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Mononuclear nickel complexes assembled into two-dimensional networks *via* hydrogen bonds and π–π stacking interactions

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Three monomeric nickel complexes [Ni(bipy)(O_2CMe)$_2$(H_2O)$_2$] **1** (bipy = 2,2′-bipyridine), [Ni(dmbipy)(O_2CMe)$_2$(H_2O)$_2$] **2** (dmbipy = 4,4′-dimethyl-2,2′-bipyridine) and [Ni(phen)(O_2CMe)$_2$(H_2O)$_2$]·0.5H_2O **3** (phen = 1,10-phenanthroline) have been synthesized and characterized by single-crystal X-ray diffraction methods. In complexes **1** and **2** the molecules are self-assembled *via* double intermolecular hydrogen bonds to form one-dimensional infinite zigzag chains, which are stacked next to each other through the diimine aromatic rings in a zipper-like fashion, giving a novel two-dimensional co-operating structure. In **3** the molecule is linked by a hydrogen bond to form a one-dimensional chain, which is further associated with another adjacent chain *via* double hydrogen bonds forming a double chain. These double chains are intercalated to each other through the π–π interaction giving a novel two-dimensional structure.

Design and self-assembly of metal compounds into one-, two- and three-dimensional supramolecular architecture is currently attracting considerable attention for potential applications.[1,2] Three main lines of studies are adopted, based on the different nature of the interactions responsible for networking, which concern: (*i*) frames comprised of metal centers and bi- or poly-dentate ligands connected through co-ordination bonds; (*ii*) networks derived by the organization of mono- or poly-nuclear metal complexes *via* hydrogen bonds;[3–9] and (*iii*) structures assembled by π–π interaction of aromatic rings.[10] Among these notable systems, the former is connected through chemical bonds, while the last two are self-assembled by weak interactions which play vital roles in highly efficient and specific biological reactions and are essential for molecular recognition and self-organization of molecules in supramolecular chemistry. In particular, hydrogen-bond assembled molecular materials are of considerable interest, and the incorporation of a transition metal ion into hydrogen-bond systems is important in the crystal engineering of non-linear optical, conducting and ferromagnetic materials.[2c,4]

Obviously, networks of metal compounds can, in principle, be extended into two or three dimensions *via* weak interactions such as hydrogen bonds and π–π stacking interactions, though these species have attracted less attention and have rarely been reported.[6–10] Here, we report the mononuclear nickel complexes [Ni(bipy)(O_2CMe)$_2$(H_2O)$_2$] **1** (bipy = 2,2′-bipyridine), [Ni(dmbipy)(O_2CMe)$_2$(H_2O)$_2$] **2** (dmbipy = 4,4′-dimethyl-2,2′-bipyridine), [Ni(phen)(O_2CMe)$_2$(H_2O)$_2$]·0.5H_2O **3** (phen = 1,10-phenanthroline), in which the hydrophilic groups are self-assembled *via* hydrogen bonds while the hydrophobic groups are stacked *via* π–π interaction giving two-dimensional structures. The use of different polypyridyl ligands demonstrates the influence of the π system stacking on self-assembly.

Experimental

Starting materials were from commercial sources and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240Q Elemental analyzer. The FT-IR spectra were recorded on a Bruker IFS-66 spectrometer as KBr pellets (4000–400 cm^{-1}), UV/VIS spectra on a Shimadzu MPS-2000 spectrophotometer in methanol solution at room temperature.

Syntheses

[Ni(bipy)(O_2CMe)$_2$(H_2O)$_2$] 1. 2,2′-Bipyridine (0.156 g, 1.0 mmol) in methanol (5 cm^3) was added to a methanol solution (10 cm^3) containing Ni(O_2CMe)$_2$·4H_2O (0.249 g, 1.0 mmol). The blue solution was stirred at room temperature for 3 h and filtered. A blue product was obtained by diffusion of diethyl ether into the filtrate, collected by filtration, washed by acetone and diethyl ether, and dried overnight *in vacuo*. Yield: 72% (Found: C, 45.68; H, 4.73; N, 7.63. Calc. for $C_{14}H_{18}N_2NiO_6$: C, 45.53; H, 4.88; N, 7.59%). IR data (KBr, cm^{-1}): 3284vs (br), 1556vs, 1441m, 1418vs, 1334m, 1307m, 1165m, 1155m, 1051m, 1027m, 1017m, 873w, 774s, 739m, 662s and 418vw. A single crystal suitable for X-ray diffraction was obtained by diffusing diethyl ether into the methanol solution of complex **1**.

