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Crystal structure of tris(1,10-phenanthroline-*N*,*N*′)nickel(III) 1,2,4,5-benzene-tetracarboxylate, $C_{51}H_{30}N_6NiO_{12}$

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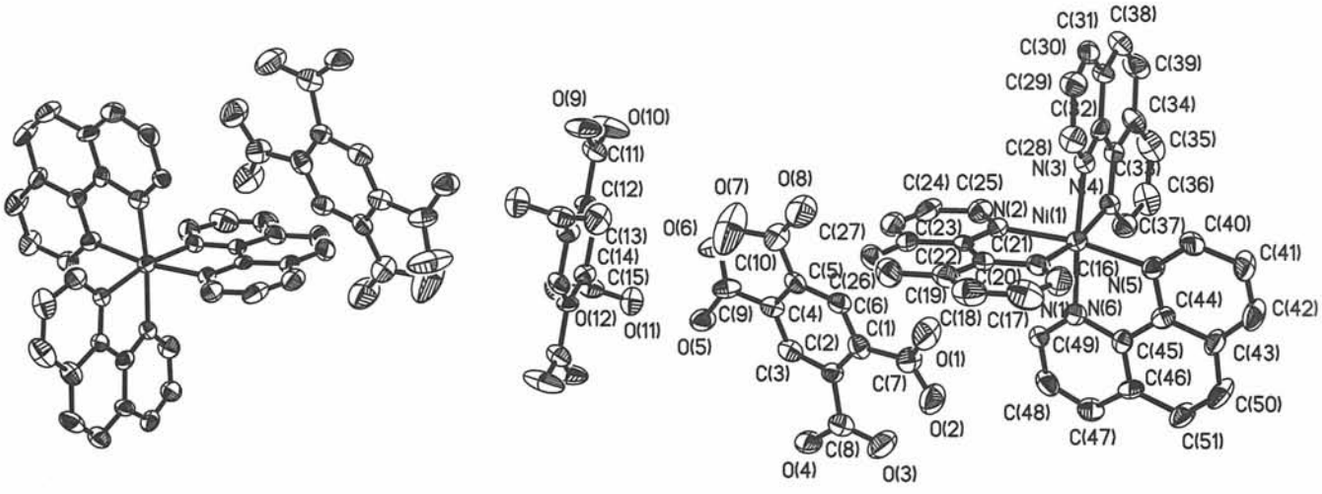

Abstract

$C_{51}H_{30}N_6NiO_{12}$, triclinic, $P\bar{1}$ (No. 2), a = 12.402(7) Å, b = 12.908(8) Å, c = 14.471(9) Å, α = 96.44(1)°, β = 106.45(1)°, γ = 105.12(1)°, V = 2101.1 Å^3, Z = 2, $R_{gt}(F)$ = 0.079, $wR_{ref}(F^2)$ = 0.170, T = 298 K.

Source of material

The title compound was synthesized with the hydrothermal method from a mixture of 1,2,4,5-benzenetetracarboxylic acid (0.60 mmol), $NiSO_4$ (0.20 mmol), 1,10-phenanthroline (1.20 mmol) and water (20.0 mL) in a 30.0 mL teflon-lined stainless steel reactor. The solution was heated to 433 K for five days. After the reaction, the system was slowly cooled to room temperature, the red prism crystals were collected and washed with distilled water. The yield is ca. 32% based on Ni(III). The substance is insoluble in water and common organic solvents.

Experimental details

The ratio $N(hkl)_{gt}/N(param)$ is relative small, because the quality of the crystal studied was low (it is very difficult to get large crystals of good quality). The anisotropy O7, O8, C27, C30 and C35 is remarkable, but a split model for these sites was not tried.

Discussion

Coordination polymers with a one-, two- or three-dimensional structure and supramolecular compounds formed by the weak interactions such as hydrogen bonds, van der Waals force, short-range exclusion force, etc, have a variety of possible applications ranging from semiconductor to catalysts and potentially valuable properties reminiscent of zeolites [1]. So, a considerable increasing attention has been focused on the synthesis or building of these coordination polymers and supramolecular compounds in recent years. However, most of coordination polymers possess poor solubility and non-stoichiometric composition owing to adsorption of coexisting ions and solvent molecules, so that it is difficult to obtain their single crystals [2]. Although many complexes with 1,2,4,5-benzenetetracarboxylic acid have been reported, which were often obtained from conventional solution reactions [3], the development of synthetic routes to systems containing 1,10-phenthanoline is less explored. Herein, considering the advantage of hydrothermal synthesis, we report synthesis and crystal structure of a new nickel complex by hydrothermal reactions of $NiSO_4$ with 1,2,4,5-benzenetetracarboxylic acid and 1,10-phenanthroline, which are apparently important for rational design and constitution of new framework structures.

