Crystal structure of [μ -13,27-di-*tert*-butyl-3,6,9,17,20,23-hexaazatri-cyclo[23,3,1,1^{11,15}]triaconta-1(28),11,13,15 (30),25,26-hexaene-29,30-diolato[$\kappa^5 N^3, N^6, N^9, O^{29}, O^{30} : \kappa^5 N^{17}, N^{20}, N^{23}, O^{29}, O^{30}$]bis(thiocyanato- κN)-nickel(II) — methanol (1:0.5), $Ni_2(C_{32}H_{52}N_6O_2)(NCS)_2 \cdot 0.5CH_3OH$

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Abstract

$C_{34.50}H_{54}N_8Ni_2O_{2.50}S_2$, triclinic, $P\bar{1}$ (no. 2), $a = 8.514(1)$ Å, $b = 10.412(1)$ Å, $c = 12.571(1)$ Å, $\alpha = 77.422(9)^\circ$, $\beta = 79.470(9)^\circ$, $\gamma = 81.725(9)^\circ$, $V = 1063.0$ Å³, $Z = 1$, $R_g(F) = 0.052$, $wR_{ref}(F^2) = 0.174$, $T = 293$ K.

Source of material

The macrocyclic 3,6,9,17,20,23-hexaaza-29,30-dihydroxy-13,27-di-*tert*-butyl-tricyclo[23,3,1,1^{11,15}]triaconta-1(28),11,13,15(30),25,26-hexaene (H_2L) ligand was synthesized according to the reported procedures [1,2]. A mixture of H_2L (0.056 g, 0.10 mmol), $Ni(OH)_2$ (0.0187 g, 0.20 mmol), and salicylic acid (0.0138 g, 0.10 mmol) was added to 10 mL methanol. Then the mixture was sealed in a 15 mL Teflon-lined reactor and heated to 150 °C for 3 days, and then slowly cooled to room temperature. Blue block-shaped crystals were collected and washed with distilled water (yield 47 %).

Experimental details

All H atoms on C and O atoms were generated geometrically and refined as riding atoms with $d(C-H) = 0.93 - 0.97$ Å, $d(O-H) = 0.82$ Å, and $U_{iso}(H) = 1.2 U_{eq}(C)$, $U_{iso}(H) = 1.5 U_{eq}(O)$, respectively. To describe the high disorder of C2 and C4 atoms their occupancy parameter were refined using FVAR instruction and the occupations of C18 and O2 were not refined.

Discussion

In the past decades, much attention has been focused on the design and synthesis of metal-organic coordination networks. Particularly, dinuclear complexes have been a fascinating area of research [3,4].

The crystal structure of the title compound is similar to the reported $[Zn_2(L)(L')_2]$ [5]. Each Ni(II) atom is six-coordinated by two O atoms from H_2L ligand and four N atoms, three of which from H_2L ligand and one from coordinating SCN^- anion in a twisted octahedral arrangement. Two Ni(II) atoms are bridged through two phenolate O atoms. The two Ni—O_{phenolate} bond distances are 2.057(2) and 2.061(2) Å, respectively. The four Ni—N bond distances are 2.113(3), 2.125(3), 2.096(3) and 2.100(4) Å, respectively.

Table 1. Data collection and handling.