[Ni(dmbipy)(O_2CMe)$_2$(H_2O)$_2$] 2. The complex was synthesized by a similar procedure using dmbipy instead of bipy. Yield: 80% (Found: C, 48.50; H, 5.61; N, 7.12. Calc. for $C_{16}H_{22}N_2NiO_6$: C, 48.35; H, 5.54; N, 7.05%). IR data (KBr, cm^{-1}): 3270vs (br), 1559vs, 1440m, 1420vs, 1337m, 1302m, 1162m, 1153m, 1054m, 1024m, 1013m, 871w, 776s, 738m, 661s and 417vw. A single crystal suitable for X-ray diffraction was obtained by diffusing diethyl ether into the methanol solution of complex **2**.

[Ni(phen)(O_2CMe)$_2$(H_2O)$_2$]·0.5H_2O 3. The complex was synthesized by a similar procedure using phen in place of bipy. Yield: 73% (Found: C, 48.02; H, 4.86; N, 6.73. Calc. for $C_{16}H_{19}N_2NiO_{6.5}$: C, 47.76; H, 4.72; N, 6.69%). IR data (KBr cm^{-1}): 3240vs (br), 1552vs, 1515s, 1428m, 1416vs, 1396s, 1336m, 1024m, 900m, 856s, 730s, 662s, 644m and 426vw. A single crystal suitable for X-ray diffraction was obtained by diffusing diethyl ether into the methanol solution of complex **3**.

X-Ray crystallography

The single crystals of complexes **1**, **2** and **3** were mounted on a glass fiber and placed on a Siemens P3/V diffractometer (graphite-monochromated Mo-Kα radiation, λ = 0.710 73 Å). The crystal class, orientation matrix, and unit-cell dimensions were determined according to established procedures; parameters were calculated from least-squares fitting of 2θ angles for 25 reflections. Three standard reflections were monitored after every 100 data measurements, showing only small random variations. The raw data were processed with a learn-profile procedure, and semiempirical absorption corrections were applied. The crystal structures were solved by direct methods using the SHELXS 97 program package,[11] and refined with full-matrix least squares on F^2 using SHELXL 97.[12] In complex **3** the lattice water molecule exhibits two-fold orientational disorder.

Table 1 Crystal data and details of the structural determinations for complexes **1**–**3** at 293(2) K

	1	**2**	**3**
Empirical formula	$C_{14}H_{18}N_2NiO_6$	$C_{16}H_{22}N_2NiO_6$	$C_{16}H_{19}N_2NiO_{6.5}$
M	369.01	397.07	402.04
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	*C*2/*c*	*Pbcn*	$P\bar{1}$
a/Å	15.383(3)	16.517(6)	7.5390(10)
b/Å	12.758(3)	13.346(6)	10.303(4)
c/Å	8.143(2)	8.148(3)	11.798(4)
α/°			106.22(2)
β/°	92.93(3)	90.0	96.10(2)
γ/°			102.25(1)
U/Å^3, Z	1596.0(6), 4	1796.1(1), 4	846.4(5), 2
D_c/Mg m^{-3}	1.536	1.468	1.578
μ/mm^{-1}	1.247	1.114	1.185
θ Range for data collection/°	2.07–25.04	1.96–25.03	2.33–26.00
Reflections collected	1458	1589	3346
Independent reflections	1409	1589	3334
Observed reflections [$I > 2\sigma(I)$]	1193	1009	2885
R, R' [$I > 2\sigma(I)$]*	0.0343, 0.0801	0.0495, 0.1054	0.0333, 0.0836
(all data)*	0.0459, 0.0856	0.0919, 0.1229	0.0420, 0.0882
Goodness of fit on F^2	1.065	1.039	1.008

* $R' = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$.