The title compound is constituted by nickel(III) ions, 1,10-phenantholine molecules and 1,2,4,5-benzenetetracarboxylate dianions. The coordination environment of nickel(III) ion involves six nitrogen atoms from three 1,10-phenthanoline molecules to form a distorted octahedron with the Ni—N bond length range of 2.056(5) Å – 2.106(4) Å. Each two the octahedrons are bridged by hydrogen bonds between three 1,2,4,5-benzenetetracarboxylate dianions and 1,10-phenthanoline molecules to finish a dimeric entity with a center of symmetry. Apparently, in the crystal structure, all carboxylate groups do not coordinate to Ni^{3+} ions, but there are some significant hydrogen bonds of three types, which are very difficult to distinguish them in the IR spectrum. The first type is observed between two carboxylate groups in a 1,2,4,5-benzenetetracarboxylate dianion, such as O(2)–H(2)···O(3); the second one is between two carboxylate groups in two adjacent 1,2,4,5-benzenetetracarboxylate dianions, such as O(11)–H(11)···O(5); the third one is between a 1,2,4,5-benzenetetracarboxylate dianion and a 1,10-phen-

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thanoline, such as C(24)–H(24)···O(1), respectively. Meanwhile, it also exists significant π-π stacking is found between 1,10-phenanthroline rings from the neighboring dimeric entities with the interplanar distance of bout 3.40 Å.

Table 1. Data collection and handling.

Crystal:	red block, size 0.10 × 0.12 × 0.29 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	5.41 cm^{-1}
Diffractometer, scan mode:	CCD area detector, 600 frames, $\Delta\omega = 2°$
$2\theta_{max}$:	50.08°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11146, 7349
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4883
$N(param)_{refined}$:	631
Programs:	SHELXS-97 [4], ORTEP-II [5]

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

Atom	Site	x	y	z	U_{iso}
H(2)	2*i*	0.6461	–0.1125	0.5923	0.133
H(7)	2*i*	0.5562	0.3698	0.7684	0.252
H(11)	2*i*	0.3114	0.2336	0.8880	0.088
H(3)	2*i*	0.4452	0.0298	0.7570	0.058
H(6A)	2*i*	0.6673	0.2022	0.5861	0.056
H(13)	2*i*	0.3229	0.4728	0.8806	0.050
H(16)	2*i*	1.2623	0.2666	0.3437	0.075
H(17)	2*i*	1.4148	0.3703	0.4809	0.097
H(18)	2*i*	1.3783	0.4544	0.6095	0.090
H(23)	2*i*	0.8118	0.3866	0.5628	0.077
H(24)	2*i*	0.6791	0.2944	0.4172	0.072
H(25)	2*i*	0.7381	0.2285	0.2922	0.060
H(26)	2*i*	1.2241	0.4921	0.6863	0.078
H(27)	2*i*	1.0335	0.4616	0.6710	0.088
H(28)	2*i*	1.1535	0.4466	0.2767	0.064
H(29)	2*i*	1.1413	0.5932	0.2046	0.063
H(30)	2*i*	0.9746	0.5766	0.0797	0.074
H(35)	2*i*	0.5658	0.0891	–0.0730	0.085
H(36)	2*i*	0.6021	–0.0460	0.0165	0.077
H(37)	2*i*	0.7584	0.0018	0.1582	0.064
H(38)	2*i*	0.7708	0.4568	–0.0343	0.075
H(39)	2*i*	0.6333	0.2890	–0.0913	0.074
H(40)	2*i*	1.1224	0.2237	0.1183	0.062
H(41)	2*i*	1.1921	0.1091	0.0329	0.072
H(42)	2*i*	1.1780	–0.0602	0.0646	0.079
H(47)	2*i*	0.8941	–0.2198	0.3747	0.067
H(48)	2*i*	0.8282	–0.0962	0.4434	0.067
H(49)	2*i*	0.8595	0.0750	0.4115	0.048
H(50)	2*i*	1.1024	–0.2117	0.1565	0.082
H(51)	2*i*	1.0148	–0.2609	0.2628	0.074

