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# Crystal structure of poly[{aqua(1,10-phenanthroline-$\kappa^2N,N'$)nickel(II)}-$\mu$-(dihydrogen-benzene-1,2,4,5-tetracarboxylate)-$\kappa^3O:O':O''$], $Ni(C_{10}H_4O_8)(C_{12}H_8N_2)(H_2O)$

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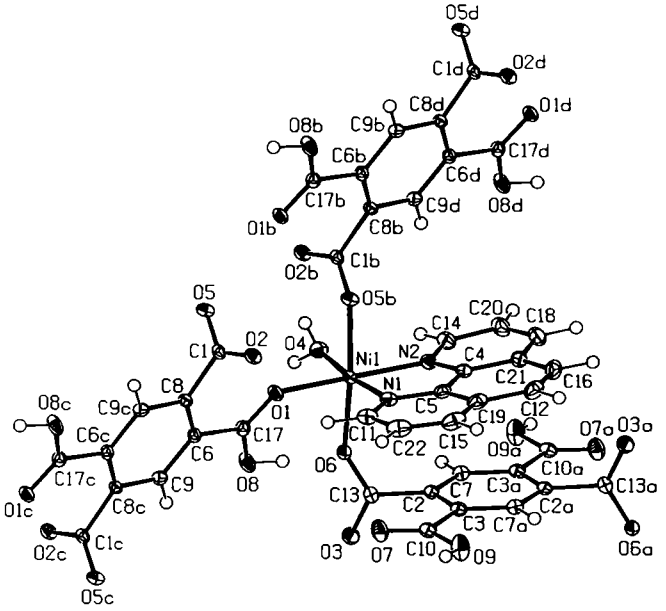
Received July 28, 2005, accepted and available on-line September 8, 2005; CCDC no. 1267/1611




## Abstract

$C_{22}H_{14}N_2NiO_9$, triclinic, $P\bar{1}$ (no. 2), $a = 9.589(5)$ Å, $b = 10.144(7)$ Å, $c = 11.312(5)$ Å, $\alpha = 87.11(2)°$, $\beta = 72.38(2)°$, $\gamma = 64.96(2)°$, $V = 946.3$ Å$^3$, $Z = 2$, $R_{gt}(F) = 0.035$, $wR_{ref}(F^2) = 0.085$, $T = 173$ K.

## Source of material

Sky blue block crystals of the title compound were synthesized by a hydrothermal method. All chemicals were of analytical purity grade and were used without further purification. A mixture of $NiCl_2 \cdot 6H_2O$ (1 mmol, 0.238 g), 1,2,4,5-benzenetetracarboxylic anhydride (1 mmol, 0.218 g), 1,10-phenanthroline monohydrate (1 mmol, 0.198 g), NaOH (2 mmol, 0.080 g) and distilled water (5 ml) was located into a 30 ml Teflon-lined reactor and heated at 160 °C for 4 days. After cooling to room temperature at ca. 5 K/h, blue block crystals were isolated and washed with water and ethanol for three times, then dried in ambient.

Elemental analysis: found – C, 52.02 %; H, 2.84 %; N, 5.54 %; calc. for $C_{22}H_{14}N_2NiO_9$ – C, 51.91 %; H, 2.77 %; N, 5.50 %.

## Discussion

The self-assembly of metal ions with aromatic carboxylates is a rapidly developing research field of modern coordination chemistry, because of the aggregation of metal ions and these carboxylate ligands in versatile binding modes, such as monodentate, chelating bidentate, bridging bidentate and bridging tridentate. Hereby, 1,2,4,5-benzenetetracarboxylic acid ($H_4TCB$) is a good bridging ligand, and numerous complexes with $H_4TCB$ anions have been prepared, such as that of Co(II) [1-3], Ni(II) [4,5], Tl(I) [6], Cu(II) [4,7,8], Zn(II) [9]. Especially, the metal-1,10-phenanthroline (phen) system has been well studied and displays a diversity of structures.

The title compound, $[Ni_2(H_2TCB)_2(phen)_2(H_2O)_2]_n$, forms a 2D polymer. The Ni atom is six-coordinated by four O atoms from three pyromellitate anions ($H_2TCB$) and one water molecule, and two N atoms from a phen ligand. The environment of the Ni atom is a slightly distorted octahedron. The structure is isotypic to the structure of the Co(II) analogue [1] and has only slightly different structural parameters. The distances range from 2.048(2) Å to 2.093(2) Å for Ni—O and from 2.083(2) Å to 2.127(2) Å for Co—O; and the distances are 2.054(2) Å, 2.059(2) Å for Ni—N and 2.103(2) Å, 2.110(2) Å for Co—N [1].The $H_2btc$ anions act as bidentate or tetradentate ligands bridging two or four Ni ions. In bidentate one, only two carboxylate groups are linked to two different Ni atom, while other two carboxylate groups remain free. There are three kinds of intralayer hydrogen bonds between water-carboxyl and carboxyl-carboxyl which contribute to the stabilization of the structure.

