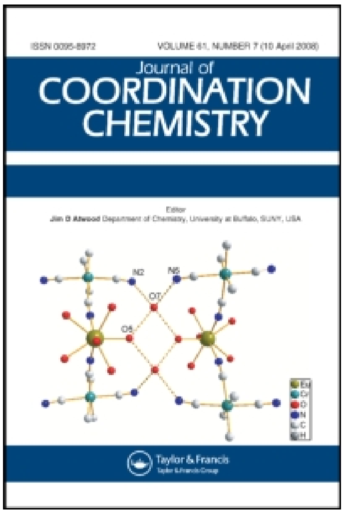

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# Nickel(II) complexes of tridentate anthracene based Schiff bases: syntheses, properties and crystal structures

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# Nickel(II) complexes of tridentate anthracene based Schiff bases: syntheses, properties and crystal structures

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The crystal and molecular structures of Ni(II) complexes with two tridentate anthracene-containing Schiff bases are reported. The Schiff bases were prepared by condensation of 9-anthraldehyde with diethylenetriamine (adien) and with dipropylenetriamine (adipn). Complexes synthesized from $Ni(O_2CCH_3)_2 \cdot 4H_2O$ and the ligands (1 : 1 mol ratio) crystallize from methanol as $[Ni(adien)(O_2CCH_3)_2(H_2O)]$ (**1**) and $[Ni(adipn)(O_2CCH_3)_2] \cdot 2CH_3OH$ (**2** $\cdot 2CH_3OH$) in space groups $P2_1/n$ and $P2_12_12_1$, respectively. In **1**, the distorted octahedral $N_3O_3$ coordination sphere around the metal ion is formed by the *meridional* $N_3$-donor adien, two mutually *trans* unidentate acetates and one water molecule. The $N_3O_3$ coordination sphere constituted by the $N_3$-donor adipn, one unidentate acetate and one bidentate acetate in **2** can be best described as trigonal bipyramidal. The secondary amine-N of adipn, the O-atom of the unidentate acetate and the midpoint of the two O-atoms of the bidentate acetate occupy the three equatorial positions and two imine-N atoms of adipn lie in axial sites. In the crystal lattice, molecules of **1** exist as discrete dimers due to intermolecular hydrogen bonding and $\pi$–$\pi$ interactions. In contrast, self-assembly of **2** via intermolecular $\pi$–$\pi$ interactions leads to a one-dimensional supramolecular structure.

*Keywords:* Ni(II) complexes; Anthracene; Schiff bases; Crystal structures; Intermolecular interactions; Self-assembly

## 1. Introduction

Self-assembly of coordination complexes of transition metal ions via non-covalent intermolecular interactions into various extended networks is an area of immense research activity [1–5]. Interest in such networks is primarily due to their potential applications as molecule-based materials. Recently we reported self-assembly of some 3d metal ion complexes of Schiff bases and reduced Schiff bases via various types of hydrogen bonding and $\pi$–$\pi$ interactions into one-dimensional (including helical),

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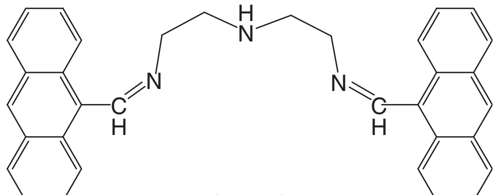
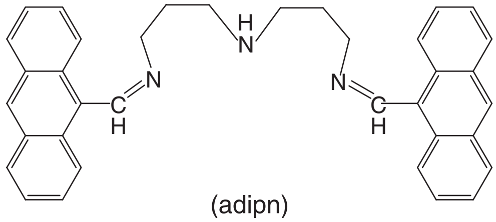


(adien)



(adipn)

two-, and three-dimensional supramolecular structures [6–15]. The nature and directionality of the intermolecular interactions and the ensuing supramolecular structures are typically controlled by the ligand, nature and positions of substituents and the coordination geometry. The tridentate anthracene-based neutral Schiff base ligands adien and adipn (above) are expected to participate in weak intermolecular interactions involving the extended $\pi$-cloud of the anthracene moiety and the secondary amine N–H group.