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}
Ni(1)	2*i*	0.9816(1)	0.2062(1)	0.2700(1)	0.050(1)	0.0341(8)	0.040(1)	0.0158(7)	0.0178(8)	0.0096(7)
N(1)	2*i*	1.1322(9)	0.2879(6)	0.3863(7)	0.063(8)	0.036(6)	0.035(7)	0.014(5)	0.010(6)	0.010(5)
N(2)	2*i*	0.9060(9)	0.2745(6)	0.3649(7)	0.048(7)	0.031(5)	0.037(7)	0.013(5)	0.015(6)	0.007(5)
N(3)	2*i*	0.9995(8)	0.3437(7)	0.2031(7)	0.044(7)	0.041(6)	0.034(7)	0.014(5)	0.014(5)	0.008(5)
N(4)	2*i*	0.8275(7)	0.1522(7)	0.1489(6)	0.058(7)	0.039(6)	0.033(7)	0.018(5)	0.012(5)	0.007(5)
N(5)	2*i*	1.0617(7)	0.1228(7)	0.1930(7)	0.044(6)	0.041(6)	0.051(7)	0.017(5)	0.024(5)	0.014(5)
N(6)	2*i*	0.9485(7)	0.0606(6)	0.3209(7)	0.036(6)	0.045(6)	0.043(7)	0.015(5)	0.016(5)	0.013(5)
O(1)	2*i*	0.7431(8)	0.0758(7)	0.5284(7)	0.104(8)	0.078(7)	0.125(9)	0.032(6)	0.093(7)	0.036(6)
O(2)	2*i*	0.6878(7)	–0.0819(7)	0.5622(7)	0.125(8)	0.075(6)	0.104(9)	0.045(6)	0.078(7)	0.028(6)
O(3)	2*i*	0.5798(8)	–0.1710(7)	0.6646(7)	0.138(9)	0.065(6)	0.13(1)	0.054(6)	0.080(8)	0.036(6)
O(4)	2*i*	0.5058(7)	–0.1222(6)	0.7750(7)	0.099(7)	0.052(5)	0.080(8)	0.028(5)	0.047(6)	0.035(5)
O(5)	2*i*	0.3923(7)	0.1755(6)	0.8279(6)	0.072(6)	0.066(6)	0.075(8)	0.037(5)	0.042(5)	0.032(5)
O(6)	2*i*	0.3787(9)	0.2891(8)	0.7297(9)	0.15(1)	0.125(9)	0.21(1)	0.105(8)	0.134(9)	0.122(9)
O(7)	2*i*	0.583(1)	0.4074(7)	0.7333(9)	0.21(1)	0.068(7)	0.24(2)	–0.021(7)	0.18(1)	–0.015(8)
O(8)	2*i*	0.637(1)	0.3841(7)	0.6105(8)	0.18(1)	0.061(6)	0.14(1)	0.032(7)	0.111(9)	0.042(7)
O(9)	2*i*	0.5481(6)	0.7410(6)	0.8839(6)	0.064(6)	0.052(5)	0.090(8)	–0.001(5)	0.002(5)	0.043(5)
O(10)	2*i*	0.3683(8)	0.6341(7)	0.8107(7)	0.090(8)	0.078(7)	0.087(9)	–0.012(6)	–0.026(6)	0.052(6)
O(11)	2*i*	0.2605(6)	0.2311(6)	0.9143(6)	0.048(5)	0.050(5)	0.066(7)	–0.003(4)	0.023(5)	–0.003(5)
O(12)	2*i*	0.2268(7)	0.3353(6)	1.0261(6)	0.064(6)	0.070(6)	0.085(8)	0.016(5)	0.050(6)	0.016(5)
C(1)	2*i*	0.6193(9)	0.061(1)	0.6262(8)	0.041(8)	0.068(9)	0.041(9)	0.017(7)	0.013(7)	0.011(7)
C(2)	2*i*	0.5513(9)	0.0067(9)	0.6803(8)	0.043(8)	0.046(8)	0.042(9)	0.017(6)	0.012(6)	0.013(6)
C(3)	2*i*	0.4904(9)	0.0649(9)	0.7216(8)	0.041(8)	0.049(8)	0.050(9)	0.005(6)	0.011(6)	0.017(7)
C(4)	2*i*	0.4923(9)	0.1691(9)	0.7139(8)	0.032(8)	0.051(8)	0.049(9)	0.012(6)	0.015(6)	0.020(7)
