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Versatile Ligands for the Construction of Layered Metal-Containing Networks

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The synthetic opportunities furnished by organic synthesis and the inherent structure-directing possibilities of coordination complexes have been combined in the assembly of a series of layered metal-containing hybrid materials. The supramolecular assembly relies on self-complementary non-covalent interactions, and in five of the six structures presented herein, N–H···O=C hydrogen bonds between acetamide moieties on neighbouring ligands provide the primary structure-direction tool as intended. The distances between metal ions are controlled by ligand···ligand hydrogen bonds and reside within a narrow and tuneable range. The following crystal structures are reported: [Cu(4-(3-pyridyl)-1-acetamidobenzene)$_2$(1,1,1,5,5,5-hexafluoro-2,4-pentanedione)$_2$] **1**; [Cu(4-(acetamidomethyl)pyridine)$_2$(1,1,1,5,5,5-hexafluoro-2,4-pentanedione)$_2$]·2CH$_2$Cl$_2$ **2**; [Cu(3-acetamidopyridine)$_2$(1,1,1,5,5,5-hexafluoro-2,4-pentanedione)$_2$] **3**; [Ni(3-acetamidopyridine)$_2$(1,3-diphenyl-1,3-propanedione)$_2$]·2CH$_2$Cl$_2$ **4**; [Ni(3-acetamidopyridine)$_2$(1,3-diphenyl-1,3-propanedione)$_2$] **5**; and [Co(2-acetamidopyridine)$_2$(1,3-diphenyl-1,3-propanedione)$_2$]·2CH$_2$Cl$_2$ **6**.

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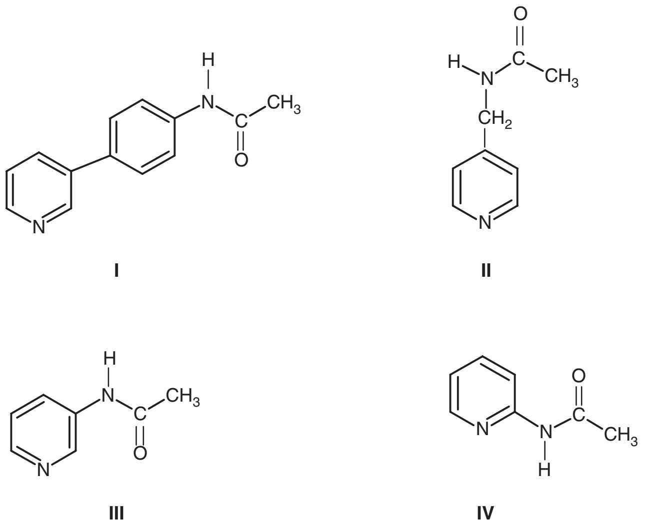
Introduction

Many strategies based on coordinate-covalent bonds have been employed in the synthesis of hybrid materials containing networks with predictable connectivity and dimensionality, typically through the use of bridging ligands such as 4,4′-bipyridine, dicarboxylates, bis(amides), bis(lactams), and bis(pyridones).[1] At the same time, the strength and directionality of hydrogen bonds have offered supramolecular pathways towards the directed assembly of extended organic networks and multicomponent supermolecules.[2] Although both strategies have enjoyed considerable success, much less work has been carried out on the assembly of metal-containing networks using a combination of metal–ligand and hydrogen-bond interactions.[3] This approach may in some cases have certain advantages, as it combines the strength of the coordinate-covalent bond with the flexibility of the softer hydrogen-bond interactions, which can offer a self-correcting assembly process, and desirable physical properties such as enhanced solubility in a range of organic solvents.[4] An important role in this approach is played by versatile bifunctional ligands that contain both metal-coordinating sites and functionalities that provide opportunities for organizing complex molecules into infinite architectures through supramolecular chemistry and non-covalent interactions.

We are currently assembling a library of reliable ligands that can be employed in the construction of coordination networks with controllable metrics with a view to preparing porous solids with well-defined and accessible channels. In the present study, we have taken advantage of the robust self-complementary hydrogen-bonding capability of the amide functionality (as a result of strong N–H···O=C hydrogen bonds), and the reliable metal-coordinating ability of pyridine.[5] More specifically, we have employed a series of acetamido(pyridine)-based compounds as such species are also present in several biologically relevant systems.[6] The four ligands **I–IV** (Scheme 1) used in the present work contain an acetamido group attached at different positions on a pyridine ring. Although complexes of some amidopyridine derivatives have previously been reported, such efforts have primarily involved the formation of 1-D and 2-D coordination networks, by the interaction of metal ions with double-ended bis(amidopyridine) ligands.[7]



Scheme 1.