Metal coordination to adien and adipn creates two five- and two six-membered chelate rings, respectively. This difference may cause subtle changes in the coordination sphere and its geometry with respect to the number and coordination mode of ancillary ligands. As a result the directionality of intermolecular interactions and the self-assembly pattern of the complexes may differ drastically. Crystal structures of the Ni(II) complexes, [Ni(adien)($O_2CCH_3$)$_2$($H_2O$)] (**1**) and [Ni(adipn)($O_2CCH_3$)$_2$] (**2**), described in the following account, provide very good examples for this suggestion.

## 2. Experimental

### 2.1. *Materials*

The Schiff bases adien and adipn were prepared in ~80% yield by condensation of two mole equivalents of 9-anthraldehyde with one mole equivalent of the corresponding triamine in methanol. All other chemicals and solvents used in this work were of analytical grade, available commercially, and were used without further purification.

### 2.2. *Physical measurements*

Microanalytical (C, H, N) data were obtained with a Thermo Finnigan Flash EA1112 instrument. Infrared spectra were collected (KBr pellets) on a Jasco-5300 FT-IR spectrophotometer. A Shimadzu 3101-PC spectrophotometer was used to record electronic spectra. Solution electrical conductivities were measured with a Digisun DI-909 conductivity meter. A Sherwood Scientific balance was used for magnetic susceptibility measurements. Diamagnetic corrections calculated from Pascal's constants [16] were used to obtain molar paramagnetic susceptibilities.

### 2.3. *[Ni(adien)($O_2CCH_3$)$_2$($H_2O$)] (1)*

A dichloromethane solution (10 $cm^3$) of adien (120 mg, 0.25 mmol) was added to a methanol solution (30 $cm^3$) of $Ni(O_2CCH_3)_2 \cdot 4H_2O$ (62 mg, 0.25 mmol). The mixture was stirred at room temperature for 12 h and then evaporated to one third of the initial volume. The green solid that separated out was collected by filtration, washed with cold methanol followed by *n*-hexane and dried in air. Yield: 140 mg (75%). Anal. Calcd for $NiC_{38}H_{37}N_3O_5$ (%): C, 67.67; H, 5.53; N, 6.23. Found: C, 67.42; H, 5.34; N, 6.27. Selected infrared bands ($cm^{-1}$): 3300 (br), 1653 (m), 1560 (s), 1404 (s), 1333 (m), 1263 (w), 1115 (m), 1049 (m), 1015 (m), 891 (s), 847 (w), 795 (w), 733 (s), 656 (m), 519 (s), 447 (w). Electronic spectrum in $CH_2Cl_2$, $\lambda_{max}$/nm ($\varepsilon$/$M^{-1}\,cm^{-1}$): 895 (30), 560sh (45), 390 (14,100), 370 (14,600), 352 (9,700), 335sh (4,900), 320sh (2,400). Magnetic moment at 298 K: 3.21 $\mu_B$.

### 2.4. *[Ni(adipn)($O_2CCH_3$)$_2$]2$CH_3OH$·(2·2$CH_3OH$)*

The complex was prepared in 80% yield from one mole equivalent each of adipn and $Ni(O_2CCH_3)_2 \cdot 4H_2O$ by following the same procedure as described for **1**. Anal. Calcd for $NiC_{42}H_{47}N_3O_6$ (%): C, 67.39; H, 6.33; N, 5.61. Found: C, 67.23; H, 6.24; N, 5.52. Electronic spectrum in $CH_2Cl_2$, $\lambda_{max}$/nm ($\varepsilon$/$M^{-1}\,cm^{-1}$): 990 (10), 593 (22), 387 (16,700), 370 (17,300), 351 (11,300), 335sh (5,600), 320sh (2,400). Selected infrared bands ($cm^{-1}$): 3390 (br), 1643 (s), 1586 (s), 1547 (s), 1435 (s), 1385 (s), 1157 (m), 1105 (m), 1061 (s), 953 (m), 910 (w), 889 (s), 843 (w), 793 (m), 727 (s), 654 (m), 623 (w), 582 (w), 517 (s), 463 (m). Magnetic moment at 298 K: 3.06 $\mu_B$.

