

Mechanochemical Control of Synthesis and Structures of Aqua-Bridged Binuclear Nickel(II) Benzoate Complexes

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Synthetic and structural aspects of a few binuclear nickel(II) complexes, having two bridging carboxylate groups and aqua groups are reported. Intramolecular O–H...O hydrogen bonding interactions between the bridging aqua group and the monodentate benzoate groups stabilises the bridging structures. Aqua-bridged nickel(II) benzoate complex is

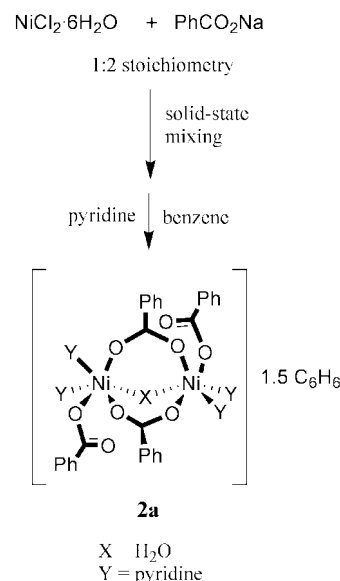
stable irrespective of solvent system and also can include solvent molecules such as toluene and benzene. A mixed chloro, aqua and 4-chloro-benzoato-bridged Ni^{II} binuclear complex was synthesised and structurally characterised. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2006)

Introduction

The crystal structures of the active sites of binuclear nickel(II) metallo-enzymes have shown that the metal centres are bridged by carboxylates as well as water or hydroxide ions.^[1] The binuclear metal active site of the urease isolated from *Klebsiella aerogenes*, has aqua-bridged binuclear nickel(II) centres with pseudo-octahedral and square-pyramid geometry around the nickel ions.^[2] So the design of binuclear aqua-bridged nickel(II) complexes is important in biological modelling.^[3] Study of the structure and properties of binuclear transition-metal complexes containing bridging groups such as aqua groups^[3] are expected to increase our understanding of the crucial factors that determine the catalytic activity of metalloenzymes.^[4] We recently described the synthesis and catalytic activity of a binuclear nickel(II) benzoate complex that contains an aqua group in the bridging position.^[5] We also communicated that the solid state and solution synthetic route results in a variation of the structure of nickel carboxylate complexes.^[5] In the biological environment the reactions of substrates takes place in confined media, so, it is necessary to understand how different types of motifs can be developed from the complexes that have close structural resemblance to biological active sites. It is also necessary to understand the stability of such complexes in the presence of various neutral molecules in the lattice. With these objectives in mind we investigated multiple component solid-state synthesis of binuclear nickel(II) carboxylate complexes and the structural aspects of aqua-bridged nickel complexes in the presence of different neutral molecules in the lattice.

Results and Discussion

We have observed that the reaction of nickel(II) chloride hexahydrate, and sodium benzoate in 1:2 stoichiometry (Scheme 1) in the solid-state followed by addition of pyridine gave the nickel(II) benzoate complex, **2a**. The synthetic procedure is important because the analogous reaction in solution results in the formation of a mononuclear species.^[6] The complex is soluble in chloroform, benzene or toluene and could subsequently be crystallised from benzene in *P2₁/c* space group as light blue blocks. The crystal structure of **2a** shows that each of the nickel centres have octahedral geometry involving two bridging benzoate groups (Figure 1), two coordinated pyridine molecules and a monodentate benzoate apart from a bridging aqua group;



Scheme 1.