All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the ligands were generated geometrically (C–H 0.96 Å), assigned isotropic thermal parameters. Crystal data as well as details of data collection and refinement for the complexes are summarized in Table 1. Selected bond distances and angles are listed in Table 2.

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Results and Discussion

Syntheses and characterization of complexes

Aromatic diimine compounds such as bipy and phen may be used as ligands to generate models of metalloenzyme active sites[13] and the sites of molecular recognition.[14] They have strong stacking interactions with the side chain aromatic ring of amino acids, and were used to observe the stacking interaction in solution and the solid state.[14] Recently, we have noticed some interesting phenomena during the systematic observation of the reactions between bipy and divalent metal acetates. First, the different metal ions can influence the structure assembly, for example treatment of metal acetates with bipy in methanol solution produces linear trinuclear complexes $[M_3(bipy)_2(O_2CMe)_6]$ (M = Mn, Fe or Co),[15] a dinuclear complex $[Cd_2(bipy)_2(O_2CMe)_4(H_2O)_2]$[16] or a monomeric complex $[Ni(bipy)(O_2CMe)_2(H_2O)_2]$ under similar reaction conditions. Secondly, the presence of a high ionic strength anion such as ClO_4^- resulted in mono- or di-nuclear complexes. For example, treatment of the reaction solution of **1** with 1.5 equivalents $NaClO_4$ led to the formation of $[Ni(bipy)_2(O_2CMe)][ClO_4]\cdot H_2O$.[16] Interestingly, a similar procedure applied to the analogous solution containing Cu^{2+} or Zn^{2+} ion gave a dinuclear complex $[M_2(bipy)_2(\mu\text{-}O_2CMe)_3][ClO_4]$ (M = Cu or Zn).[17] This indicated that an equilibrium was existent in solution; when the solvent of the reaction solution was allowed to evaporate slowly or when a hydrophobic solvent, diethyl ether, was added a neutral mono-, di- or tri-nuclear complex was obtained. If $NaClO_4$ was added to the solution the reaction was driven to the formation of a thermodynamically preferred product.

The IR spectra of complexes **1**, **2** and **3** display an intense and broad band centered at 3284, 3270 and 3240 cm^{-1}, respectively. These bands can be assigned to ν(O–H) of the aqua ligand, and the broadness is indicative of hydrogen bonds, in accord with the crystal structures. The symmetric and asymmetric stretching vibrations of acetate ligands display characteristic absorption bands at 1556, 1559 and 1552 and 1418, 1420 and 1416 cm^{-1} for complexes **1**, **2** and **3**, respectively. The Δ values [$\nu_{asym}(CO_2) - \nu_{sym}(CO_2)$] are 138, 139 and 136 cm^{-1} for complexes **1**, **2** and **3**, respectively, which are markedly less than those of the unidentate complexes ($\Delta \gg 160$ cm^{-1}), but are similar to those of the bidentate bridging complexes ($\Delta \leqslant 160$ cm^{-1}).[18] This observation suggests that the geometry of the acetate group is similar to that of bidentate bridging, and can be rationalized by the effect of hydrogen bonds. There exists a strong 'pulling effect' on the non-co-ordinated oxygen of the acetate group, from two hydrogen bonds, one intra- and one inter-molecular. This makes the otherwise very 'asymmetric' terminal unidentate acetate group much more 'symmetric' than in the normal non-hydrogen-bonded case, and may be regarded as a 'pseudo-bridging' arrangement.[18]