### 2.5. *X-ray crystallography*

Single crystals were grown by slow evaporation of methanol solutions of the complexes. X-ray data for both **1** and **2**·2$CH_3OH$ were collected on an Enraf-Nonius Mach-3 diffractometer using graphite-monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å). In each case, data were collected by the $\omega$-scan method and the stability of the crystal was monitored by measuring the intensities of three check reflections after every 1.5 h during data collection. No decay was observed during data collection for either crystal. Absorption corrections were applied to each data set based on $\psi$-scans [17] of selected reflections. Programs of the WinGX package [18] were used for data reductions and absorption corrections. Structures were solved by direct methods and refined on $F^2$ by full-matrix least-squares procedures. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms of the water molecule in **1** were located in a difference map and refined with $U_{iso}(H) = 1.5U_{eq}(O)$. All other hydrogen atoms were included in the structure factor calculations at idealized positions by using a riding model, but not refined. SHELX-97 programs [19] were used for structure solution and refinement. ORTEX6a [20] and Platon [21] packages were used for molecular graphics. Significant crystallographic data for **1** and **2**·2$CH_3OH$ are summarized in table 1.

Table 1. Crystallographic data for **1** and **2** · $2CH_3OH$.

| Complex | **1** | **2** · $2CH_3OH$ |
|---|---|---|
| Empirical formula | $NiC_{38}H_{37}N_3O_5$ | $NiC_{42}H_{47}N_3O_6$ |
| Molecular weight | 674.42 | 748.54 |
| Crystal system | Monoclinic | Orthorhombic |
| Space group | $P2_1/n$ | $P2_12_12_1$ |
| $a$ (Å) | 12.741(1) | 11.852(2) |
| $b$ (Å) | 13.053(1) | 17.443(4) |
| $c$ (Å) | 23.164(3) | 18.760(5) |
| $\beta$ (°) | 91.89(4) | |
| $V$ (Å$^3$) | 3850.3(7) | 3878.4(15) |
| $Z$ | 4 | 4 |
| $F$(000) | 1416 | 1584 |
| $\rho_{\mathrm{Calcd}}$(g cm$^{-3}$) | 1.163 | 1.282 |
| $\mu$ (mm$^{-1}$) | 0.546 | 0.550 |
| Reflections collected | 5266 | 4949 |
| Unique reflections | 4991 | 4270 |
| Reflections with $I > 2\sigma(I)$ | 2890 | 2403 |
| Parameters | 430 | 471 |
| $R$ [$I > 2\sigma(I)$] | 0.0528 | 0.0825 |
| $Rw$ [$I > 2\sigma(I)$] | 0.1257 | 0.2043 |
| Goodness-of-fit on $F^2$ | 1.001 | 1.059 |
| Largest peak and hole (e Å$^{-3}$) | 0.472, −0.477 | 0.778, −0.750 |

## 3. Results and discussion

Room temperature (298 K) magnetic moments are 3.21 and 3.06 $\mu_B$ for **1** and **2** · $2CH_3OH$, respectively. These values indicate an S = 1 spin state for the metal ions in both complexes. In solutions, the complexes are electrically non-conducting. Thus, the acetate ions are coordinated to the metal ion in each complex. In the infrared spectra of the complexes a broad band near 3300 cm$^{-1}$ is due to water and methanol molecules present. The stretch expected from the secondary amine N–H is buried under this band. The C=N stretch of the ligand appears as a strong band at 1560 and 1585 cm$^{-1}$ for **1** and **2** · $2CH_3OH$, respectively. In **1** both acetate ligands are unidentate while in **2** · $2CH_3OH$ one acetate is unidentate and the other one is bidentate (*vide infra*). Two medium to strong bands observed at 1653 and 1333 cm$^{-1}$ for **1** and 1643 and 1385 cm$^{-1}$ for **2** · $2CH_3OH$ are attributed to $\nu_{\mathrm{asym}}$ and $\nu_{\mathrm{sym}}$ stretches of monodentate acetates [22]. Two more strong bands observed at 1547 and 1435 cm$^{-1}$ in the spectrum of **2** · $2CH_3OH$ are most likely due to $\nu_{\mathrm{asym}}$ and $\nu_{\mathrm{sym}}$ stretches of bidentate acetate [22]. In the electronic spectra two weak absorptions observed at 895 and 560 nm for **1** and at 990 and 593 nm for **2** · $2CH_3OH$ are assigned to d–d bands [23, 24]. Below 400 nm the spectroscopic profiles of both complexes and the free Schiff bases are very similar. This suggests that intense absorptions observed in the range 390–320 nm are due to intraligand transitions.