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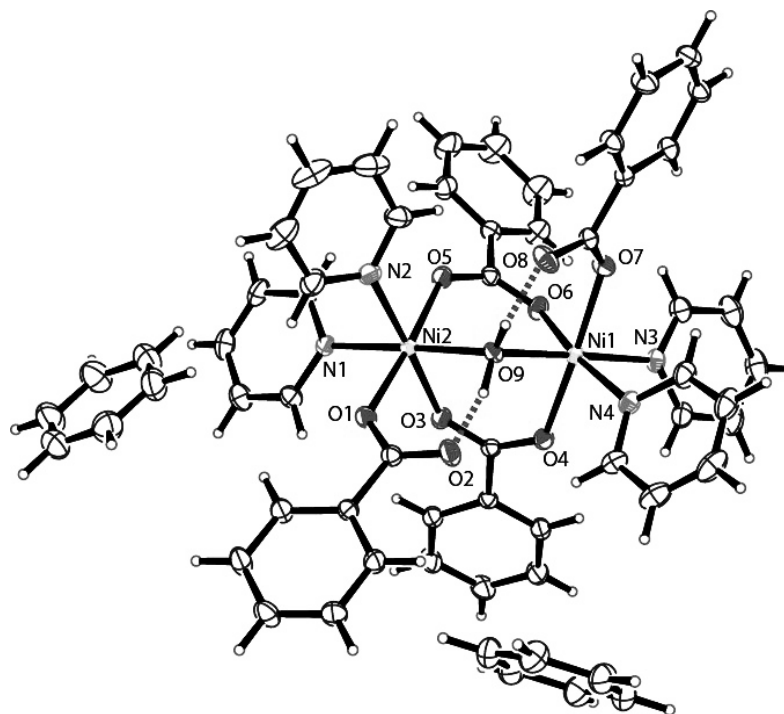


Figure 1. Crystal structure of **2a** with included benzene molecules (thermal ellipsoids drawn to 30% probability).

the Ni(1)⋯Ni(2) distance in this complex is 3.506(3) Å. The monodentate benzoate groups are intramolecularly hydrogen-bonded to the bridging aqua group through O(9)–H⋯O(2) [2.565(3) Å, 166(3)°] and O(9)–H⋯O(8) [2.572(3) Å, 170(3)°] interactions. The Ni(1)–O(9) and Ni(2)–O(9) bond lengths in this complex are 2.093(2) and 2.094(2) Å while the corresponding Ni(1)–O(9)–Ni(2) bond angle is 113.7(8)°.

There is a distorted octahedral geometry around each of the nickel centres. The compound has an absorption maximum at 645 nm due to a 3A_2 to 3T_1 transition arising from d^8 -electronic configuration in a weak field. The assembly is stabilised by weak aromatic C–H⋯ π interactions ($d_{C\cdots\pi}$ 3.87 Å) involving the C60–H of the benzene molecule as the donor and the aromatic ring of the benzoate groups of the molecule as the acceptor. In this case, the self-assembly of the binuclear nickel(II) benzoate complex leads to the inclusion of two benzene molecules in the crystal lattice that are stabilised by weak intermolecular C–H⋯ π interactions.

The complex $[\text{Ni}_2(\text{H}_2\text{O})(\text{O}_2\text{CPh})_4(\text{Py})_4]$ when crystallised from toluene results in the formation of a polymorph that contains included benzoic acid and toluene molecules and we have reported this structure in the past.^[5] When this complex was dissolved in ethanol and layered over water the complex $[\text{Ni}_2(\text{H}_2\text{O})(\text{O}_2\text{CPh})_4(\text{Py})_4]\text{H}_2\text{O}$ (**2b**) was crystallised; the crystals were found to have crystallised in the orthorhombic *Pbcn* space group. The structure of this complex is shown in Figure 2. Intra-molecular O(4)–H⋯O(2) [2.573(17) Å, 166(3)°] hydrogen bonding interactions are also observed between the bridging aqua group and the monodentate benzoate group as shown in Figure 2. It is observed that the Ni(1)–O(4) bond length in **2b** is

2.104(9) Å, which is slightly longer than that in **2a**, while the Ni(1)–O(4)–Ni(1') bond angle is 115.25(8)°. This complex, **2b**, is a polymorph of **2a** and is characterised by a similar binuclear nickel(II) core except for the presence of a lattice water molecule that is intermolecularly hydrogen-bonded to the monodentate benzoate group through O(6)–H⋯O(2) [2.910(2) Å, 164(3)°] interactions. Solid-state FT-IR spectroscopy of this complex shows broad signals at 3537 and 3478 cm^{-1} arising from intramolecular and intermolecularly hydrogen bonded O–H stretching vibrations. In methanol, the UV/Visible spectrum of **2b** shows an absorption band at 648 nm that may be assigned to the 3A_2 to 3T_1 transition.