Systematic structural studies of organic salts and co-crystals have demonstrated that the structural behaviour and pattern preference of the N–H moiety depend on the position of

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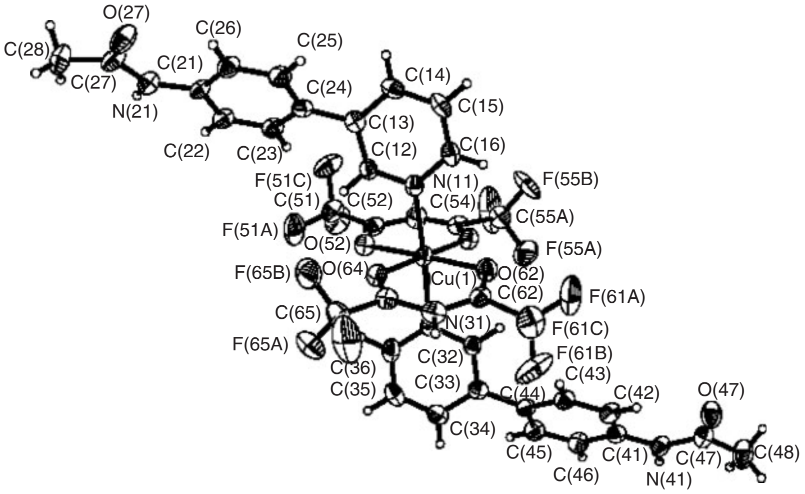

Fig. 1. Molecular geometry of **1**.

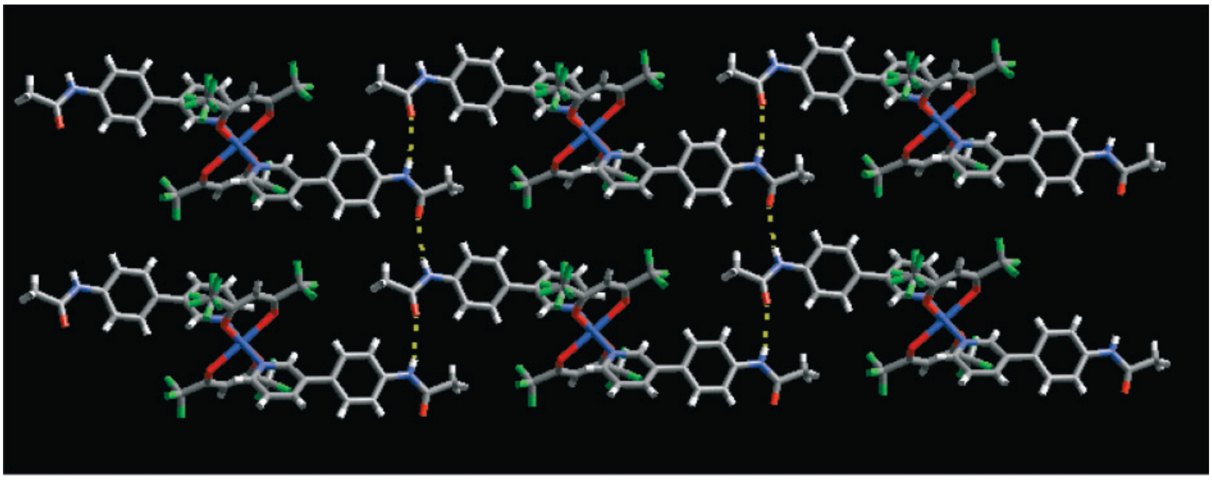

Fig. 2. Two-dimensional layer in the structure of **1** generated by symmetry-related N–H···O hydrogen bonds.

the acetamido group with respect to the heterocyclic nitrogen atom.[8] A search of the Cambridge Structural Database (CSD) shows that a catemeric N–H···O=C is unlikely to form if the acetamido group is positioned *ortho* to a pyridine nitrogen atom (2-acetamidopyridines). However, if the acetamido group is located either *meta* or *para* to a pyridine nitrogen atom (3- and 4-acetamidopyridines), then the most likely structural outcome is a self-complementary N–H···O=C (amide–amide) motif. In order to exploit the latter synthon, we decided to focus on 3- and 4-substituted acetamidopyridines as our bifunctional ligands in an attempt to construct metal-containing 1-D and 2-D architectures (although one example of a structure with an *ortho*-substituted ligand is also included).