### 3.1. *Description of molecular structures*

The structures of **1** and **2** · $2CH_3OH$ are illustrated in figures 1 and 2, respectively. Bond parameters associated with the metal ions are listed in table 2. In each of the two complex molecules, the metal ion lies in an $N_3O_3$ coordination sphere. In **1**, the coordination sphere is comprised of the adien, two unidentate acetates

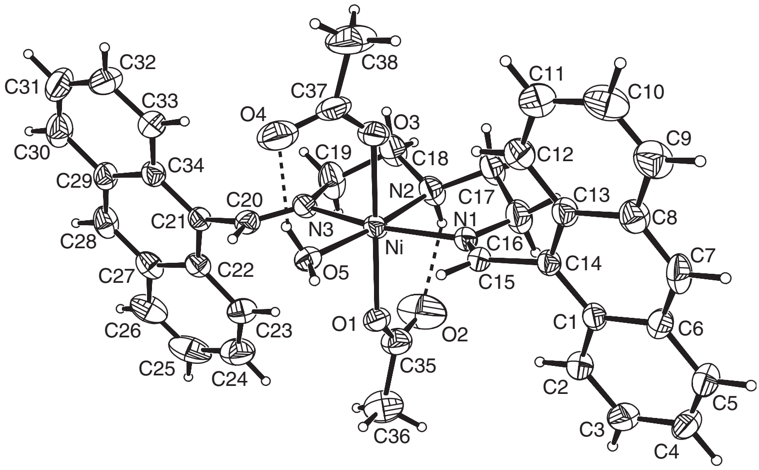


Figure 1. Molecular structure and atom numbering scheme of [Ni(adien)$(O_2CCH_3)_2(H_2O)$] (**1**). All non-hydrogen atoms are represented by 25% probability thermal ellipsoids. Dashed lines indicate intramolecular hydrogen bonds.

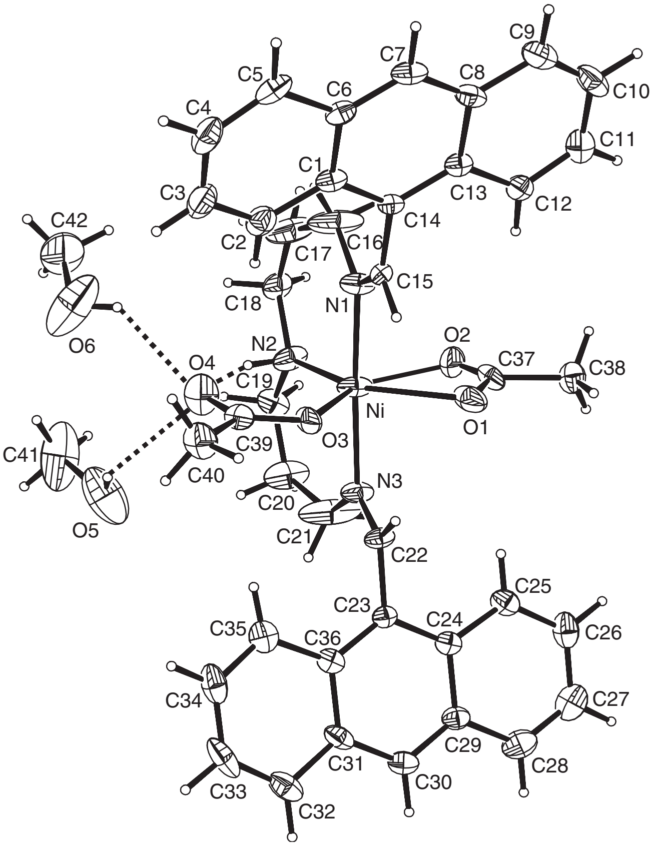


Figure 2. Structure and atom numbering scheme of [Ni(adipn)$(O_2CCH_3)_2(H_2O)$] · $2CH_3OH$ (**2** · $2CH_3OH$). All non-hydrogen atoms are represented by 15% probability thermal ellipsoids. Hydrogen bonds are indicated by dashed lines.