Addition of pyridine to a mixture of nickel(II) chloride hexahydrate, 1-naphthoic acid and potassium hydroxide in toluene/methanol (1:1 v/v) gave a blue solution, from which the corresponding aqua-bridged binuclear complex, $[\text{Ni}_2(\text{H}_2\text{O})(\text{O}_2\text{Cnp})_4(\text{Py})_4]$ (**2c**), was obtained (where Np is naphthyl). The crystal structure of the complex is shown in Figure 3 (a), which shows that the bridging aqua group is hydrogen bonded to the monodentate naphthoate group through O(9)–H⋯O(8) [2.566(4) Å, 169(5)°] and O(9)–H⋯O(2) [2.533(4) Å, 162(6)°] interactions. The structure of the complex shows that the two nickel(II) centres are bridged by a water molecule and two naphthoate groups such that the Ni(1)–O(9)–Ni(2) bond angle is 117.78(9)°, with a Ni(1)⋯Ni(2) distance of 3.593(7) Å.

In a similar manner to the one discussed above, a corresponding binuclear nickel(II) complex of 2-nitrobenzoic acid was also prepared and could be crystallised from toluene as blue-green plates in the *C2/c* space group. Crystal structure analysis shows that the corresponding aqua bridge

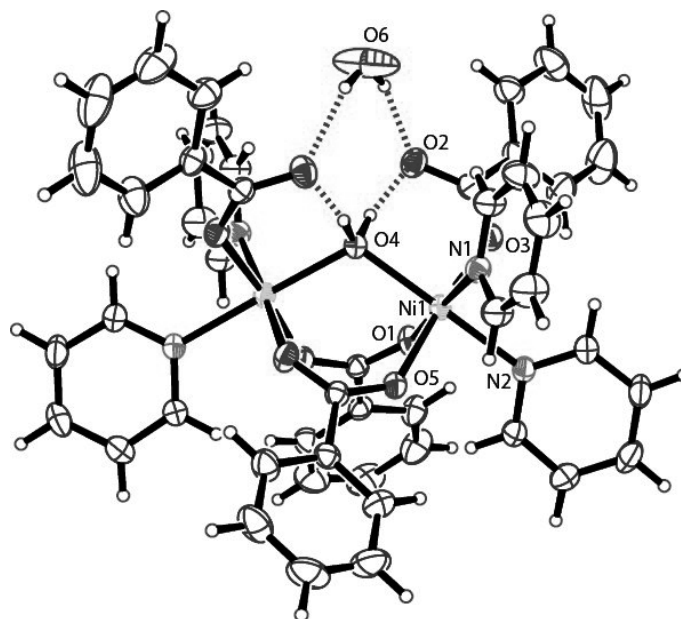


Figure 2. The structure of **2b** containing a hydrogen-bonded water molecule; symmetry for equivalent atoms $[-x, y, -z + 1/2]$ (thermal ellipsoids drawn to 30% probability).

in the binuclear nickel(II) complex with 2-nitrobenzoic acid **2d** is structurally similar to that of **2c** (Figure 3, b). It is observed that solvent molecules are not included in the crystal lattice of this complex apparently due to the steric crowding caused by the nitro substituent on the aromatic carboxylic acid molecules. As described earlier, each nickel(II) centre in complex **2d** is coordinated to the monodentate benzoate groups and two pyridine molecules, apart from the two bridging benzoate and bridging aqua group, which gives a six-coordinate octahedral geometry. The aqua molecule in this complex is intramolecularly hydrogen bonded to the monodentate benzoate through O(9)–H $\cdots$ O(2) [2.571(16) Å, 167(2) $^\circ$] interactions; in this case the

Ni(1)–O(9) bond length is 2.089(9) Å with the Ni(1)–O(9)–Ni(2) bond angle being 117.05(8) $^\circ$.

So far in the above reactions we have obtained systematically aqua-bridged complexes, starting from nickel(II) chloride as the inorganic salt. However, in the reaction of 4-chlorobenzoic acid under analogous conditions a chloro-bridged complex $[\text{Ni}_2(\text{H}_2\text{O})(\text{Cl})(\text{O}_2\text{CAr})_3(\text{Py})_4]$ (**2e**) was formed. The crystal structure of this complex revealed the presence of an aqua bridge (Figure 4) and a benzoate bridge unlike complexes **2a–2d**, along with a chloride bridging group between the two nickel centres. In this case the presence of three monodentate 4-chlorobenzoate groups led to the binuclear tribridged $[\text{Ni}_2(\text{H}_2\text{O})(\text{Cl})(\text{O}_2\text{CAr})_3(\text{Py})_4]$