A complication that may arise when utilizing hydrogen bonds as the primary synthetic tool of hybrid materials is potential interference from counterions that often accompany the metal ions. Many common anions such as chloride, nitrate, and sulfate are powerful hydrogen-bond acceptors that can readily disrupt the intended intermolecular ligand–ligand hydrogen bonds. Therefore, in order to avoid or at least minimize this potential problem, we opted to use charge-neutral metal–ligand complexes as building blocks,[9] such as copper(II) 1,1,1,5,5,5-hexafluoro-2,4-pentanedione [$Cu(hfac)_2$], cobalt(II) 1,3-diphenyl-1,3-propanedione [$Co(DBM)_2$], and nickel(II) 1,3-diphenyl-1,3-propanedione [$Ni(DBM)_2$]. An additional advantage of using two chelating ligands is that the coordination chemistry is easier to control (especially in the case of the notoriously unpredictable Cu^{II} ion). Acetylacetonate (acac)-type ligands typically coordinate to M(II) metal ions in a square-planar arrangement, thus leaving the two axial sites open for coordination to a suitable ligand, which can subsequently be used for constructing the desired structural motif. The primary goal of the current particular project is to employ the C=O···H–N amide catemer as a synthetic vehicle for organizing coordination complexes into extended architectures and to begin to map out its limits and limitations as a supramolecular synthon. In the present study, we allowed ligands **I**–**IV** to react with a series of acac-based Cu^{II}, Ni^{II}, and Co^{II} complexes, and we obtained crystals suitable for single-crystal X-ray diffraction in six cases reported here: [Cu(4-(3-pyridyl)-1-acetamidobenzene)$_2$(hfac)$_2$] **1**; [Cu(4-(acetamidomethyl)pyridine)$_2$(hfac)$_2$]·$2CH_2Cl_2$ **2**; [Cu(3-acetamidopyridine)$_2$(hfac)$_2$] **3**; [Ni(3-acetamidopyridine)$_2$(DBM)$_2$]·$2CH_2Cl_2$ **4**; [Ni(3-acetamidopyridine)$_2$(DBM)$_2$] **5**; [Co(2-(acetamidopyridine)$_2$(DBM)$_2$]·$2CH_2Cl_2$ **6**.

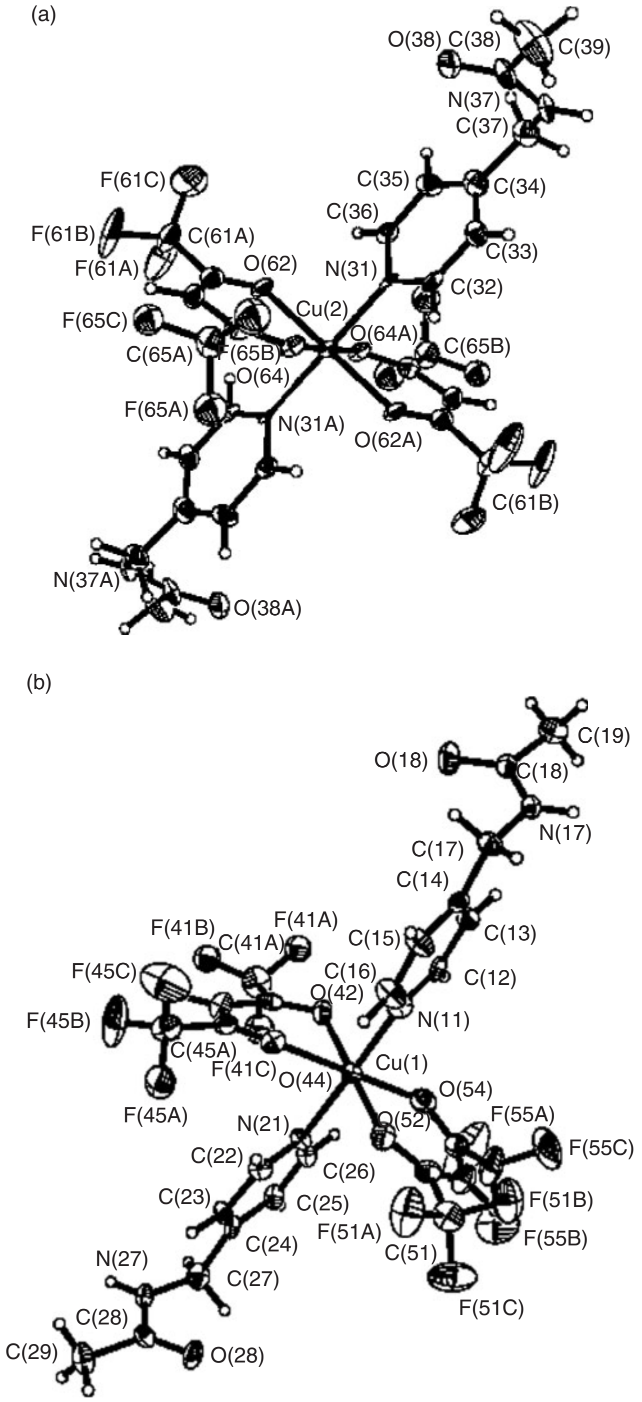

Fig. 3. Molecular geometries of the two unique complexes in **2**.

