Crystal structure of 7,15,23,31-tetramethyl-3,11,19,27-tetraazopentacyclo[27.16.16$^{11.27}$.4.4$^{11.27}$.3.3$^{5.9}$.3$^{13.17}$.3$^{21.25}$.1.1$^{5.9}$.1$^{13.17}$.1$^{21.25}$]triaconta-1(32),5,7,9(34),13,15,17(35),21,23,25(36),29(33),30-dodecaarene-33,34,35,36-tetraol, $C_{44}H_{56}N_4O_4$

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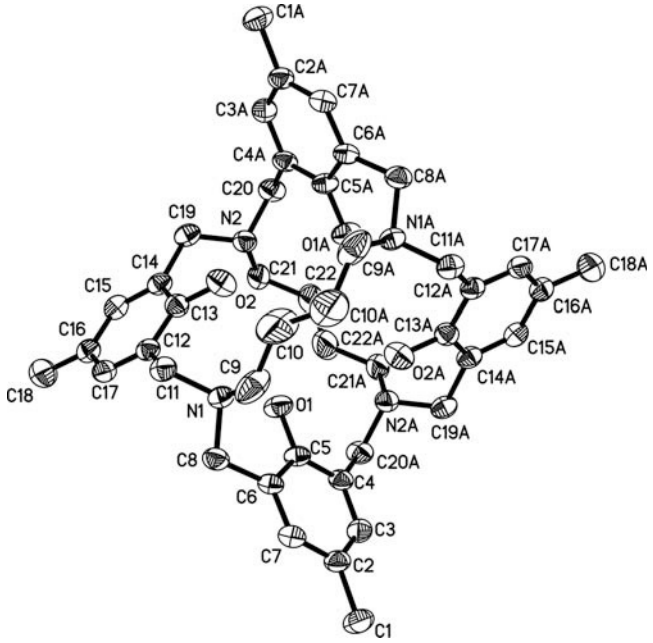

Abstract

$C_{44}H_{56}N_4O_4$, monoclinic, *C*12/*c*1 (no. 15), a = 23.216(2) Å, b = 14.0445(9) Å, c = 13.064(1) Å, β = 118.413(9)°, V = 3746.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.076, $wR_{ref}(F^2)$ = 0.186, T = 293 K.

Source of material

The macrocyclic ligand H_2L was prepared as reported earlier [1]. A methanol solution (30 mL) containing H_2L (0.44 g, 1 mmol) was heated to boiling and then slowly treated with a methanol solution (20 mL) of 4-methyl-2,6-diformyl (0.33 g, 2 mmol). After stirring for 1 h, an orange precipitate was obtained. Then a amount of solid $NaBH_4$ was added to the solution. The solid material gradually went into solution, and ultimately an almost colorless solution was obtained over a period of 0.5 h. This was filtered, and to the filtrate was added slowly 30 mL of water with stirring. The resulting solution was allowed to stand overnight, during which period the product separated out as colorless crystals. The product was collected by filtration and recrystallized from methanol/water (yield 35 % or more). The product (0.077 g, 0.1 mmol) and $Ni(OAc)_2 \cdot 6H_2O$ (0.050 g, 0.2 mmol) were dissolved in DMF (5 mL) and water (5 mL). The mixture sealed in a 15 mL Teflon-lined stainless steel autoclave, and heated at 100 °C for 4 days under autogenous pressure. Afterward, the reaction system was gradually cooled to room temperature at a rate of 10 °C/h. Light green crystals were obtained in a 34 % yield.

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 or 1.5 U_{eq}(C). The hydroxy H atom were located from difference Fourier map and refined with U_{iso}(H) = 1.5 U_{eq}(O). The huge residual values are caused by the vibration of the terminal C21 and C22 atoms at room temperature.

Discussion

Recently, the study of metal complexes with phenol-based macrocyclic compartmental ligands has become important in view of their significance as biomimetric catalysts in the process of oxygenation [2]. Several classes of macrocyclic ligands have been synthesized [3].