Crystal:	blue block, size 0.12 × 0.15 × 0.18 mm
Wavelength:	Mo $K\alpha$ radiation (0.71069 Å)
μ :	10.23 cm ⁻¹
Diffraction, scan mode:	Oxford Diffraction Gemini R Ultra, ω
$2\theta_{max}$:	58.22°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9726, 4890
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 3712
$N(param)_{refined}$:	255
Programs:	SHELXS-97 [6], SHELXL-97 [7]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U_{iso}
H(1A)	2i	0.68	1.0865	0.1967	0.0911	0.155
H(1B)	2i	0.68	0.9921	0.0764	0.0959	0.155
H(1C)	2i	0.68	0.9703	0.1434	0.1986	0.155
H(2A)	2i	0.68	0.9523	0.4026	0.1162	0.114
H(2B)	2i	0.68	0.8198	0.3445	0.2114	0.114
H(2C)	2i	0.68	0.7700	0.4426	0.1064	0.114
H(4A)	2i	0.68	0.6064	0.2696	0.0836	0.127
H(4B)	2i	0.68	0.6631	0.1883	0.1930	0.127
H(4C)	2i	0.68	0.6864	0.1235	0.0889	0.127
H(1'1)	2i	0.32	1.0869	0.1952	0.0888	0.155
H(1'2)	2i	0.32	0.9896	0.0753	0.0983	0.155
H(1'3)	2i	0.32	0.9724	0.1461	0.1985	0.155
H(2'1)	2i	0.32	0.6577	0.3978	0.0729	0.140
H(2'2)	2i	0.32	0.7971	0.4336	0.1234	0.140
H(2'3)	2i	0.32	0.6836	0.3296	0.1935	0.140
H(4'1)	2i	0.32	0.6204	0.1907	0.0760	0.118
H(4'2)	2i	0.32	0.7026	0.1061	0.1743	0.118
H(4'3)	2i	0.32	0.7610	0.0798	0.0545	0.118
H(6)	2i		0.6605	0.3874	-0.0685	0.051
H(7)	2i		1.1192	0.2453	-0.0744	0.049
H(11A)	2i		1.2732	0.4277	-0.2945	0.049

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Table 2. Continued.

Atom	Site	Occ.	x	y	z	U _{iso}
H(11B)	2i		1.3068	0.2856	-0.2244	0.049
H(12A)	2i		0.6092	0.4331	-0.3133	0.053
H(12B)	2i		0.5545	0.5097	-0.2160	0.053
H(13A)	2i		1.2131	0.1121	-0.2847	0.061
H(13B)	2i		1.3158	0.0954	-0.3989	0.061
H(14A)	2i		1.0641	0.0599	-0.4148	0.060
H(14B)	2i		0.9836	0.1805	-0.3603	0.060
H(15A)	2i		0.8313	0.6660	-0.2645	0.059
H(15B)	2i		0.6621	0.7493	-0.2497	0.059

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U _{iso}
H(16A)	2i		0.7164	0.8766	-0.4271	0.060
H(16B)	2i		0.8620	0.8794	-0.3670	0.060
H(18A)	2i		1.4706	0.0378	-0.2405	0.130
H(18B)	2i		1.6425	0.032	-0.3110	0.130
H(18C)	2i		1.5421	0.1691	-0.3034	0.130
H(1')	2i		1.3744	0.2849	-0.4011	0.045
H(2')	2i		0.9894	0.2548	-0.5387	0.048
H(3')	2i		0.5963	0.6607	-0.3768	0.045
H(2)	2i	0.25	1.5594	0.0826	-0.1227	0.132