Results

The crystal structure of **1** contains the expected six-coordinated copper(II) complex. The geometry at the $\mathrm{Cu^{II}}$ centre is a 4+2 coordination, resulting from two *O*,*O*′-chelating hexafluoro-2,4-pentanedionato ions and two 4-(3-pyridyl)-1-acetamidobenzene ligands coordinated through their pyridine nitrogen atoms, in *trans* positions, with Cu–N distances of 2.021(3) and 2.022(3) Å, respectively. The two axial pyridine rings are coplanar. The chelate rings formed by the 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato ligands are planar with *cis* angles ranging between 88° and 92°, with the acute angles being associated with the bite of the chelate ring. The benzene rings of 4-(3-pyridyl)-1-acetamidobenzene molecules are slightly twisted (~30°) with respect to the plane of pyridine (py) rings and the amide groups in the complex are arranged in a *trans*-fashion with respect to the N(py)–Cu–N(py) axis (Fig. 1).

The N–H groups on both ligands engage in N–H···O hydrogen bonds with a C=O moiety from a ligand on a neighbouring complex, (N21···O47, 3.153(4) Å and (N41···O27, 3.075(4) Å), producing an infinite 2-D layer (Fig. 2).

The crystal structure of **2** contains two crystallographically independent 4+2 copper(II) ions as well as two molecules of methylene chloride. One of the two copper ions is positioned on an inversion centre, with four oxygen atoms, from two *O*,*O*′-chelating hexafluoro-2,4-pentanedionato anions occupying the four equatorial coordination sites, with *cis* angles of 85° and 95°, with the smaller angle being associated with the bite of the chelate. The Cu–O bond lengths are 1.988(5) and 2.331(5) Å, respectively, and the two 4-(acetamidomethyl)pyridine ligands are occupying the axial sites through their pyridine nitrogen atoms with a Cu–N bond distance of 1.981(6) Å (Fig. 3a).

The geometry around the second copper(II) ion in the crystal structure of **2** can also be described as having a 4+2 coordination; see Fig. 3b. Again the two *O*,*O*′-chelating hexafluoro-2,4-pentanedionato anions are occupying the four equatorial coordination sites, with *cis* angles of 85°, 89°, 92°, and 95°, with the two short angles being associated with the bite of the chelate. The two 4-(acetamidomethyl)pyridine ligands are occupying the axial sites through their pyridine nitrogen atoms at an N–Cu–N angle of 176°. The four different Cu–O bond lengths fall in the range 2.050(6)–2.193(6) Å and the two Cu–N bond distances are 1.971(7) and 2.012(6) Å, respectively.

As was the case with the structure of **1**, the amide groups in neighbouring complex ions are interlinked through N–H···O hydrogen bonds (N17···O38, 2.806(8) Å, N27···O18, 2.848(9) Å and N37···O28, 2.858(9) Å) to produce infinite 2-D sheets; see Fig. 4.

The central motif in the crystal structure of **3** is a 4+2 hexacoordinated copper(II) complex where the metal ion is located on an inversion centre. The two chelating 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato anions occupy the equatorial plane, whereas the two 3-acetamidopyridine molecules complete the complex ion by coordinating through their pyridine nitrogen atoms with a Cu–N distance of 2.007(3) Å (Fig. 5).

The pyridine rings of two amide ligands are coplanar and the amide groups in the complex are oriented *trans* with respect to the N–M(II)–N axis. The chelate rings formed by the anionic acac ligands have *cis* angles of 87° and 93°, with the short angle, as expected, being associated with the bite of the chelate ring. The N–H group of one amide ligand and the C=O group on a pyridyl ligand on an adjacent complex engage in self-complementary N–H···O hydrogen bonds, N13···O21, 2.791(4) Å. As the metal ion is located on an inversion centre, there are two symmetry-related N–H···O=C catemers, leading to an infinite 2-D sheet structure; see Fig. 6.

The crystal structure of **4** shows that each nickel(II) ion is coordinated by two unique 1,3-diphenyl-1,3-propanedionato ions and two 3-acetamidopyridine molecules with two additional methylene chloride molecules present in the lattice. The chelate rings have *cis* angles ranging from 87° to 92° and in contrast to **1**–**3**, the acute angles in this complex are associated with the non-biting sides. The two 3-acetamidopyridine molecules are occupying the *trans* positions with Ni–N distances of 2.095(2)

