Crystal structure of [3,6,9,12,20,23,26,29-octaaza-35,36-dihydroxy-16,33-dimethyl-tricyclo[29.3.1.1^{14,18}]hexatriacona-1(35),18(36),15,17,31,33-hexaene]bis(thiocyanato-κN)dinickel(II) — methanol — water (1:2:2), $Ni_2(NCS)_2(C_{36}H_{62}N_8O_2) \cdot 2CH_3OH \cdot 2H_2O$

Li-Hui Zhang[I], Dao-Cheng Xia[II] and Jian-Fang Ma[*,I]

[I] Northeast Normal University, Department of Chemistry, Changchun 130024, P. R. China
[II] Yuncheng University, Department of Chemistry, Yuncheng 044000, P. R. China

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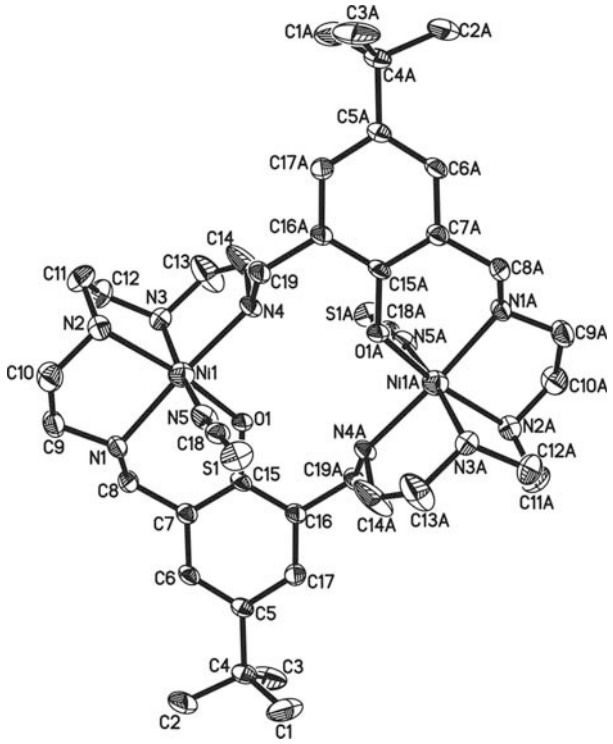

Abstract

$C_{40}H_{74}N_{10}Ni_2O_6S_2$, triclinic, $P\bar{1}$ (no. 2), a = 9.038(1) Å, b = 11.178(2) Å, c = 12.925(2) Å, α = 68.21(1)°, β = 79.17(1)°, γ = 85.80(1)°, V = 1190.9 Å^3, Z = 1, $R_{gt}(F)$ = 0.075, $wR_{ref}(F^2)$ = 0.199, T = 293 K.

Source of material

The macrocyclic 3,6,9,17,20,23-hexaaza-29,30-dihydroxy-13,27-dimethyltricyclo[23,3,1,1^{11,15}]triaconta-1(28),11,13,15(30),25,26-hexaene ligand (H_2L) was synthesized according to the reported procedures [1,2]. A mixture of H_2L (0.058 g, 0.10 mmol) in methanol (10 mL) was stirred at room temperature, then $Ni(ClO_4)_2 \cdot 6H_2O$ (0.037 g, 0.10 mmol) was added to the solution. The mixture was stirred for 30 min. Purple crystals were obtained by slow evaporation of the solution at ambient temperature after several days (yield 80 %) .

Experimental details

All H atoms on C atoms were generated geometrically and refined as riding atoms with d(C—H) = 0.93 - 0.97 Å, and U_{iso}(H) = 1.2 U_{eq}(C) or U_{iso}(H) = 1.5 U_{eq}(N,methyl). The methanol O atom and water O atom are disordered. The water H atoms and methanol H atoms were not located from a difference Fourier map. The large R values are caused by the low quality of the crystal.

Discussion

In the past decades, much attention has been focused on the design and synthesis of metal-organic coordination networks. Dinuclear Ni(II) cores have attracted much interest as a result of their siganificance in biological systems [3-5].

The title crystal structure is a symmetric dinuclear Ni(II) complex. Ni(II) is six-coordinated by one O atom and five N atoms. Each Ni(II) cation adopts a twisted octahedral coordination by five N atoms, four of them from L^{2-} ligand and one from NCS^- anion, and one O atom from L^{2-} ligand. The separation of Ni···Ni is 5.4 Å. The N_5O coordination moieties are situated on different sides of the molecule. The Ni—$O_{phenolate}$ bond distance is 2.057(3) Å. The Ni—N bond distances are 2.084(2), 2.114(2), 2.122(2), 2.157(2) and 2.167(2) Å.