Crystal structures

Crystal structures of complexes **1**, **2** and **3** reveal that each nickel(II) ion is ligated by a diimine ligand and two terminal unidentate acetates, and further co-ordinated by two aqua ligands forming a slightly distorted NiN_2O_4 octahedron as shown in Figs. 1 and 2 with the atom numbering scheme. In complexes **1** and **2** the molecule has a crystallographically imposed two-fold axis passing through the nickel ion, and the two oxygen atoms from a pair of acetate ligands occupy the two axial positions with O(1)–Ni(1)–O(1a) 179.3(1)° for complex **1** and 178.7(2)° for **2**. In contrast, the two aqua ligands occupy the axial positions with O(1w)–Ni(1)–O(2w) 178.45(7)° for complex **3**; this may be attributed to the stronger stacking interaction of phen than bipy ligands (see below). The bond angles around the Ni^{2+} ion at the equatorial plane defined by N(1), N(1a), O(1w) and O(1wa) in complexes **1** and **2**, and N(1), N(2), O(1) and O(3) in **3**, sum to 360° within experimental error, showing that they are coplanar. The Ni–N bond distances are 2.069(2), 2.067(4) and 2.070(2) Å, those of Ni–O (aqua) are 2.082(2), 2.077(3) and 2.072(2) Å, and those of Ni–O (acetate) are 2.079(2), 2.077(3) and 2.054(2) Å for complexes **1**, **2** and **3**, respectively, which are comparable with those of other nickel(II) complexes.[20] Each aqua ligand is further stabilized by forming a strong intramolecular hydrogen bond with the unco-ordinated acetate oxygen atom at 2.620(3) Å, D–H···A 153.2° (A = hydrogen-bond acceptor, D = hydrogen-bond donor) for complex **1**, 2.620(5) Å, 153.2° for **2** and 2.589(3) Å, 164.0° and 2.624(3) Å, 152.8° for **3**. The bond length differences of the C–O at the acetate group are trivial in complexes **1** (0.009 Å) and **2** (0.014 Å) due to the hydrogen-bond effect, giving rise to

Table 2 Selected bond distances (Å) and angles (°)*

Complex **1**

Ni(1)–O(1w)	2.082(2)	C(6)–O(2)	1.244(4)
Ni(1)–N(1)	2.069(2)	O(2a)···O(1w)	2.620(3)
Ni(1)–O(1)	2.079(2)	O(2b)···O(1w)	2.776(3)
O(1)–C(6)	1.253(3)		

N(1)–Ni(1)–N(1a)	78.97(13)	N(1)–Ni(1)–O(1)	88.67(8)
N(1a)–Ni(1)–O(1)	90.80(8)	O(1)–Ni(1)–O(1a)	179.31(11)
O(1wa)–Ni(1)–N(1)	171.61(8)	O(1w)–Ni(1)–O(1wa)	94.39(11)
N(1)–Ni(1)–O(1w)	93.42(9)	O(1)–Ni(1)–O(1wa)	87.93(8)
O(1)–Ni(1)–O(1w)	92.54(8)	O(1)–C(6)–O(2)	124.7(3)
O(1w)–H(1A)···O(2a)	153.2	O(1w)–H(1B)···O(2b)	155.6
H(1B)–O(1w)–H(1A)	104.9		

Symmetry codes: a $-x, y, -z + \frac{1}{2}$; b $-x, 1 - y, 1 - z$.

Complex **2**

Ni(1)–O(1w)	2.077(3)	O(2)–C(7)	1.252(5)
Ni(1)–N(1)	2.067(4)	O(2a)···O(1w)	2.620(5)
Ni(1)–O(1)	2.077(3)	O(2b)···O(1w)	2.788(5)
O(1)–C(7)	1.266(5)		

N(1)–Ni(1)–N(1a)	78.57(19)	N(1)–Ni(1)–O(1wa)	170.87(13)
N(1)–Ni(1)–O(1w)	93.52(13)	O(1wa)–Ni(1)–O(1w)	94.71(17)
N(1)–Ni(1)–O(1a)	91.38(13)	O(1w)–Ni(1)–O(1a)	88.06(13)
N(1)–Ni(1)–O(1)	87.59(13)	O(1w)–Ni(1)–O(1)	92.84(13)
O(1a)–Ni(1)–O(1)	178.67(17)	O(2)–C(7)–O(1)	123.8(5)
O(1w)–H(1A)···O(2a)	153.2	O(1w)–H(1B)···O(2b)	162.5
H(1B)–O(1w)–H(1A)	103.0		

Symmetry codes: a $-x, y, \frac{1}{2} - z$; b $1 - x, 1 - y, -z$.