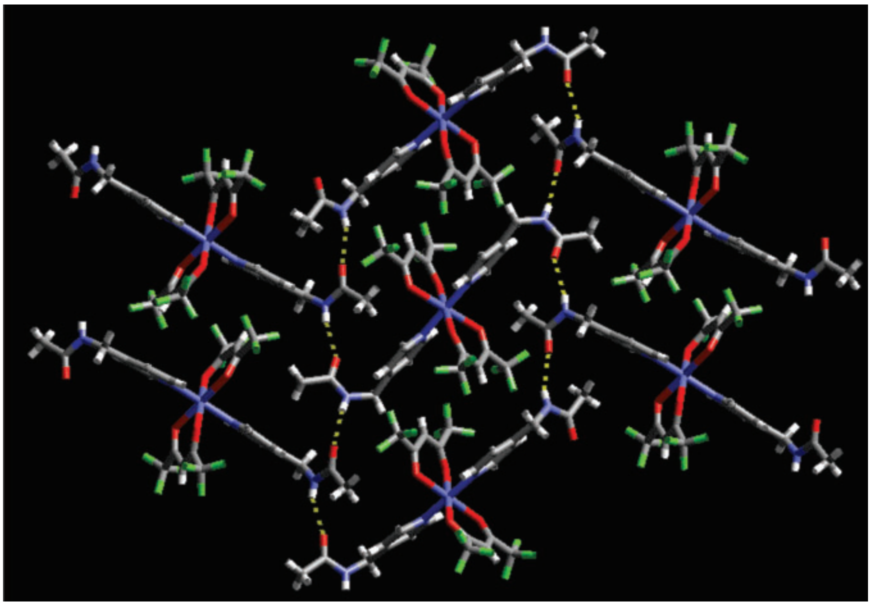

Fig. 4. Two-dimensional layer in the structure of **2** generated by N–H· · ·O hydrogen bonds.

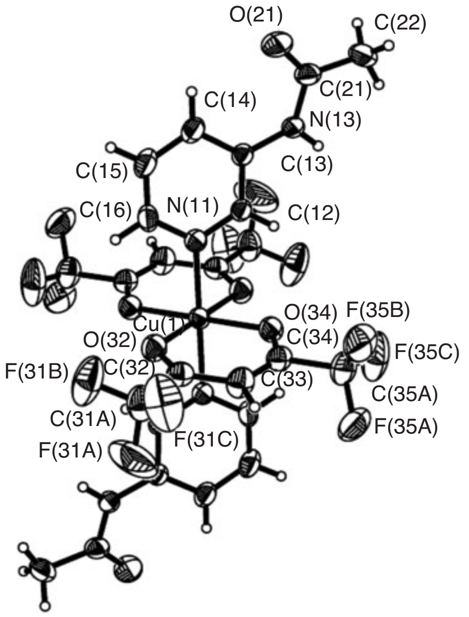

Fig. 5. Molecular geometry and thermal ellipsoids (50%) for the complex ion in **3**.

and 2.108(2) Å, respectively, and the two amide groups are oriented in a *trans* manner (Fig. 7).

Again, ligands on adjacent complex ions form two intermolecular N–H· · ·O=C hydrogen bonds, N23· · ·O17, 2.967(3) Å and N13· · ·O27, 2.819(3) Å, respectively resulting in a 2-D sheet structure, (Fig. 8).

The crystal structure determination of **5** shows that each nickel(II) ion is coordinated by two unique 1,3-diphenyl-1,3-propanedionato ions and two 3-acetamidopyridine molecules in a 4+2 manner, but this time there is no solvent present in the lattice (these crystals were grown from acetonitrile, whereas **4** was obtained from CH_2Cl_2). The two symmetry-related axial ligands display Ni–N(py) distances of 2.1188(12) Å and the amide groups are again arranged in a *trans* fashion (Fig. 9).

Pyridine-based ligands on adjacent complex ions form intermolecular N–H· · ·O=C hydrogen bonds, N13· · ·O17, 2.9696(18) Å, resulting in a 2-D sheet structure (Fig. 10).

The crystal structure of **6** contains a 4+2 cobalt(II) complex as well as two molecules of methylene chloride. Each metal complex is located on a crystallographic inversion centre with an octahedral geometry constructed from two chelating anions and two 2-acetamidopyridine molecules (Fig. 11).

The chelate rings are almost planar with *cis* angles of 90.6° and 90.4° but two phenyl groups on each 1,3-diphenyl-1,3-propanedionato ion are slightly twisted with respect to each other. The two *trans*-2-acetamidopyridine molecules are coordinated to the central metal(II) ion with Co–N distances of 2.2332(9) Å. In contrast to previous cases **1**–**5**, the N–H group of each amide ligand is involved in intracomplex N–H· · ·O hydrogen bonding with an oxygen atom from the nearest acac ligand, N12· · ·O23, 2.8984(13) Å. As the most prominent hydrogen-bond donors in the compound, the N–H moieties, are occupied with intramolecular interactions, there are no other structure-directing complementary intermolecular interactions that can connect discrete metal complexes into specific and recognizable networks.