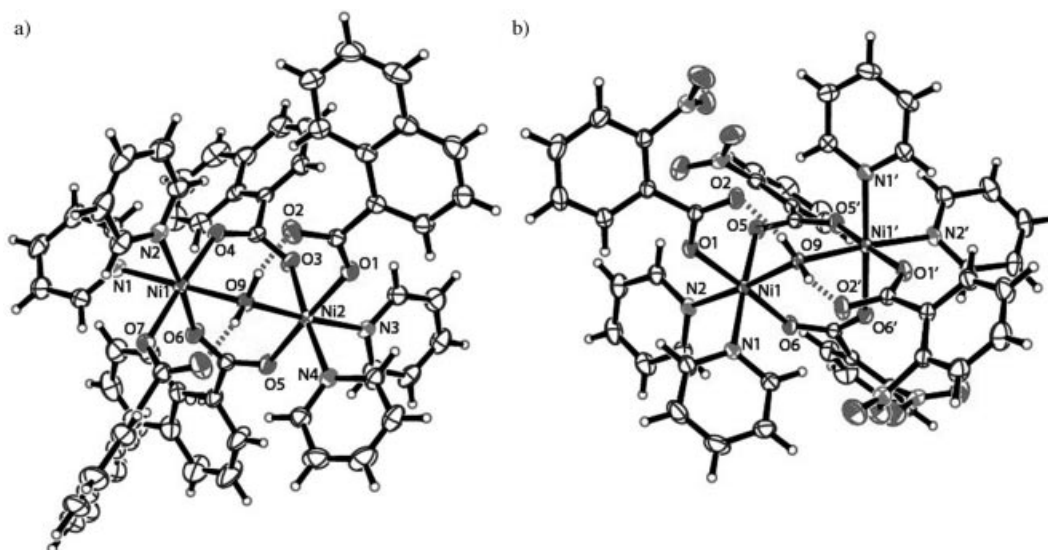


Figure 3. Crystal structures of (a) **2c** and (b) **2d** showing the intramolecular hydrogen bonding interactions between the bridging aqua molecule and the monodentate carboxylate groups (thermal ellipsoids drawn to 30% probability).

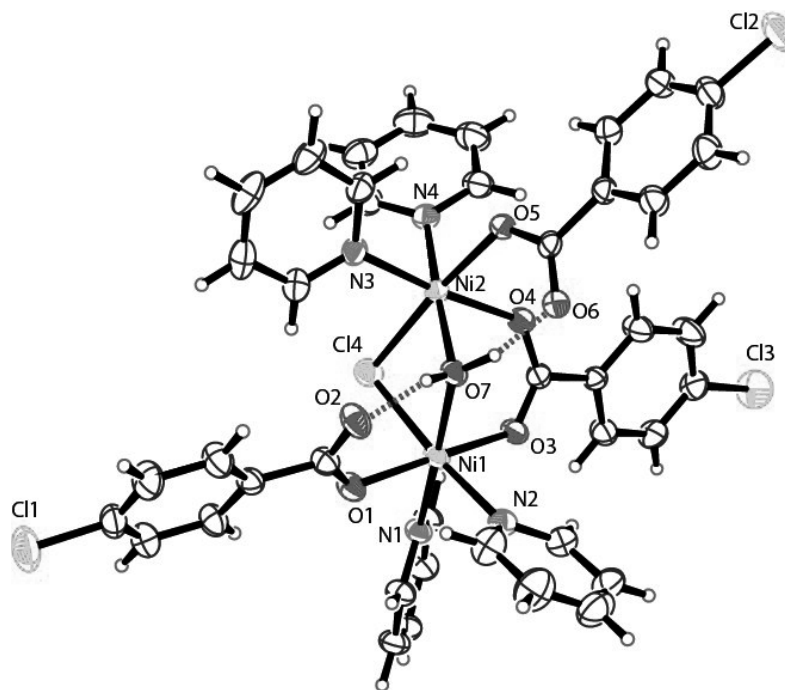


Figure 4. Crystal structure of **2e** (thermal ellipsoids drawn to 30% probability).

complex, (**2e**) as shown in Figure 4. The complex also has distorted octahedral geometry around the nickel centres and has an electronic absorption at 633 nm due to the 3A_2 to 3T_1 transition.