Complex **3**

Ni(1)–O(1w)	2.073(2)	O(3)–C(15)	1.242(3)
Ni(1)–O(2w)	2.072(2)	O(4)–C(15)	1.251(3)
Ni(1)–N(1)	2.072(2)	O(1w)···O(2)	2.589(3)
Ni(1)–N(2)	2.068(2)	O(1wa)···O(4)	2.770(3)
Ni(1)–O(1)	2.075(2)	O(1)···O(2wb)	2.788(3)
Ni(1)–O(3)	2.033(2)	O(2w)···O(4)	2.624(3)
O(1)–C(13)	1.270(3)	O(3w)···O(1w)	2.885
O(2)–C(13)	1.237(3)		

O(3)–Ni(1)–N(2)	172.83(8)	O(3)–Ni(1)–N(1)	93.69(8)
N(2)–Ni(1)–N(1)	79.73(8)	O(3)–Ni(1)–O(2w)	90.94(7)
N(2)–Ni(1)–O(2w)	86.27(8)	N(1)–Ni(1)–O(2w)	90.01(7)
O(3)–Ni(1)–O(1w)	87.57(7)	N(2)–Ni(1)–O(1w)	95.16(8)
N(1)–Ni(1)–O(1w)	89.66(7)	O(2w)–Ni(1)–O(1w)	178.45(7)
O(3)–Ni(1)–O(1)	89.87(8)	N(2)–Ni(1)–O(1)	96.70(7)
N(1)–Ni(1)–O(1)	176.43(8)	O(2w)–Ni(1)–O(1)	89.65(7)
O(1w)–Ni(1)–O(1)	90.77(7)	O(1)–C(13)–O(2)	124.6(2)
O(3)–C(15)–O(4)	125.6(2)	O(1w)–H(1A)···O(2)	164.0
O(2w)–H(2A)···O(4)	152.8	O(1w)–H(1B)···O(4a)	170.9
O(2w)–H(2B)···O(1b)	166.0	H(1A)–O(1w)–H(1B)	98.2
H(2A)–O(2w)–H(2B)	106.9	O(1w)···O(3w)···O(1wc)	155.62

Symmetry codes: a $1 + x, y, z$; b $-x, -y, -z$; c $1 - x, -y, 1 - z$.

* A and B represent geometrically generated hydrogen atoms.

what may be regarded as a 'pseudo-bridging' arrangement of the terminal acetate group.[18] This is also observed in complex **3**, in which the difference between C(15)–O(4) and C(15)–O(3) is 0.009 Å. The distance C(13)–O(1) [1.270(3) Å] is significantly longer than C(13)–O(2) [1.237(3) Å], due to the co-ordinated O(1) atom forming an intermolecular hydrogen bond with O(2wb) from an adjacent aqua ligand.

The crystal structures of complexes **1** and **2** consist of similar two-dimensional organizations. Interestingly, the hydrophilic groups recognize each other *via* intermolecular hydrogen bonds to form one-dimensional infinite zigzag chains viewed along the *a* axis as shown in Fig. 3. Each pair of aqua ligands forms a donor hydrogen bond with an unco-ordinated acetate oxygen atom from an adjacent molecule, while each pair of unco-ordinated acetate oxygen atoms forms an acceptor hydrogen bond with an aqua ligand from the adjacent molecule. Each molecule is associated with two adjacent molecules each through one donor and one acceptor hydrogen bond, *i.e.* of the AD=DA type, giving one-dimensional chains in the lattice (see Fig. 3). In these chains the hydrogen bonds are 2.77 (D–H···A 155.6°) and 2.78 Å (162.5°) for complexes **1** and **2**, respectively. The Ni···Ni intermolecular distances bridged by these double hydrogen bonds are 7.08 Å for complex **1** and 7.06 Å for complex **2**, and the distances between every second Ni^{2+} in the chain are 8.14 Å for **1** and 8.15 Å for **2**. It is also interesting that, in complexes **1** and **2**, the hydrophobic bipyridyl groups are thus alternatively extended outwards at both sides of the chain; each pair of adjacent bipyridyl groups at the same side forms one pitch of the chain, and is virtually oriented in a parallel fashion with a separation at 7.02 and 7.31 Å for complexes **1** and **2**, respectively. Intercalation of each bipyridyl group at one side of a chain into each pit of an adjacent chain in a zipper-like