Discussion

Single-crystal X-ray analysis of **1**–**6** has demonstrated that the self-complementary N–H· · ·O=C intermolecular ligand· · ·ligand hydrogen-bond interaction is present as long as the N–H donor is not forced into an intramolecular interaction as a result of *ortho*-substitution of the pyridyl backbone. The *O*,*O*′-chelating anions employed in the present study, hexafluoro-2,4-pentanedionate and 1,3-diphenyl-1,3-propanedionate, occupy the four equatorial sites around the metal(II) ions, and when the amide moiety is located so close to the equatorial plane, the N–H group is essentially pre-organized for an intramolecular N–H· · ·O interaction (as seen in the structure of **6**). However, if the N–H moiety is given the structural freedom (as is the case with the *meta*- and *para*-substituted pyridine-based ligands) to select a hydrogen-bond acceptor, the carbonyl moiety is the preferred interaction site in each case **1**–**5**. The nature of the metal ion

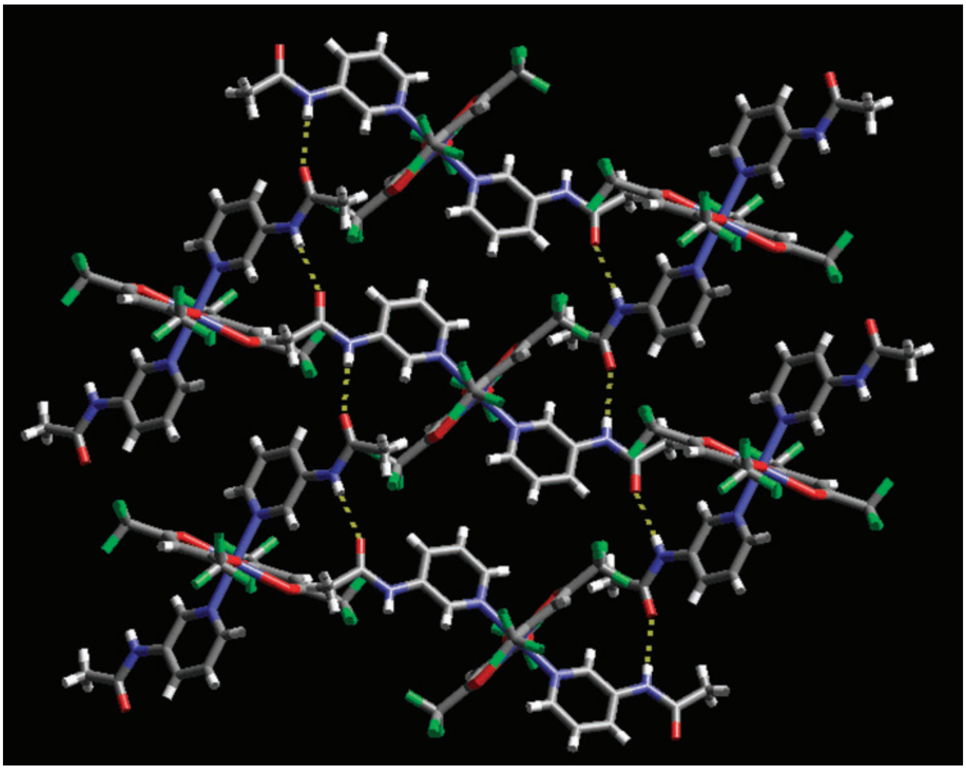

Fig. 6. Two-dimensional layer in the structure of **3** generated by symmetry-related N–H···O hydrogen bonds.

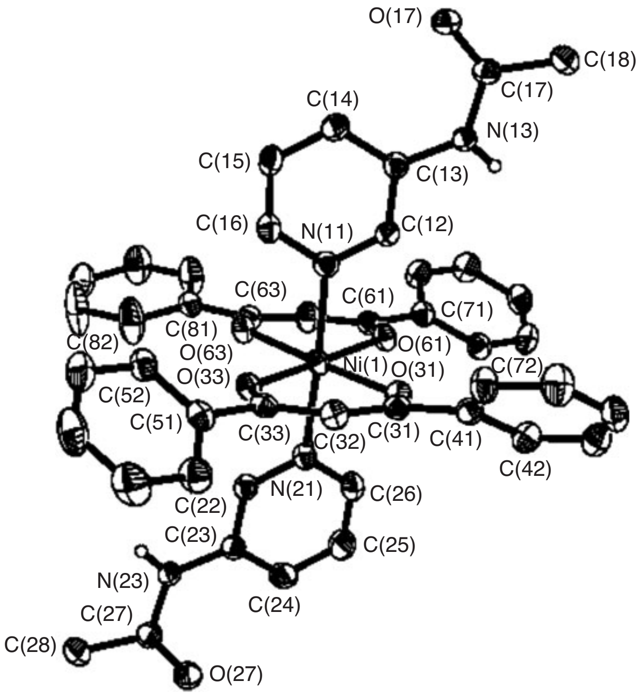

Fig. 7. Molecular geometry and thermal ellipsoids (50%) for the complex ion in **4** (solvent molecules not shown).