Table 1. Data collection and handling.

Crystal:	purple block, size 0.12 × 0.15 × 0.18 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.32 cm^{-1}
Diffractometer, scan mode:	Oxford Diffraction Gemini R Ultra, ω
$2\theta_{max}$:	50.4°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12424, 4209
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2749
$N(param)_{refined}$:	301
Programs:	SHELXS-97 [6], SHELXL-97 [7]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	2*i*	0.7973	0.5433	0.4506	0.127
H(1B)	2*i*	0.7773	0.4921	0.5829	0.127
H(1C)	2*i*	0.6354	0.5201	0.5238	0.127
H(2A)	2*i*	0.5475	0.3028	0.6402	0.121
H(2B)	2*i*	0.6916	0.2772	0.6966	0.121
H(2C)	2*i*	0.6508	0.1835	0.6412	0.121
H(3A)	2*i*	0.9627	0.3514	0.4509	0.131

* Correspondence author (e-mail: majf247nenu@yahoo.com.cn)

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(3B)	2*i*	0.9022	0.2133	0.5287	0.131
H(3C)	2*i*	0.9408	0.3090	0.5828	0.131
H(6)	2*i*	0.5364	0.1989	0.5067	0.046
H(8A)	2*i*	0.3816	0.0974	0.4413	0.050
H(8B)	2*i*	0.4565	0.0850	0.3260	0.050
H(9A)	2*i*	0.1036	0.0990	0.4253	0.065
H(9B)	2*i*	0.1789	0.0355	0.3382	0.065
H(10A)	2*i*	–0.0513	0.1158	0.2909	0.074
H(10B)	2*i*	–0.0161	0.2509	0.2918	0.074
H(11A)	2*i*	0.0946	0.1554	0.0263	0.072
H(11B)	2*i*	0.0288	0.0554	0.1458	0.072
H(12A)	2*i*	0.2584	–0.0127	0.1867	0.066

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(12B)	2*i*	0.2742	0.0025	0.0596	0.066
H(13A)	2*i*	0.5490	0.1780	–0.0515	0.123
H(13B)	2*i*	0.3990	0.1415	–0.0751	0.123
H(14A)	2*i*	0.3481	0.3141	–0.1481	0.130
H(14B)	2*i*	0.5129	0.3460	–0.1476	0.130
H(17)	2*i*	0.8063	0.4899	0.3009	0.050
H(19A)	2*i*	0.2057	0.5422	–0.0563	0.052
H(19B)	2*i*	0.1680	0.4400	–0.1037	0.052
H(1N)	2*i*	0.245(4)	0.245(3)	0.348(2)	0.080
H(2N)	2*i*	0.047(8)	0.273(5)	0.119(6)	0.080
H(3N)	2*i*	0.443(4)	0.123(5)	0.123(2)	0.080
H(4N)	2*i*	0.423(4)	0.453(2)	–0.065(2)	0.080