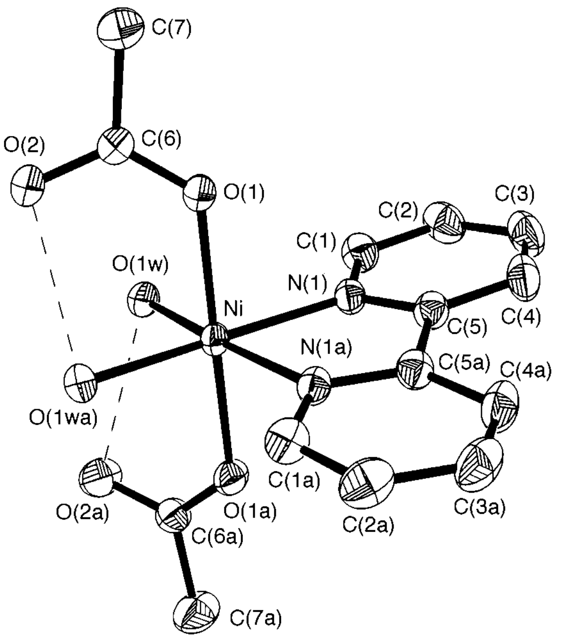

Fig. 1 An ORTEP[19] view (35% probability) of the molecular structure of complex **1** with the intramolecular hydrogen bonds and atom-numbering scheme

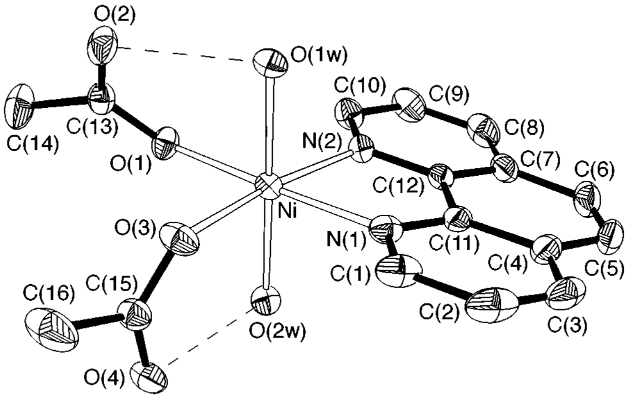

Fig. 2 An ORTEP view of the molecular structure of complex **3**. Details as in Fig. 1

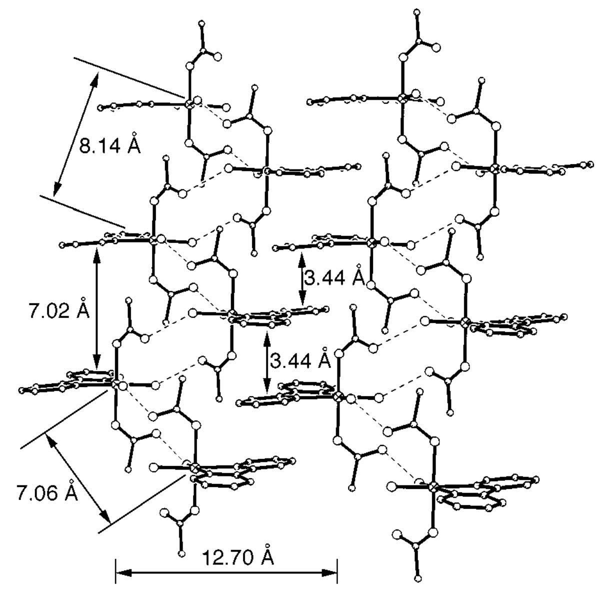

Fig. 3 View of the packing and double hydrogen-bond-linked zigzag chains in complex **1** along the *a* axis