C(5)	2*i*	0.567(1)	0.2255(9)	0.6676(8)	0.048(8)	0.052(8)	0.032(8)	0.013(7)	0.007(6)	0.009(6)
C(6)	2*i*	0.6233(9)	0.1666(9)	0.6221(8)	0.051(8)	0.047(8)	0.046(9)	0.015(7)	0.019(7)	0.018(7)
C(7)	2*i*	0.688(1)	0.017(1)	0.568(1)	0.051(9)	0.07(1)	0.07(1)	0.024(8)	0.034(8)	0.022(9)
C(8)	2*i*	0.547(1)	–0.104(1)	0.711(1)	0.06(1)	0.06(1)	0.06(1)	0.020(8)	0.019(8)	0.022(8)
C(9)	2*i*	0.416(1)	0.219(1)	0.762(1)	0.06(1)	0.043(8)	0.08(1)	0.016(7)	0.022(8)	0.029(8)
C(10)	2*i*	0.598(1)	0.346(1)	0.665(1)	0.052(9)	0.052(9)	0.08(1)	0.010(7)	0.029(8)	0.009(8)
C(11)	2*i*	0.462(1)	0.650(1)	0.871(1)	0.06(1)	0.052(9)	0.04(1)	0.006(8)	0.008(7)	0.016(7)
C(12)	2*i*	0.488(1)	0.5755(8)	0.9376(8)	0.045(8)	0.030(7)	0.043(9)	0.010(6)	0.014(7)	0.017(6)
C(13)	2*i*	0.3951(9)	0.4845(8)	0.9290(8)	0.037(8)	0.043(7)	0.030(8)	–0.001(6)	0.001(6)	0.006(6)
C(14)	2*i*	0.406(1)	0.4078(8)	0.9919(9)	0.039(8)	0.036(7)	0.053(9)	0.008(6)	0.026(7)	0.017(6)
C(15)	2*i*	0.290(1)	0.320(1)	0.9776(9)	0.040(9)	0.048(8)	0.06(1)	0.005(7)	0.007(7)	0.021(7)
C(16)	2*i*	1.245(1)	0.301(1)	0.395(1)	0.06(1)	0.08(1)	0.05(1)	0.031(8)	0.008(9)	0.004(8)
C(17)	2*i*	1.337(1)	0.363(1)	0.478(1)	0.07(1)	0.09(1)	0.08(1)	0.017(9)	0.02(1)	0.03(1)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(18)	2*i*	1.316(1)	0.413(1)	0.554(1)	0.07(1)	0.06(1)	0.06(1)	0.011(8)	–0.009(9)	0.010(8)
C(19)	2*i*	1.199(1)	0.4012(9)	0.551(1)	0.07(1)	0.044(8)	0.05(1)	0.011(8)	0.009(9)	0.013(7)
C(20)	2*i*	1.108(1)	0.3389(8)	0.4618(9)	0.07(1)	0.034(7)	0.039(9)	0.021(7)	0.021(8)	0.015(6)
C(21)	2*i*	0.987(1)	0.3274(8)	0.4502(9)	0.08(1)	0.029(7)	0.041(9)	0.025(7)	0.034(8)	0.023(6)
C(22)	2*i*	0.961(1)	0.3764(9)	0.531(1)	0.09(1)	0.032(7)	0.05(1)	0.027(8)	0.036(9)	0.020(7)
C(23)	2*i*	0.837(1)	0.3593(9)	0.513(1)	0.10(1)	0.048(9)	0.08(1)	0.031(9)	0.06(1)	0.029(8)
C(24)	2*i*	0.759(1)	0.3051(9)	0.427(1)	0.07(1)	0.043(8)	0.09(1)	0.029(8)	0.05(1)	0.027(8)
C(25)	2*i*	0.795(1)	0.2642(8)	0.3528(9)	0.048(9)	0.046(7)	0.06(1)	0.014(7)	0.019(8)	0.011(7)
C(26)	2*i*	1.166(1)	0.4496(9)	0.629(1)	0.09(1)	0.043(8)	0.05(1)	0.003(8)	0.012(9)	–0.002(7)
C(27)	2*i*	1.053(2)	0.434(1)	0.618(1)	0.13(2)	0.044(9)	0.05(1)	0.02(1)	0.04(1)	0.016(8)
C(28)	2*i*	1.084(1)	0.4392(9)	0.2264(9)	0.046(9)	0.052(8)	0.05(1)	0.006(7)	0.010(7)	0.007(7)