does not affect the resulting structure notably because in each case, the metal ion is 'strapped into' a fixed geometry dictated by the two anionic chelating ligands. All six complex ions have a 4+2 coordination with the two chelating ligands located in the equatorial plane. The charge balance that results when combining M^{II} ions with two acac ligands also removes the need for possibly disruptive counterions, which undoubtedly facilitates the supramolecular synthetic strategy. The importance of using chelating ligands for controlling the coordination geometry, and thereby also the structural role of the complex ion itself, is illustrated by a previously reported crystal structure of a five-coordinate Cu^{II} complex comprising two 4-acetamidopyridine, two acetate ions and a water molecule in the first coordination sphere; in this case the amide···amide hydrogen bond is disrupted by the water molecule, and the result is a complex 3-D architecture.[10]

It is interesting to note that **1**–**5** form layered structures as dictated by the ligand···ligand hydrogen bonds; however, as soon as the intermolecular interaction is prevented (as in **6**, when the amide is now in the *ortho*-position), the layers are no longer present.

Furthermore, in all the layered structures, the metal···metal distances are in the 9–11-Å range as a result of the 1-D amide α-network. The second dimension of the layer unit cell varies more because the size of the ligand shows greater variation (Fig. 12).

Even though the five layered structures **1**–**5** display very similar structural chemistry, the crystallographic symmetry varies between them (layers are related by either translation, inversion, or by a glide plane).

The self-complementary acetamido moiety has also been previously utilized in the preparation of a series of silver(I)-containing 2-D architectures,[11] and it is clear that this particular supramolecular synthon is robust enough to organize relatively large complex ions into desired extended networks. Some 50 crystal structures containing silver(I) ions and acetamido-substituted pyridyl-based ligands were found in the CSD database and approximately half of those contained extended networks assembled via self-complementary N–H···O=C hydrogen bonds. In most of the structures that

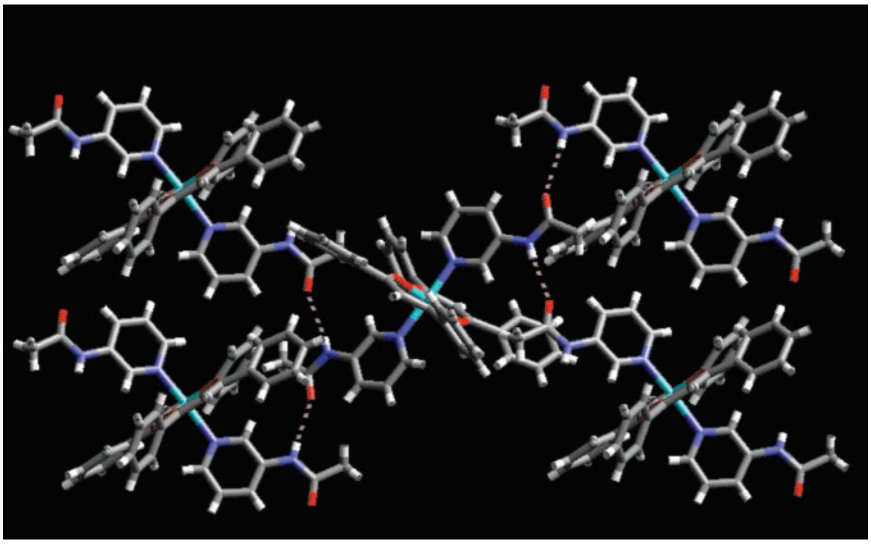

Fig. 8. Two-dimensional layer in the crystal structure of **4** generated by two unique N–H···O hydrogen bonds.

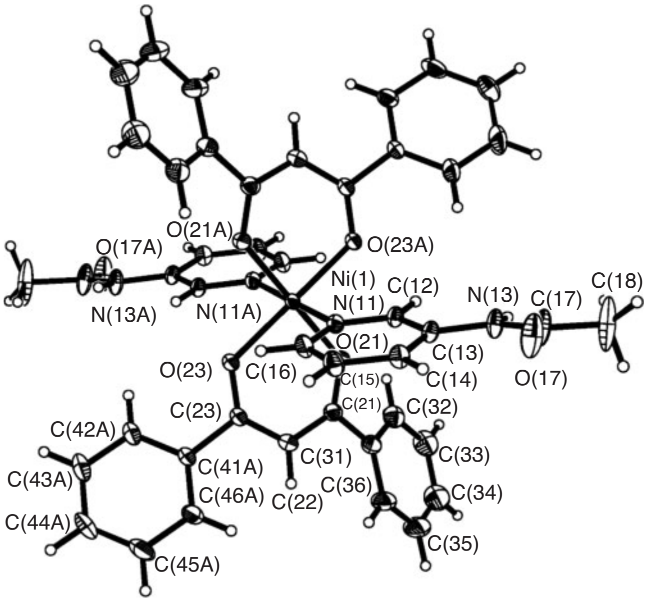

Fig. 9. Molecular geometry and thermal ellipsoids (50%) for the complex ion in **5**.