It is observed that in complex **2e**, the bridging aqua molecule is intramolecularly hydrogen bonded to the carboxylate units of the monodentate 4-chlorobenzoate groups via O(7)–H $\cdots$ O(2) [2.593(3) Å, 165(3)°] and O(7)–H $\cdots$ O(6) [2.561(3) Å, 165(4)°] interactions. The corresponding Ni(1)–O(7) and Ni(2)–O(7) bond lengths are 2.126(2) and 2.121(2) Å respectively while the Ni(1)–O(7)–Ni(2) bond angle is found to be 101.18(9)°. Although the Ni(1) $\cdots$ Ni(2) distance is 3.281(2) Å it is substantially shorter than **2a** or **2c** (Table 1). The reported values for Ni $\cdots$ Ni distance of separation in aqua-bridged complexes ranges from 3.497–3.676 Å.^[7] However, the effect of the substituent on the aromatic ring as well as solvation on the Ni–O_{aqua}–Ni angle becomes prominent in the complexes **2c** and **2d**, which are close to the reported bond angles.^[7] When the Ni–O_{aqua}–Ni angles among **2a** and **2b** are compared it is found that **2a** < **2b**. This happens because the hydrogen bonding interaction of the bridging water molecules in each case is different. In the case of complex **2b**, the hydrogen bonding interaction involving the interstitial water molecules draws

the carbonyl closer, making the Ni–O_{aqua}–Ni bond angle smaller than in **2a**. In the case of complex **2e** the bond angle is the smallest in comparison to **2a**–**2d** because both the chloro and aqua groups bridge it.

Conclusion

In summary, we have described the synthetic and structural aspects of a few binuclear nickel(II) complexes, having two bridging carboxylate groups and aqua groups. Intramolecular O–H $\cdots$ O hydrogen bonding interactions between the bridging aqua group and the monodentate benzoate groups are observed in these complexes which add to the stability of the bridging structure. From this structural study on aqua-bridged structures we could show the structural implications of solvent molecules in different types of co-crystals. Aqua-bridged nickel(II) benzoate complexes are stable irrespective of solvent system and also can include solvent molecules such as toluene and benzene. A mixed chloro, aqua and 4-chloro-benzoato-bridged Ni^{II} binuclear complex is formed from the reaction of 4-chlorobenzoate with nickel(II) chloride in the presence of pyridine. This suggests that a substituent on the aromatic ring has a role in deciding the mechanochemical process during the solid-state synthesis.

Experimental Section

The reagents used were procured from commercial sources (Sigma–Aldrich or Fluka) and used as received unless otherwise stated. Solvents such as benzene, toluene, methanol and acetonitrile were distilled and used.

Table 1. Bond lengths (in Å) and angles (in °).

	2a	2b	2c	2d	2e
Ni(1)–O _{aqua}	2.094(2)	2.139(2)	2.088(2)	2.089(9)	2.126(2)
Ni(2)–O _{aqua}	2.094(2) ^[a]	2.143(2)	2.108(2)	2.089(9) ^[a]	2.121(2)
Ni(1)–O _{aqua} –Ni(2)	113.7(8)	111.87(11)	117.78(9)	117.05(8)	101.18(9)
Ni(1) $\cdots$ Ni(2)	3.506(5)	3.554(3)	3.593(7)	3.563(6)	3.281(2)

[a] Symmetry equivalence Ni(1) and Ni(2) in **2a** and **2d**.

Table 2. Crystal data and refinement parameters for **2a–e**.