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2** $\cdot$ $2CH_3OH$.

| | | | |
|---|---|---|---|
| **1** | | | |
| Ni–O(1) | 2.092(3) | Ni–N(1) | 2.058(4) |
| Ni–O(3) | 2.119(4) | Ni–N(2) | 2.052(4) |
| Ni–O(5) | 2.054(3) | Ni–N(3) | 2.049(4) |
| O(1)–Ni–O(3) | 173.72(15) | O(3)–Ni–N(3) | 94.14(15) |
| O(1)–Ni–O(5) | 86.80(14) | O(5)–Ni–N(1) | 102.00(16) |
| O(1)–Ni–N(1) | 91.66(14) | O(5)–Ni–N(2) | 174.67(16) |
| O(1)–Ni–N(2) | 96.20(16) | O(5)–Ni–N(3) | 92.95(15) |
| O(1)–Ni–N(3) | 90.00(14) | N(1)–Ni–N(2) | 82.35(17) |
| O(3)–Ni–O(5) | 88.27(15) | N(1)–Ni–N(3) | 165.03(17) |
| O(3)–Ni–N(1) | 85.55(15) | N(2)–Ni–N(3) | 82.68(16) |
| O(3)–Ni–N(2) | 89.01(18) | | |
| **2** $\cdot$ $2CH_3OH$ | | | |
| Ni–O(1) | 2.183(10) | Ni–N(1) | 2.079(7) |
| Ni–O(2) | 2.386(11) | Ni–N(2) | 1.983(7) |
| Ni–O(3) | 2.054(7) | Ni–N(3) | 2.092(7) |
| O(1)–Ni–O(2) | 57.3(3) | O(2)–Ni–N(3) | 89.9(4) |
| O(1)–Ni–O(3) | 96.5(3) | O(3)–Ni–N(1) | 86.5(3) |
| O(1)–Ni–N(1) | 87.8(3) | O(3)–Ni–N(2) | 118.6(4) |
| O(1)–Ni–N(2) | 144.9(4) | O(3)–Ni–N(3) | 88.3(4) |
| O(1)–Ni–N(3) | 87.7(3) | N(1)–Ni–N(2) | 93.4(3) |
| O(2)–Ni–O(3) | 153.7(4) | N(1)–Ni–N(3) | 172.7(3) |
| O(2)–Ni–N(1) | 92.5(4) | N(2)–Ni–N(3) | 93.5(3) |
| O(2)–Ni–N(2) | 87.6(4) | | |

Table 3. Hydrogen bond distances (Å) and angles (°) for **1** and **2** $\cdot$ $2CH_3OH$.

| D–H···A | d(D–H) | d(H···A) | d(D···A) | D–H···A |
|---|---|---|---|---|
| **1** | | | | |
| N(2)–H(2N)···O(2) | 0.91 | 2.11 | 2.923(7) | 147.6 |
| O(5)–H(5B)···O(4) | 0.83(5) | 1.85(5) | 2.615(5) | 152(5) |
| O(5)–H(5A)···O(1)[a] | 0.86(5) | 1.86(5) | 2.718(5) | 173(5) |
| **2** $\cdot$ $2CH_3OH$ | | | | |
| O(5)–H(5M)···O(4) | 0.82 | 2.37 | 2.92(2) | 124.2 |
| O(6)–H(6M)···O(4) | 0.82 | 2.3 | 2.86(2) | 126.6 |
| N(2)–H(2N)···O(4) | 0.91 | 2.21 | 2.987(13) | 142.3 |

[a] Symmetry transformation used to generate equivalent atoms is $-x$, $-y$, $1-z$.

and a water molecule. Adipn, a unidentate and a bidentate acetate form the coordination sphere around the metal ion in **2** $\cdot$ $2CH_3OH$. The methanol molecules and the N–H group of adipn are hydrogen bonded to the uncoordinated O-atom of the unidentate acetate (figure 2, table 3). In **1**, the N–H group of adien and the water molecule are involved in two intramolecular hydrogen bonds with uncoordinated O-atoms of the unidentate acetates (figure 1, table 3).