In the title crystal structure, the intramolecular hydrogen bonds involving the phenolic oxygens are of particular importance because the macrocyclic cation is stabilized by these bonds. The N···O distances are in the range 2.738 (5) - 3.04 (1) Å, while the O–H···N angles vary between 135° and 140°, which indicates that the intramolecular hydrogen bonds are quite strong. The C—O and C—N bond lengthes are in the range of 1.37 to 1.45 Å, respectively. The bond distances and bond angles are all in normal range.

Table 1. Data collection and handling.

Crystal:	green block, size 0.23 × 0.29 × 0.37 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.80 cm^{-1}
Diffractometer, scan mode:	Oxford Diffraction Gemini R Ultra, ω
$2\theta_{max}$:	58.36°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	14927, 4471
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1623
$N(param)_{refined}$:	241
Programs:	SHELXS-97 [4], SHELXL-97 [5]

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

Atom	Site	x	y	z	U_{iso}
H(8A)	8*f*	–0.2037	0.1058	0.7058	0.077
H(8B)	8*f*	–0.2070	0.0037	0.6548	0.077
H(9A)	8*f*	–0.1575	0.3645	0.3988	0.080
H(9B)	8*f*	–0.1446	0.3729	0.5275	0.080
H(16)	8*f*	0.0489	0.3565	0.3820	0.076
H(3)	8*f*	–0.2300	0.2389	0.2905	0.075
H(14)	8*f*	0.1738	0.1468	0.5494	0.076
H(7)	8*f*	–0.2652	0.0212	0.4470	0.073
H(18A)	8*f*	0.0680	0.0015	0.5813	0.072
H(18B)	8*f*	0.1434	0.0144	0.6274	0.072
H(10A)	8*f*	–0.0552	0.3671	0.3801	0.073
H(10B)	8*f*	–0.0838	0.2638	0.3653	0.073
H(1A)	8*f*	–0.3304	0.0340	0.2434	0.128
H(1B)	8*f*	–0.2938	0.0783	0.1803	0.128
H(1C)	8*f*	–0.3442	0.1397	0.1997	0.128
H(22A)	8*f*	–0.0025	0.0167	0.8273	0.282
H(22B)	8*f*	–0.0056	–0.0933	0.8210	0.282
H(17A)	8*f*	0.2047	0.2641	0.4512	0.142
H(17B)	8*f*	0.1762	0.3656	0.4500	0.142
H(17C)	8*f*	0.1444	0.3019	0.3380	0.142
H(19A)	8*f*	–0.0528	0.4645	0.5430	0.110
H(19B)	8*f*	0.0128	0.4071	0.5911	0.110
H(21A)	8*f*	–0.1074	–0.0327	0.6374	0.125
H(21B)	8*f*	–0.1041	–0.0896	0.7429	0.125
H(20A)	8*f*	–0.0494	0.4639	0.7027	0.241
H(20B)	8*f*	–0.0501	0.3537	0.7036	0.241
H(1O)	8*f*	–0.105(5)	0.180(5)	0.718(7)	0.301
H(2O)	8*f*	–0.044(5)	0.199(7)	0.558(8)	0.301