	2a	2b	2c	2d	2e
Formula	C ₅₇ H ₅₁ N ₄ Ni ₂ O ₉	C ₄₈ H ₄₄ N ₄ Ni ₂ O ₁₀	C ₆₄ H ₅₀ N ₄ Ni ₂ O ₉	C ₄₈ H ₃₈ N ₈ Ni ₂ O ₁₇	C ₄₁ H ₃₄ Cl ₄ N ₄ Ni ₂ O ₇
Mol. weight	1053.40	954.29	1136.50	1116.28	953.94
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	<i>P2₁/c</i>	<i>Pbcn</i>	<i>P2₁/c</i>	<i>C2/c</i>	<i>P2₁/c</i>
Temperature [K]	296	296	296	296	296
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
<i>a</i> [Å]	10.7917(2)	14.2706(6)	10.490(4)	15.9027(5)	12.9935(5)
<i>b</i> [Å]	38.3193(7)	21.2846(8)	20.917(9)	13.5204(5)	14.3654(5)
<i>c</i> [Å]	12.5877(2)	15.2229(6)	25.180(11)	23.6140(10)	22.6612(8)
<i>a</i> [°]	90	90	90	90	90
<i>β</i> [°]	91.3750(1)	90	96.16(3)	99.906(2)	97.762(3)
<i>γ</i> [°]	90	90	90	90	90
<i>V</i> [Å ³]	5203.90(16)	4623.9(3)	5493.0(4)	5001.6(3)	4191.1(3)
<i>Z</i>	4	4	4	4	4
Density [Mg m ^{−3}]	1.345	1.371	1.374	1.482	1.512
Abs. coeff. [mm ^{−1}]	0.784	0.876	0.748	0.834	1.207
Abs. correction	none	none	none	none	none
<i>F</i> (000)	2196	1984	2360	2296	1952
Total no. of reflections	50748	34247	39758	21611	41439
Reflections, <i>I</i> > 2σ(<i>I</i>)	12870	5768	12863	6153	10403
Max. 2θ [°]	28.33	28.32	28.28	28.33	28.32
Ranges (<i>h</i> , <i>k</i> , <i>l</i>)	−11 ≤ <i>h</i> ≤ 14 −51 ≤ <i>k</i> ≤ 45 −16 ≤ <i>l</i> ≤ 16	−13 ≤ <i>h</i> ≤ 19 −28 ≤ <i>k</i> ≤ 28 −16 ≤ <i>l</i> ≤ 20	−13 ≤ <i>h</i> ≤ 13 −27 ≤ <i>k</i> ≤ 27 −27 ≤ <i>l</i> ≤ 33	−16 ≤ <i>h</i> ≤ 21 −17 ≤ <i>k</i> ≤ 16 −31 ≤ <i>l</i> ≤ 31	−16 ≤ <i>h</i> ≤ 17 −19 ≤ <i>k</i> ≤ 19 −30 ≤ <i>l</i> ≤ 30
Complete to 2θ (%)	99.1	99.9	94.4	98.9	99.7
Refinement method	full-matrix least squares on <i>F</i> ²	full-matrix least squares on <i>F</i> ²	full-matrix least squares on <i>F</i> ²	full-matrix least squares on <i>F</i> ²	full-matrix least squares on <i>F</i> ²
Data/restraints/parameters	12870/0/657	5768/0/298	12863/0/720	6153/0/343	10403/0/531
Goof (<i>F</i> ²)	1.016	1.021	0.948	0.993	0.974
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	0.0417	0.0332	0.0472	0.0319	0.0451
<i>R</i> indices (all data)	0.0761	0.0556	0.1025	0.0452	0.1146

The X-ray data were collected at 296 K with Mo-*K*_α radiation ($\lambda = 0.71073$ Å) with a Bruker Nonius SMART CCD diffractometer equipped with a graphite monochromator (Table 2). The SMART software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated using SAINT software. The structures were solved by direct methods and refined by full-matrix least-squares calculations using the SHELXTL software.^[8] All the non-H atoms were refined in the anisotropic approximation against *F*² of all reflections. The H-atoms, except those attached to N, O and F were placed at their calculated positions and refined in the isotropic approximation; those attached to heteroatoms (N, O and F) were located in the difference Fourier maps, and refined with isotropic displacement coefficients.

CCDC numbers 614270–614274 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Preparation of 2a: Nickel(II) chloride hexahydrate (0.238 g, 1 mmol) and sodium benzoate (0.28 g, 2 mmol) were finely ground in a mortar and heated at 100 °C for 15 min. The solid mixture was cooled to room temperature and transferred into a round-bottomed flask and benzene (20 mL) was added and the heterogeneous mixture was stirred at room temp. for 5 min followed by the addition of pyridine (0.158 g, 2 mmol). The blue supernatant liquid was filtered off and was left undisturbed. Blue crystals were collected after 3 d and dried in air. Yield: 0.371 g, 34% (based on Ni). FT-IR (KBr): $\tilde{\nu} = 3412$ (b), 3065 (w), 3032 (w), 1630 (s), 1602 (m), 1572 (m), 1530 (w), 1481 (w), 1445 (m), 1394 (s), 1215 (m), 1067 (m),