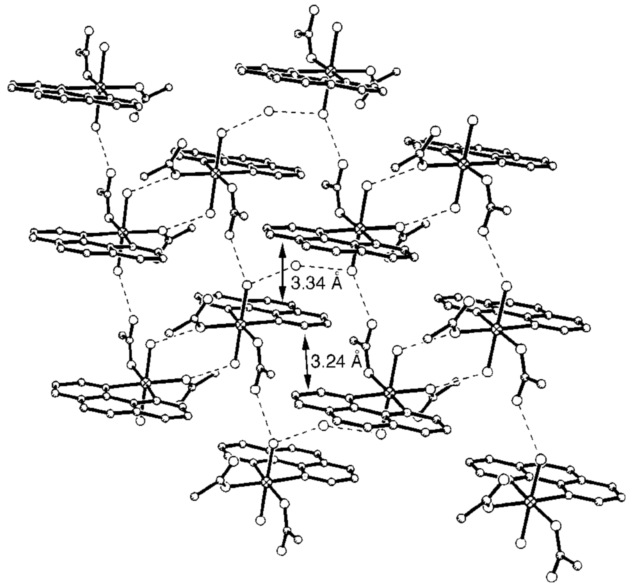

Fig. 4 View of the two-dimensional network in complex **3** along the *b* axis

fashion extends the structure into a two-dimensional network, where the close interchain bipyridyl groups, being arranged in an off-set fashion, have an average face-to-face distance of 3.44 Å for complex **1** and 3.60 Å for **2**, respectively, showing significant π–π stacking interaction.[9,10,14] The chain-to-chain spacing (13.34 Å) and the interchain bipyridyl stacking distance (3.60 Å) in complex **2** are both markedly larger than the corresponding values in **1** (12.70 and 3.44 Å), which can be attributed to the repulsion of the methyl groups of dmbipy in complex **2**.

The crystal structure of complex **3** is very different from that of **1** and **2**. One aqua ligand donates an intermolecular hydrogen bond to an unco-ordinated acetate oxygen atom from an adjacent molecule with A · · · D 2.770(3) Å (D–H · · · A 170.9°), forming a one-dimensional single chain, as shown in Fig. 4. Within this chain the Ni · · · Ni distance is 7.54 Å. The single chain is further associated with another single chain through double hydrogen bonds between the other aqua ligand and one of the co-ordinated acetate oxygen atoms [O(1) · · · O(2wb) 2.788(3) Å, D–H · · · A 166.0°] (Fig. 4), giving rise to a double chain supported by 5.2 Å. These double chains are further assembled *via* hydrogen bonds and π–π stacking interactions. Every lattice water is connected to two aqua ligands from two double chains by hydrogen bonds at O(3w) · · · O(1w) 2.885 Å, O(1w) · · · O(3w) · · · O(1wc) 155.6° (Fig. 4). The aqua molecule O(1w) not only co-ordinates to Ni^{2+} but also donates two hydrogen bonds to two oxygen atoms of acetates, and additionally accepts a hydrogen bond from the lattice water. In these double chains the hydrophobic phen rings are oriented outwards in a similar fashion to that found in both complexes **1** and **2**, and therefore resulting in analogous intercalation into the adjacent double chains. The interchain stacking interaction between the phen is also in an off-set fashion with average face-to-face distances of 3.34 and 3.24 Å, showing markedly stronger interaction between the phen ligands in complex **3** than those between the bipyridyl ligands in **1** (3.44 Å) and **2** (3.60 Å). This may be ascribed to the larger π system in the phen ligand. Such stronger π–π interactions result in the different geometries and packing arrangements of complexes **3** and **1** and **2**. In **3** the bulky acetate groups (relative to water) occupy the equatorial plane (see above) to meet the needs of space for the stronger π–π stacking, and result in the different intermolecular hydrogen bonds and the different structural arrangements. The Ni · · · Ni distance bridged by double hydrogen bonds is 5.46 Å, and the interchain spacing between the double chains is 13.17 Å in complex **3**.

Conclusion

Three monomeric nickel complexes have been synthesized and characterized by single-crystal X-ray diffraction methods. The complexes were self-assembled into two dimensional networks *via* intermolecular hydrogen bonds and π–π stacking interactions. The structures described demonstrated that intermolecular hydrogen bonds and aromatic ring interactions have enormous potential for assembling multicomponent systems in which the subunits are metal complexes. This contribution adds several new features to the fast developing field of supramolecular chemistry and aids in the fundamental understanding of molecular recognition and systematic rationalization of molecular aggregation in inorganic crystal engineering.

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