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*		0.738(1)	0.4895(7)	0.5199(7)	0.142(8)	0.058(4)	0.078(5)	0.005(5)	–0.057(5)	–0.034(4)
C(2)	2*i*		0.650(1)	0.2716(8)	0.6357(5)	0.091(6)	0.117(7)	0.036(3)	–0.026(5)	–0.018(4)	–0.022(4)
C(3)	2*i*		0.9014(8)	0.3020(9)	0.5213(6)	0.063(5)	0.152(8)	0.072(5)	0.042(5)	–0.048(4)	–0.060(5)
C(4)	2*i*		0.7419(7)	0.3529(5)	0.5236(4)	0.049(3)	0.053(3)	0.033(3)	0.007(3)	–0.019(2)	–0.013(2)
C(5)	2*i*		0.6820(6)	0.3449(5)	0.4233(4)	0.043(3)	0.043(3)	0.028(3)	0.003(2)	–0.013(2)	–0.009(2)
C(6)	2*i*		0.5751(6)	0.2550(5)	0.4343(4)	0.041(3)	0.045(3)	0.023(2)	0.001(2)	–0.009(2)	–0.004(2)
C(7)	2*i*		0.5232(6)	0.2446(5)	0.3432(4)	0.037(3)	0.041(3)	0.031(3)	0.001(2)	–0.008(2)	–0.009(2)
C(8)	2*i*		0.4108(7)	0.1451(5)	0.3609(4)	0.051(4)	0.034(3)	0.033(3)	–0.006(2)	–0.011(2)	–0.001(2)
C(9)	2*i*		0.1459(7)	0.1165(6)	0.3464(5)	0.044(4)	0.064(4)	0.042(3)	–0.010(3)	0.000(3)	–0.007(3)
C(10)	2*i*		0.0281(7)	0.1775(7)	0.2742(5)	0.038(4)	0.079(5)	0.062(4)	–0.004(3)	–0.004(3)	–0.021(3)
C(11)	2*i*		0.1083(7)	0.1178(7)	0.1047(6)	0.045(4)	0.069(4)	0.077(4)	–0.006(3)	–0.016(3)	–0.036(4)
C(12)	2*i*		0.2593(7)	0.0494(6)	0.1106(6)	0.054(4)	0.039(3)	0.073(4)	–0.001(3)	–0.012(3)	–0.019(3)
C(13)	2*i*		0.441(1)	0.1922(7)	–0.0409(6)	0.181(9)	0.051(4)	0.057(4)	0.012(5)	0.031(5)	–0.026(3)
C(14)	2*i*		0.418(1)	0.3118(7)	–0.0990(5)	0.200(9)	0.060(4)	0.036(3)	0.040(5)	0.019(5)	–0.013(3)
C(15)	2*i*		0.5773(6)	0.3315(5)	0.2325(4)	0.039(3)	0.040(3)	0.022(2)	0.004(2)	–0.012(2)	–0.004(2)
C(16)	2*i*		0.6882(6)	0.4211(5)	0.2189(4)	0.037(3)	0.043(3)	0.029(2)	–0.002(2)	–0.013(2)	–0.005(2)
C(17)	2*i*		0.7357(6)	0.4278(5)	0.3122(4)	0.038(3)	0.045(3)	0.038(3)	–0.005(2)	–0.014(2)	–0.008(2)
C(18)	2*i*		0.1657(7)	0.5547(5)	0.1650(4)	0.048(3)	0.038(3)	0.032(3)	0.002(3)	–0.013(2)	–0.011(2)
C(19)	2*i*		0.2487(6)	0.4904(5)	–0.1004(4)	0.039(3)	0.051(3)	0.031(3)	–0.007(3)	–0.014(2)	0.000(2)
C(20)	2*i*		0.759(1)	–0.141(1)	0.297(1)	0.092(8)	0.081(6)	0.15(1)	0.000(6)	0.010(7)	–0.019(7)
N(1)	2*i*		0.2743(5)	0.2035(4)	0.3118(3)	0.033(2)	0.042(2)	0.029(2)	–0.003(2)	–0.002(2)	–0.008(2)
N(2)	2*i*		0.0950(5)	0.2203(4)	0.1524(4)	0.033(3)	0.045(3)	0.043(3)	0.005(2)	–0.008(2)	–0.010(2)
N(3)	2*i*		0.3842(5)	0.1375(4)	0.0809(4)	0.035(3)	0.037(2)	0.046(2)	0.003(2)	–0.010(2)	–0.016(2)
N(4)	2*i*		0.3614(5)	0.4018(4)	–0.0419(3)	0.049(3)	0.032(2)	0.025(2)	0.004(2)	–0.008(2)	–0.006(2)
N(5)	2*i*		0.2257(6)	0.4620(4)	0.1623(4)	0.063(3)	0.040(3)	0.039(2)	0.009(2)	–0.006(2)	–0.013(2)
O(1)	2*i*		0.5346(4)	0.3248(3)	0.1415(3)	0.035(2)	0.047(2)	0.029(2)	–0.005(2)	–0.011(2)	–0.011(2)
O(2)	2*i*	0.50	0.724(2)	0.145(1)	0.095(1)	0.07(1)	0.064(9)	0.078(8)	0.025(7)	–0.020(7)	–0.025(7)
O(2')	2*i*	0.50	0.776(2)	0.193(1)	0.096(1)	0.048(8)	0.062(8)	0.065(6)	0.015(6)	–0.012(6)	–0.025(6)
O(3')	2*i*	0.80	0.658(1)	–0.054(1)	0.226(2)	0.090(8)	0.15(1)	0.37(2)	0.006(7)	–0.06(1)	–0.11(1)
O(3)	2*i*	0.20	0.717(3)	–0.045(2)	0.322(2)	0.09(2)	0.05(1)	0.05(1)	0.02(1)	0.02(1)	–0.01(1)
Ni(1)	2*i*		0.3147(1)	0.29711(7)	0.13405(6)	0.0530(5)	0.0500(5)	0.0499(5)	0.0048(4)	–0.0145(4)	–0.0161(3)
S(1)	2*i*		0.0762(2)	0.6875(1)	0.1682(1)	0.052(1)	0.0484(9)	0.068(1)	0.0161(7)	–0.0167(8)	–0.0309(7)

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