1037 (m), 814 (m), 757 (m), 716 (s), 696 (s), 676 (s) cm^{−1}. $\lambda_{\text{max}}(\text{methanol}) = 645$ nm, $\epsilon = 18.91$ M^{−1}cm^{−1}, 383 nm, $\epsilon = 65.6$ M^{−1}cm^{−1}

Preparation of 2b: Benzoic acid (0.24 g, 2 mmol), potassium hydroxide (0.116 g, 2 mmol) and nickel(II) chloride hexahydrate (0.238 g, 1 mmol) were finely ground in the mortar and heated at 100 °C for 15 min. The solid mixture was cooled to room temperature and transferred into a round-bottomed flask. Toluene (20 mL) was added to the solid mass and the heterogeneous mixture was stirred at room temperature for 5 min. To this mixture pyridine (0.158 g, 2 mmol) was added. The residue was filtered off and the blue filtrate was left undisturbed. From this solution blue crystals were obtained after 3 d and dried in air. The blue crystals were further dissolved in ethanol and water (1:1) mixture (5 mL) to obtain crystals of **2b**. Yield: 0.553 g, 58% (based on Ni). FT-IR (KBr): $\tilde{\nu} = 3537$ (w), 3478 (w), 3060 (w), 2065 (w), 1630 (s), 1602 (m), 1572 (s), 1528 (m), 1484 (m), 1447 (s), 1397 (s), 1215 (m), 1152 (w), 1070 (m), 1039 (m), 825 (s), 760 (m), 720 (s), 697 (s), 674 (s) cm^{−1}. $\lambda_{\text{max}}(\text{methanol}) = 648$ nm, $\epsilon = 16.55$ M^{−1}cm^{−1}; 389 nm, $\epsilon = 36.63$ M^{−1}cm^{−1}.

The complexes **2c–2e** were prepared from the corresponding acid in an analogous manner to that for **2b**. However, for the crystallisations different solvents were used.

2c: Crystallised from a toluene and methanol mixture (1:1). Yield: 0.296 g, 26%. IR (KBr): $\tilde{\nu} = 3423$ (w), 3043 (m), 2071 (w), 1626 (s), 1614 (s), 1588 (w), 1525 (w), 1484 (m), 1445 (m), 1410 (s), 1374 (s), 1256 (w), 1215 (m), 1152 (w), 1070 (w), 1039 (w), 891 (w), 861 (m), 787 (s), 697 (s), 655 (m), 628 (w) cm^{−1}. $\lambda_{\text{max}}(\text{methanol})$ 649 nm, $\epsilon = 19.53$ M^{−1}cm^{−1}; 388 nm, $\epsilon = 55.45$ M^{−1}cm^{−1}.

2d: Crystallised from toluene. Yield: 0.235 g, 21%. IR (KBr): $\tilde{\nu}$ = 3445 (m), 3071 (m), 2071 (w), 1637 (s), 1604 (m), 1555 (w), 1520 (s), 1486 (m), 1448 (s), 1396 (s), 1363 (s), 1303 (w), 1218 (w), 1155 (w), 1071 (w), 858 (w), 824 (m), 781 (m), 736 (s), 701 (s) cm^{-1} . $\lambda_{\text{max}}(\text{acetonitrile}) = 638 \text{ nm}$, $\epsilon = 12.09 \text{ M}^{-1} \text{cm}^{-1}$.

2e: Crystallised from an ethanol and acetonitrile mixture (2:1). Yield: 0.134 g, 14%. IR (KBr): $\tilde{\nu}$ = 3420 (w), 3065 (w), 1703 (w), 1614 (s), 1566 (w), 1533 (w), 1484 (w), 1445 (m), 1400 (s), 1218 (m), 1166 (m), 1091 (m), 1039 (w), 1012 (w), 850 (w), 820 (m), 772 (m), 697 (m), 631 (w), 532 (s) cm^{-1} . $\lambda_{\text{max}}(\text{methanol}) 633 \text{ nm}$, $\epsilon = 24.42 \text{ M}^{-1} \text{cm}^{-1}$; 389 nm, $\epsilon = 40.92 \text{ M}^{-1} \text{cm}^{-1}$.

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