**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | blue block, size 0.40 × 0.50 × 0.50 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| $\mu$: | 10.91 cm$^{-1}$ |
| Diffractometer, scan mode: | Rigaku R-AXIS RAPID, $\omega$ |
| $2\theta_{max}$: | 54.94° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 9392, 4302 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 3\ \sigma(I_{obs})$, 3900 |
| $N(param)_{refined}$: | 308 |
| Programs: | SIR92 [10], CRYSTALS [11], PLATON [12] |

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

| Atom | Site | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|---|
| H(1) | 2*i* | 0.1742 | –0.1167 | 0.6228 | 0.050 |
| H(2) | 2*i* | 0.2227 | –0.1120 | 0.7083 | 0.050 |
| H(3) | 2*i* | –0.1792 | 0.0954 | 0.6683 | 0.050 |
| H(4) | 2*i* | –0.4644 | 0.7319 | 0.7622 | 0.050 |
| H(5) | 2*i* | 0.1554 | 0.2602 | 0.3958 | 0.014 |
| H(6) | 2*i* | –0.4754 | 0.0012 | 0.7843 | 0.013 |
| H(7) | 2*i* | –0.3065 | 0.3352 | 0.9680 | 0.019 |
| H(8) | 2*i* | –0.0368 | 0.7579 | 0.8973 | 0.031 |

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**Table 2.** Continued.

| Atom | Site | x | y | z | $U_{iso}$ |
|---|---|---|---|---|---|
| H(9) | 2*i* | 0.3784 | 0.0735 | 0.5710 | 0.022 |
| H(10) | 2*i* | −0.2937 | 0.7283 | 1.0226 | 0.024 |
| H(11) | 2*i* | 0.2230 | 0.6564 | 0.7545 | 0.032 |
| H(12) | 2*i* | 0.4542 | 0.4386 | 0.6057 | 0.031 |
| H(13) | 2*i* | 0.5517 | 0.1957 | 0.5181 | 0.028 |
| H(14) | 2*i* | −0.4299 | 0.5746 | 1.0730 | 0.023 |