The coordination geometry in **1** is distorted octahedral. Adien coordinates the metal ion *meridionally* and forms two five-membered chelate rings. Two unidentate acetates lie *trans* to each other and the water O-atom satisfies the remaining coordination site. Bite angles for the five-membered rings are very similar (82.35(17) and 82.68(16)°). All other *cis* bond angles are in the range 85.55(15)–102.00(16)°. The *trans* bond angle (165.03(17)°) involving the terminal imine N-atoms of adien is significantly less than the ideal value; the other two *trans* bond angles (173.72(15) and 174.67(16)°) are much closer. Ni–N bond lengths (2.049(4)–2.058(4) Å) are very similar. However, the Ni–O(water) bond (2.054 Å) is significantly shorter than the two Ni–O(acetate) bonds (2.092(3) and 2.119(4) Å). One of the coordinated O-atoms (O1) acts as an acceptor in intermolecular hydrogen bonding (*vide infra*). Perhaps the involvement of the uncoordinated O-atoms of the two acetates in the intramolecular hydrogen bonds and the steric constraints imposed by the resulting hydrogen bond containing six-membered rings (figure 1) also contribute to the lengthening of the Ni–O(acetate) bonds.

The coordination geometry in **2** can be best described as trigonal bipyramidal where the mid-point of the two O-atoms of the bidentate acetate, the O-atom of the unidentate acetate and the secondary amine N-atom of adipn form the trigonal plane and the two axial sites are occupied by the two imine-N atoms of adipn (figure 2). In the trigonal plane, angles are in the range 116.2–125.2°. Bite angles for the two six-membered rings formed by adipn are identical (93.4(3)° and 93.5(3)°). As expected, this value is larger than those observed for the five-membered rings formed by adien in **1**. The angle between the two axial Ni–N(imine) bonds is 172.7(3)°. Ni–N(imine) bonds (2.079(7) and 2.092(7) Å) are noticeably longer than the Ni–N(amine) bond (1.983(7) Å). Possibly, the rigidity of the tridenate planar adipn is the primary reason for shortening the Ni–N(amine) bond [25]. The bidentate acetate is unsymmetrical with respect to the two Ni–O(acetate) bond lengths (2.183(10) and 2.386(11) Å). Compared to these values the Ni–O(acetate) bond length (2.054(7) Å) for the unidentate acetate is much shorter and the difference in the coordination modes is most likely responsible for the long and short Ni–O(acetate) bond lengths.

It is interesting to note that there is a drastic change in the coordination geometries around the Ni(II) centres in **1** and **2** although the tridentate ligands adien and adipn are very similar. The spatial dispositions of the anthracenyl moieties are very similar in both complexes. Planar anthracenyl moieties (mean deviations 0.01–0.05 Å) are roughly orthogonal with the mean planes constituted by the C- and N-atoms of the azomethine, the secondary amine and the methylene groups (mean deviations 0.19 and 0.12 Å for **1** and **2**, respectively). Dihedral angles are 88.15(9) and 86.53(9)° for **1** and 84.36(15) and 87.93(15)° for **2**. The main difference between the two ligands is in the chelate ring sizes. In **1**, the *meridional* adien forms two five membered chelate rings and the bond angle at the metal centre involving the two terminal imine-N atoms is 165.03(17)°. On the other hand, adipn forms two six-membered chelate rings. As a result the N(imine)–Ni–N(imine) bond angle (172.7(3)°) in **2** is significantly larger than that in **1**. Thus, the proximity between the anthracenyl groups is enhanced in **2** compared to **1**. Perhaps, for this reason, there is not enough room for the coordination of a water molecule to complete an $N_3O$ square-plane around the metal ion in **2**. Thus, instead of a distorted octahedral environment as observed for **1**, a trigonal bipyramidal arrangement with both acetates along the two equatorial positions is preferred in **2**.