C(29)	2*i*	1.079(1)	0.5282(9)	0.183(1)	0.06(1)	0.040(8)	0.05(1)	0.006(7)	0.010(8)	0.008(7)
C(30)	2*i*	0.981(1)	0.5173(9)	0.110(1)	0.12(1)	0.030(7)	0.06(1)	0.020(8)	0.052(9)	0.018(7)
C(31)	2*i*	0.887(1)	0.4184(9)	0.0757(9)	0.060(9)	0.047(8)	0.041(9)	0.026(7)	0.024(7)	0.022(7)
C(32)	2*i*	0.902(1)	0.3326(9)	0.1267(9)	0.045(9)	0.042(7)	0.048(9)	0.023(7)	0.026(7)	0.010(7)
C(33)	2*i*	0.813(1)	0.2305(9)	0.0981(9)	0.051(9)	0.045(8)	0.037(9)	0.024(7)	0.017(7)	0.010(7)
C(34)	2*i*	0.711(1)	0.212(1)	0.013(1)	0.043(9)	0.060(9)	0.04(1)	0.004(7)	0.018(7)	0.015(8)
C(35)	2*i*	0.632(1)	0.106(1)	–0.0172(9)	0.036(9)	0.12(1)	0.06(1)	0.026(9)	0.013(7)	0.02(1)
C(36)	2*i*	0.653(1)	0.026(1)	0.037(1)	0.035(9)	0.07(1)	0.06(1)	–0.010(7)	0.008(8)	–0.004(9)
C(37)	2*i*	0.748(1)	0.0540(9)	0.1199(9)	0.06(1)	0.045(8)	0.05(1)	0.012(7)	0.017(8)	0.010(7)
C(38)	2*i*	0.783(1)	0.399(1)	–0.003(1)	0.09(1)	0.07(1)	0.05(1)	0.036(9)	0.030(9)	0.025(8)
C(39)	2*i*	0.699(1)	0.300(1)	–0.0363(9)	0.05(1)	0.09(1)	0.05(1)	0.037(8)	0.010(7)	0.028(9)
C(40)	2*i*	1.114(1)	0.1530(8)	0.1299(8)	0.07(1)	0.034(7)	0.05(1)	0.006(6)	0.034(8)	0.019(7)
C(41)	2*i*	1.157(1)	0.0852(9)	0.0788(9)	0.08(1)	0.047(8)	0.08(1)	0.011(7)	0.061(9)	0.015(8)
C(42)	2*i*	1.147(1)	–0.0149(9)	0.0973(9)	0.08(1)	0.053(9)	0.09(1)	0.022(8)	0.060(9)	0.010(8)
C(43)	2*i*	1.094(1)	–0.0534(9)	0.1623(9)	0.064(9)	0.037(7)	0.06(1)	0.020(6)	0.029(7)	0.002(7)
C(44)	2*i*	1.0499(9)	0.0186(8)	0.2120(8)	0.038(8)	0.029(6)	0.048(9)	0.004(6)	0.012(6)	0.006(6)
C(45)	2*i*	0.9901(9)	–0.0141(8)	0.2783(8)	0.034(7)	0.034(7)	0.036(8)	0.004(6)	0.006(6)	–0.003(6)
C(46)	2*i*	0.977(1)	–0.1168(8)	0.2984(9)	0.061(9)	0.030(7)	0.06(1)	0.016(6)	0.021(7)	0.020(6)
C(47)	2*i*	0.910(1)	–0.1494(9)	0.3618(9)	0.07(1)	0.039(8)	0.06(1)	0.010(7)	0.032(8)	0.024(7)
C(48)	2*i*	0.870(1)	–0.0769(9)	0.4008(8)	0.07(1)	0.055(8)	0.042(9)	0.009(7)	0.025(7)	0.015(7)
C(49)	2*i*	0.8892(8)	0.0266(8)	0.3814(7)	0.045(8)	0.045(7)	0.036(8)	0.018(6)	0.017(6)	0.011(6)
C(50)	2*i*	1.075(1)	–0.1615(9)	0.187(1)	0.08(1)	0.032(8)	0.11(1)	0.020(7)	0.051(9)	0.003(8)
C(51)	2*i*	1.023(1)	–0.1911(9)	0.2491(9)	0.08(1)	0.037(7)	0.09(1)	0.027(7)	0.054(9)	0.025(8)

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