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ni(1)	2i		1.16697(4)	0.41454(4)	-0.50589(3)	0.0275(2)	0.0263(3)	0.0314(3)	0.0011(2)	-0.0026(2)	-0.0031(2)
S(1)	2i		1.3464(1)	0.8192(1)	-0.4624(1)	0.0515(6)	0.0359(5)	0.0838(8)	-0.0011(4)	-0.0166(5)	-0.0172(5)
C(1)	2i	0.68(1)	0.9873(9)	0.1588(7)	0.1195(5)	0.121(4)	0.105(4)	0.057(3)	0.013(3)	-0.001(3)	0.015(3)
C(2)	2i	0.68	0.848(1)	0.3721(8)	0.1330(6)	0.113(5)	0.078(4)	0.037(3)	-0.013(4)	-0.006(4)	-0.015(3)
C(4)	2i	0.68	0.687(1)	0.204(1)	0.1139(8)	0.088(5)	0.104(6)	0.050(4)	-0.021(4)	0.005(4)	0.004(4)
C(1')	2i	0.32	0.9873(9)	0.1588(7)	0.1195(5)	0.121(4)	0.105(4)	0.057(3)	0.013(3)	-0.001(3)	0.015(3)
C(2')	2i	0.32	0.737(3)	0.364(2)	0.121(1)	0.110(7)	0.087(6)	0.061(6)	0.008(6)	0.009(6)	0.000(6)
C(4')	2i	0.32	0.720(3)	0.147(2)	0.097(2)	0.092(6)	0.074(6)	0.053(6)	-0.002(6)	0.008(6)	0.003(6)
C(3)	2i		0.8492(5)	0.2536(4)	0.0764(3)	0.065(2)	0.058(2)	0.032(2)	-0.005(2)	-0.001(2)	-0.001(2)
C(5)	2i		0.8832(5)	0.3033(4)	-0.0488(3)	0.052(2)	0.044(2)	0.032(2)	-0.004(2)	-0.003(1)	-0.003(1)
C(6)	2i		0.7634(4)	0.3734(4)	-0.1073(3)	0.042(2)	0.043(2)	0.036(2)	-0.003(1)	0.005(1)	-0.006(1)
C(7)	2i		1.0353(4)	0.2912(4)	-0.1100(3)	0.048(2)	0.040(2)	0.034(2)	0.000(1)	-0.010(1)	-0.004(1)
C(8)	2i		1.0686(4)	0.3445(3)	-0.2225(3)	0.038(2)	0.033(2)	0.034(2)	-0.002(1)	-0.005(1)	-0.004(1)
C(9)	2i		0.9444(4)	0.4112(3)	-0.2811(3)	0.037(1)	0.031(2)	0.031(2)	-0.000(1)	-0.003(1)	-0.005(1)
C(10)	2i		0.7889(4)	0.4239(3)	-0.2212(3)	0.037(2)	0.035(2)	0.035(2)	-0.001(1)	0.000(1)	-0.005(1)
C(11)	2i		1.2410(4)	0.3389(4)	-0.2767(3)	0.038(2)	0.049(2)	0.035(2)	-0.001(1)	-0.011(1)	-0.003(1)
C(12)	2i		0.6425(4)	0.4922(4)	-0.2737(3)	0.032(2)	0.052(2)	0.039(2)	0.001(1)	0.003(1)	-0.002(2)
C(13)	2i		1.2292(5)	0.1501(4)	-0.3630(3)	0.061(2)	0.035(2)	0.045(2)	0.010(2)	-0.002(2)	0.004(2)
C(14)	2i		1.0761(5)	0.1494(4)	-0.4093(3)	0.051(2)	0.034(2)	0.059(2)	-0.009(2)	0.005(2)	-0.005(2)
C(15)	2i		0.7440(5)	0.7124(4)	-0.3026(3)	0.059(2)	0.045(2)	0.043(2)	0.008(2)	-0.006(2)	-0.017(2)
C(16)	2i		0.8059(5)	0.8229(4)	-0.3956(3)	0.059(2)	0.038(2)	0.055(2)	0.003(2)	-0.011(2)	-0.018(2)
C(17)	2i		1.3083(4)	0.6740(3)	-0.4782(3)	0.027(1)	0.034(2)	0.040(2)	0.000(1)	-0.004(1)	-0.003(1)
C(18)	2i	0.25	1.567(2)	0.081(2)	-0.264(2)	0.066(9)	0.09(1)	0.08(1)	0.014(9)	0.015(9)	0.004(9)
N(1)	2i		1.2748(3)	0.2833(3)	-0.3794(2)	0.029(1)	0.039(2)	0.038(2)	0.004(1)	-0.002(1)	-0.000(1)
N(2)	2i		1.0848(3)	0.2362(3)	-0.5193(3)	0.033(1)	0.033(2)	0.057(2)	-0.001(1)	-0.010(1)	-0.012(1)
N(3)	2i		0.6756(3)	0.6196(3)	-0.3517(2)	0.029(1)	0.039(2)	0.039(2)	0.006(1)	-0.002(1)	-0.005(1)
N(4)	2i		1.2799(4)	0.5740(3)	-0.4893(3)	0.041(2)	0.040(2)	0.054(2)	-0.010(1)	-0.004(1)	-0.007(1)
O(1)	2i		0.9761(3)	0.4622(2)	-0.3899(2)	0.030(1)	0.038(1)	0.028(1)	0.0050(9)	0.0005(9)	-0.0001(9)
O(2)	2i	0.25	1.630(2)	0.086(1)	-0.177(2)	0.069(8)	0.055(8)	0.15(2)	-0.014(7)	-0.05(1)	-0.003(9)

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