### 3.2. *Intermolecular interactions and self-assembly*

Molecules of **1** are involved in intermolecular hydrogen bonding and $\pi$–$\pi$ interactions and form discrete dimers in the crystal lattice. In each dimeric unit, molecules are connected by two intermolecular O–H···O hydrogen bonds (figure 3, table 3). Water molecules and the metal coordinated acetate O-atoms are involved in these interactions in a reciprocal fashion. Orientations of the anthracenyl moieties in the dimer

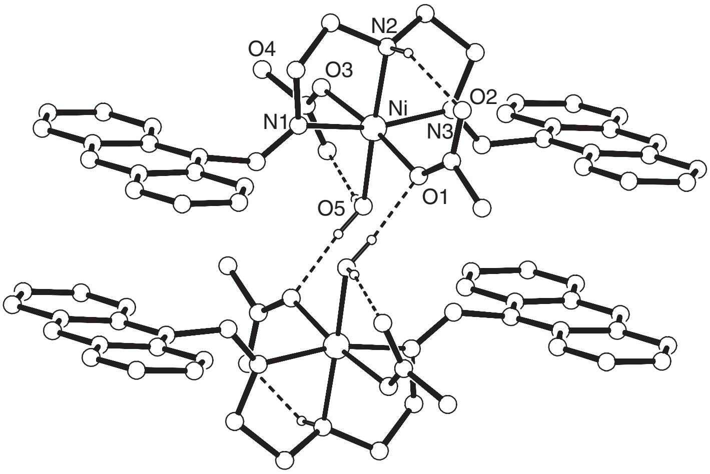


Figure 3. The dimeric structure of $[Ni(adien)(O_2CCH_3)_2(H_2O)]$ (**1**) formed through intermolecular hydrogen bonds and π–π interactions.

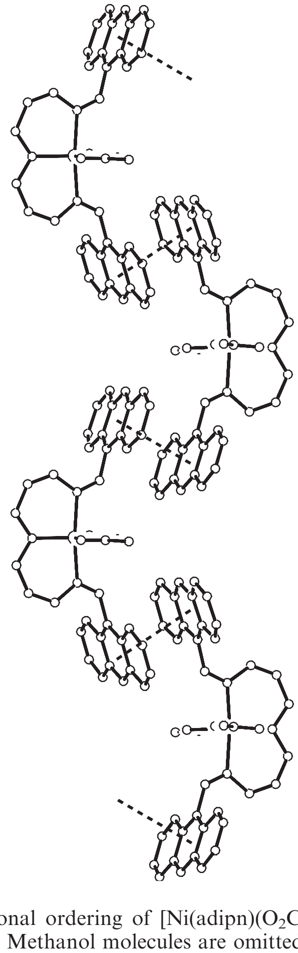


Figure 4. View of the one-dimensional ordering of $[Ni(adipn)(O_2CCH_3)_2(H_2O)] \cdot 2CH_3OH$ ($\mathbf{2} \cdot 2CH_3OH$) via π–π interactions along the *c* axis. Methanol molecules are omitted for clarity.

also suggest intermolecular $\pi$–$\pi$ interactions (figure 3). The dihedral angle (2.7(1)°) between overlapping anthracenyl fragments indicates that they are essentially parallel; the interplanar distance is 3.64 Å. Among the three rings of each anthracenyl group, two are involved in the $\pi$–$\pi$ interactions (figure 3). The centroid-to-centroid distances are 3.88 Å (rings C1–C6 and C21, C22, C27–C29, C34) and 3.90 Å (rings C1, C6–C8, C13, C14 and C22–C27). There is no significant inter-dimer short contact or non-covalent interaction.

Involvement of the anthracenyl fragments of the complex molecules in intermolecular $\pi$–$\pi$ interactions leads to an infinite one-dimensional arrangement of the **2** · $2CH_3OH$ units in the crystal lattice (figure 4). The dihedral angle and the interplanar distance for the overlapping anthracenyl groups are 1.6(3)° and 3.46 Å, respectively. In contrast to **1**, all three rings of each anthracene moiety are involved in $\pi$–$\pi$ interactions. The centroid-to-centroid distances are in the range 3.75–3.86 Å. Parallel chains of **2** · $2CH_3OH$ propagate along the *b* axis and there is no significant inter-chain short contact or non-covalent interaction.

## Supplementary material

Crystallographic data (excluding structure factors) are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk) on request, quoting deposition numbers CCDC 274876 and CCDC 274877 for **1** and **2** · $2CH_3OH$, respectively.

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