)	0.042(2)	0.037(2)	0.032(2)	0.003(2)	–0.007(2)	–0.018(2)
C(5)	2*i*		0.2317(4)	0.1085(4)	0.8567(4)	0.030(2)	0.041(2)	0.035(2)	0.005(2)	–0.003(2)	–0.020(2)
C(6)	2*i*		0.2653(4)	0.0715(4)	0.7557(3)	0.027(2)	0.037(2)	0.033(2)	0.002(1)	–0.007(1)	–0.018(2)
C(7)	2*i*		0.7202(4)	0.1253(4)	0.6461(4)	0.027(2)	0.048(2)	0.041(2)	0.005(2)	–0.013(2)	–0.025(2)
C(8)	2*i*		0.1364(4)	0.0211(4)	0.7189(4)	0.025(2)	0.049(2)	0.045(2)	0.008(2)	–0.009(2)	–0.029(2)
C(9)	2*i*		0.3072(6)	0.1966(5)	1.0044(4)	0.058(3)	0.061(3)	0.045(2)	–0.002(2)	–0.009(2)	–0.034(2)
C(10)	2*i*		0.7107(6)	0.3690(4)	0.4789(4)	0.054(3)	0.040(2)	0.049(2)	–0.009(2)	–0.006(2)	–0.024(2)
C(11)	2*i*		0.6613(6)	0.4576(4)	0.3556(4)	0.056(3)	0.037(2)	0.055(3)	–0.007(2)	–0.004(2)	–0.021(2)
C(12)	2*i*		0.4981(5)	0.4153(4)	0.3498(5)	0.036(2)	0.045(2)	0.067(3)	0.008(2)	–0.009(2)	–0.027(2)
C(13)	2*i*		0.1667(5)	–0.2318(5)	0.8633(4)	0.042(2)	0.051(2)	0.039(2)	–0.008(2)	0.004(2)	–0.016(2)
C(14)	2*i*		0.3323(6)	–0.2671(5)	0.8923(4)	0.057(3)	0.061(3)	0.040(2)	–0.003(2)	–0.015(2)	–0.014(2)
C(15)	2*i*		0.4303(6)	–0.3654(5)	0.8418(4)	0.057(3)	0.046(2)	0.046(2)	0.006(2)	–0.022(2)	–0.011(2)
C(16)	2*i*	0.50	1.072(1)	0.5341(9)	0.1819(8)	0.076(6)	0.030(4)	0.033(4)	–0.017(4)	–0.017(4)	0.012(3)
N(1)	2*i*		0.5130(4)	0.3048(3)	0.3034(3)	0.028(2)	0.037(2)	0.046(2)	–0.001(1)	–0.008(1)	–0.015(2)
N(2)	2*i*		0.7435(4)	0.2189(3)	0.5035(3)	0.021(2)	0.049(2)	0.043(2)	–0.004(1)	–0.001(1)	–0.027(2)
N(3)	2*i*		0.1651(4)	–0.1241(4)	0.7282(3)	0.024(2)	0.053(2)	0.041(2)	–0.004(1)	–0.005(1)	–0.027(2)
O(1)	2*i*		0.4621(3)	0.0405(3)	0.5866(2)	0.030(1)	0.040(1)	0.034(1)	–0.009(1)	0.002(1)	–0.023(1)
O(2)	2*i*	0.50	1.080(1)	0.6064(9)	0.2471(9)	0.092(6)	0.081(6)	0.080(6)	–0.044(5)	–0.018(5)	–0.011(5)
Zn(1)	2*i*		0.62953(5)	0.13073(4)	0.41421(4)	0.0251(2)	0.0337(2)	0.0322(2)	–0.0017(2)	–0.0040(2)	–0.0170(2)
Cl(1)	2*i*		1.1294(1)	0.2216(1)	0.3556(1)	0.0301(5)	0.0781(8)	0.0836(8)	–0.0020(5)	–0.0102(5)	–0.0484(7)

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