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	8*f*	–0.1109(1)	0.2216(2)	0.6675(2)	0.063(2)	0.064(2)	0.062(2)	–0.017(1)	0.010(1)	0.006(1)
O(2)	8*f*	–0.0085(1)	0.1500(2)	0.5685(2)	0.064(2)	0.061(2)	0.092(2)	0.004(1)	0.035(2)	0.015(2)
N(2)	8*f*	–0.1151(1)	0.0496(2)	0.7540(2)	0.053(2)	0.049(2)	0.047(2)	0.000(1)	0.014(1)	0.003(1)
N(1)	8*f*	–0.0665(1)	0.3247(2)	0.5155(3)	0.053(2)	0.061(2)	0.058(2)	0.007(2)	0.021(2)	0.010(2)
C(12)	8*f*	0.0335(2)	0.1867(3)	0.5325(3)	0.052(2)	0.050(3)	0.059(2)	–0.006(2)	0.023(2)	–0.005(2)
C(8)	8*f*	–0.1844(2)	0.0643(3)	0.6709(3)	0.052(2)	0.070(3)	0.061(2)	–0.012(2)	0.020(2)	0.001(2)
C(6)	8*f*	–0.1945(2)	0.1075(3)	0.5583(3)	0.040(2)	0.058(3)	0.055(2)	0.000(2)	0.016(2)	0.004(2)
C(13)	8*f*	0.0923(2)	0.1387(3)	0.5640(3)	0.055(2)	0.045(2)	0.050(2)	0.000(2)	0.018(2)	–0.009(2)
C(11)	8*f*	0.0161(2)	0.2668(3)	0.4632(3)	0.060(2)	0.051(3)	0.050(2)	0.009(2)	0.018(2)	0.000(2)
C(5)	8*f*	–0.1586(2)	0.1884(3)	0.5626(3)	0.045(2)	0.050(3)	0.052(2)	0.002(2)	0.010(2)	0.003(2)
C(9)	8*f*	–0.1376(2)	0.3329(3)	0.4738(3)	0.056(2)	0.064(3)	0.070(2)	0.014(2)	0.021(2)	0.023(2)
C(16)	8*f*	0.0600(2)	0.3023(3)	0.4285(3)	0.068(2)	0.060(3)	0.053(2)	–0.003(2)	0.022(2)	0.000(2)
C(3)	8*f*	–0.2206(2)	0.2056(3)	0.3581(3)	0.056(2)	0.071(3)	0.054(2)	0.018(2)	0.020(2)	0.016(2)
C(14)	8*f*	0.1341(2)	0.1771(3)	0.5280(3)	0.054(2)	0.076(3)	0.054(2)	0.000(2)	0.021(2)	–0.009(2)
C(7)	8*f*	–0.2421(2)	0.0764(3)	0.4510(3)	0.046(2)	0.059(3)	0.067(3)	0.001(2)	0.019(2)	–0.001(2)
C(2)	8*f*	–0.2566(2)	0.1245(3)	0.3489(3)	0.046(2)	0.066(3)	0.055(2)	0.010(2)	0.015(2)	–0.001(2)
C(4)	8*f*	–0.1719(2)	0.2395(3)	0.4618(3)	0.043(2)	0.058(3)	0.057(2)	0.009(2)	0.016(2)	0.013(2)
C(18)	8*f*	0.1050(2)	0.0432(3)	0.6257(3)	0.063(2)	0.051(3)	0.060(2)	0.004(2)	0.023(2)	–0.012(2)
C(10)	8*f*	–0.0517(2)	0.3076(3)	0.4204(3)	0.065(2)	0.049(3)	0.055(2)	0.006(2)	0.018(2)	0.005(2)
C(15)	8*f*	0.1197(2)	0.2591(3)	0.4613(3)	0.066(3)	0.070(3)	0.056(2)	–0.005(2)	0.026(2)	–0.007(2)
C(1)	8*f*	–0.3113(2)	0.0910(3)	0.2323(3)	0.068(2)	0.106(4)	0.064(3)	0.004(2)	0.016(2)	–0.007(2)
C(22)	8*f*	–0.0180(3)	–0.0364(7)	0.7732(5)	0.137(6)	0.46(1)	0.076(4)	0.217(8)	0.027(3)	0.038(5)
C(17)	8*f*	0.1654(2)	0.3015(3)	0.4215(4)	0.086(3)	0.114(4)	0.094(3)	–0.010(3)	0.050(3)	0.006(3)
C(19)	8*f*	–0.0307(2)	0.4070(4)	0.5839(4)	0.077(3)	0.130(4)	0.079(3)	–0.024(3)	0.044(2)	–0.035(3)
C(21)	8*f*	–0.0891(2)	–0.0323(4)	0.7214(4)	0.145(4)	0.097(4)	0.058(3)	0.056(3)	0.039(3)	0.013(3)
C(20)	8*f*	–0.0249(2)	0.4082(7)	0.7019(4)	0.098(5)	0.42(1)	0.104(5)	–0.086(5)	0.066(4)	–0.124(6)

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