**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* | 0.03068(3) | 0.14402(3) | 0.76434(2) | 0.0108(2) | 0.0134(2) | 0.0128(2) | −0.0061(1) | −0.0038(1) | 0.0004(1) |
| O(1) | 2*i* | −0.1471(2) | 0.0768(2) | 0.8601(2) | 0.0142(7) | 0.0245(8) | 0.0152(8) | −0.0126(6) | −0.0048(6) | 0.0042(6) |
| O(2) | 2*i* | 0.3069(2) | −0.1587(2) | 0.8510(2) | 0.0144(7) | 0.0161(8) | 0.0180(8) | −0.0060(6) | −0.0056(6) | −0.0019(6) |
| O(3) | 2*i* | −0.1970(2) | 0.2666(2) | 0.4778(2) | 0.0286(9) | 0.0229(9) | 0.0207(9) | −0.0152(7) | −0.0138(7) | 0.0047(7) |
| O(4) | 2*i* | 0.1858(2) | −0.0549(2) | 0.6666(2) | 0.0217(8) | 0.0156(8) | 0.0179(8) | −0.0059(6) | −0.0093(7) | −0.0016(6) |
| O(5) | 2*i* | 0.1471(2) | 0.0807(2) | 0.9009(2) | 0.0133(7) | 0.0171(7) | 0.0152(8) | −0.0043(6) | −0.0065(6) | −0.0009(6) |
| O(6) | 2*i* | −0.0749(2) | 0.1826(2) | 0.6216(2) | 0.0190(8) | 0.0191(8) | 0.0168(8) | −0.0120(7) | −0.0086(6) | 0.0062(6) |
| O(7) | 2*i* | −0.3761(2) | 0.4910(2) | 0.7101(2) | 0.0184(8) | 0.0237(9) | 0.028(1) | −0.0119(7) | −0.0001(7) | −0.0015(7) |
| O(8) | 2*i* | −0.2387(2) | 0.0459(2) | 0.7083(2) | 0.0271(9) | 0.038(1) | 0.0133(8) | −0.0252(8) | −0.0067(7) | 0.0061(7) |
| O(9) | 2*i* | −0.3905(2) | 0.7161(2) | 0.7187(2) | 0.0173(8) | 0.0206(9) | 0.034(1) | −0.0080(7) | 0.0085(7) | −0.0082(7) |
| N(1) | 2*i* | −0.1035(2) | 0.3472(2) | 0.8602(2) | 0.0138(9) | 0.0147(9) | 0.0153(9) | −0.0040(7) | −0.0060(7) | −0.0001(7) |
| N(2) | 2*i* | 0.1896(2) | 0.2358(2) | 0.6903(2) | 0.0154(9) | 0.0170(9) | 0.0144(9) | −0.0083(7) | −0.0058(7) | 0.0016(7) |
| C(1) | 2*i* | 0.2667(3) | −0.0350(2) | 0.9018(2) | 0.0113(9) | 0.018(1) | 0.0104(9) | −0.0090(8) | −0.0019(8) | 0.0020(8) |
| C(2) | 2*i* | −0.0615(3) | 0.3946(2) | 0.5262(2) | 0.016(1) | 0.014(1) | 0.012(1) | −0.0072(8) | −0.0069(8) | 0.0018(8) |
| C(3) | 2*i* | −0.1529(3) | 0.5356(2) | 0.5859(2) | 0.0130(9) | 0.016(1) | 0.0117(9) | −0.0056(8) | −0.0042(8) | 0.0007(8) |
| C(4) | 2*i* | 0.1352(3) | 0.3726(2) | 0.7421(2) | 0.018(1) | 0.018(1) | 0.014(1) | −0.0089(9) | −0.0086(8) | 0.0037(8) |
| C(5) | 2*i* | −0.0240(3) | 0.4337(2) | 0.8325(2) | 0.019(1) | 0.016(1) | 0.015(1) | −0.0067(9) | −0.0092(9) | 0.0030(8) |
| C(6) | 2*i* | −0.3726(3) | 0.0207(2) | 0.9156(2) | 0.0107(9) | 0.0123(9) | 0.014(1) | −0.0057(8) | −0.0023(8) | 0.0011(7) |
| C(7) | 2*i* | 0.0904(3) | 0.3605(2) | 0.4402(2) | 0.015(1) | 0.014(1) | 0.014(1) | −0.0051(8) | −0.0043(8) | 0.0002(8) |
| C(8) | 2*i* | 0.3855(2) | −0.0198(2) | 0.9582(2) | 0.0097(9) | 0.0119(9) | 0.016(1) | −0.0044(7) | −0.0047(8) | 0.0007(7) |
| C(9) | 2*i* | −0.4863(3) | 0.0010(2) | 0.8750(2) | 0.014(1) | 0.015(1) | 0.013(1) | −0.0056(8) | −0.0048(8) | 0.0014(8) |
| C(10) | 2*i* | −0.3182(3) | 0.5767(2) | 0.6782(2) | 0.015(1) | 0.018(1) | 0.014(1) | −0.0064(8) | −0.0049(8) | 0.0000(8) |
| C(11) | 2*i* | −0.2478(3) | 0.3987(3) | 0.9466(2) | 0.017(1) | 0.023(1) | 0.019(1) | −0.0054(9) | −0.0070(9) | 0.0016(9) |
| C(12) | 2*i* | 0.0087(4) | 0.6562(3) | 0.8579(3) | 0.041(2) | 0.016(1) | 0.026(1) | −0.013(1) | −0.019(1) | 0.0037(9) |
| C(13) | 2*i* | −0.1200(3) | 0.2759(2) | 0.5436(2) | 0.013(1) | 0.015(1) | 0.013(1) | −0.0066(8) | −0.0016(8) | −0.0017(8) |
| C(14) | 2*i* | 0.3377(3) | 0.1746(3) | 0.6097(2) | 0.017(1) | 0.024(1) | 0.021(1) | −0.0088(9) | −0.0051(9) | 0.0012(9) |
| C(15) | 2*i* | −0.2426(3) | 0.6277(3) | 0.9796(2) | 0.030(1) | 0.017(1) | 0.021(1) | −0.001(1) | −0.011(1) | −0.0027(9) |
| C(16) | 2*i* | 0.1586(4) | 0.5977(3) | 0.7749(2) | 0.041(2) | 0.024(1) | 0.025(1) | −0.022(1) | −0.018(1) | 0.009(1) |
| C(17) | 2*i* | −0.2408(3) | 0.0492(2) | 0.8235(2) | 0.013(1) | 0.0136(9) | 0.015(1) | −0.0059(8) | −0.0027(8) | 0.0009(8) |
| C(18) | 2*i* | 0.3844(3) | 0.3851(3) | 0.6289(2) | 0.026(1) | 0.036(1) | 0.023(1) | −0.021(1) | −0.012(1) | 0.009(1) |
| C(19) | 2*i* | −0.0877(3) | 0.5754(3) | 0.8896(2) | 0.029(1) | 0.016(1) | 0.018(1) | −0.007(1) | −0.013(1) | 0.0020(9) |
| C(20) | 2*i* | 0.4396(3) | 0.2459(3) | 0.5774(2) | 0.017(1) | 0.034(1) | 0.024(1) | −0.014(1) | −0.0047(9) | 0.005(1) |
| C(21) | 2*i* | 0.2272(3) | 0.4534(3) | 0.7141(2) | 0.027(1) | 0.023(1) | 0.019(1) | −0.016(1) | −0.013(1) | 0.0072(9) |
| C(22) | 2*i* | −0.3212(3) | 0.5392(3) | 1.0082(2) | 0.019(1) | 0.026(1) | 0.019(1) | −0.000(1) | −0.0040(9) | −0.003(1) |

*Acknowledgment.* Financial support from Kyoto University Foundation is gratefully acknowledged.

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