did not contain an N–H···O=C synthon, the N–H moiety was instead engaged in charge-assisted hydrogen bonds with a strong hydrogen-bond acceptor such as a nitrate or sulfate ion. The relative positions of the hydrogen-bonding site with respect to the pyridyl nitrogen atom is also of considerable importance, because in the absence of more strongly chelating ligands (such as acac), 2-acetamidopyridine acts as a bis(N,O)chelator that prevents any structure-directing intermolecular N–H···O=C hydrogen bonds from forming.[12] For the N-oxide analogue of 2-acetamidpyridine, a seven-membered chelate is not formed, however, and instead the ligand is binding to the metal ion only through the N-oxide moiety.[13]

In the structures of **1**–**6**, the central metal complex is charge-neutral, which removes the need for counterions, which emphasizes the importance of minimizing the number of structurally competing factors if a desired supramolecular goal is to be attained in a reasonable yield. Furthermore, an amide moiety should be placed either *meta* or *para* with respect to the coordinating pyridyl nitrogen atom in order to avoid a bis(N,O) chelating mode or an intramolecular N–H···O hydrogen bond if an acac-based ligand (a strong hydrogen-bond acceptor) is used as a way of controlling coordination geometry and charge of the complex ion. We are currently exploring how amide···amide hydrogen bonds can be utilized for the construction of 3-D architectures with accessible cavities with controllable size and shape.

Experimental

All chemicals were purchased from Aldrich and used without further purification. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected.

Synthesis of Ligands

Synthesis of 4-(Bromo)acetamidobenzene

Acetic anhydride (5 mL) was added dropwise to 4-bromoaniline (5.16 g; 30 mmol) and the mixture was heated under reflux for 30 min. The excess acetic anhydride and acetic acid produced during the reaction were removed on a rotary evaporator, and the precipitates thus obtained on cooling were recrystallized from methanol. Yield 70%. Mp 173–174°C. $\nu_{\max}$(KBr)/cm^{-1} 3293m (ν(NH)), 1669vs (ν(C=O)), 1534vs (ν(amide II)). δ_{H} (400 MHz, CDCl$_3$) 7.41 (br s, 4H), 7.34 (s, 1H), 2.17 (s, 3H).

*Synthesis of 4-(3-Pyridyl)-acetamidobenzene, **I** (Scheme 1)*

A mixture of 4-bromo-1-acetamidobenzene (2.14 g, 10 mmol), 3-pyridylboronic acid (1.58 g, 10.33 mmol), sodium carbonate (0.700 g, 6.6 mmol), and *trans*-dichlorobis(triphenylphosphine) palladium(II) (0.180 g; 0.25 mmol) was weighed in a round-bottom flask and acetonitrile (35 mL) and water (35 mL) were added to it. After passing through nitrogen for 10 min, the solution was heated at 80°C under a nitrogen atmosphere. The reaction was monitored by TLC and on completion (24 h) was allowed to cool to room temperature. The solution was then diluted with 150 mL of ethyl acetate, and washed with water (3 × 100 mL), followed by saturated aqueous sodium chloride solution (2 × 100 mL). The organic layer was separated and dried over magnesium sulfate. After removing the solvent on a rotary evaporator, the residue was chromatographed on silica

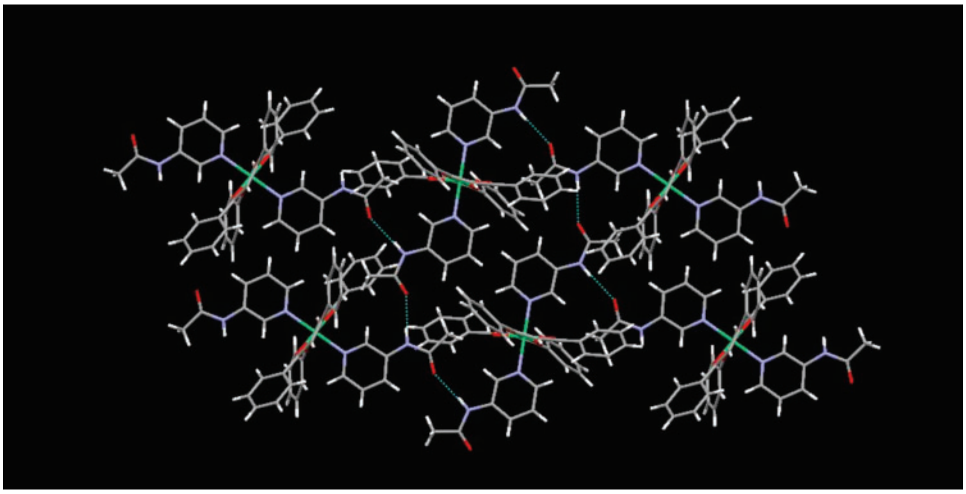

Fig. 10. Two-dimensional layer in the crystal structure of **5** generated by symmetry-related N–H· · ·O hydrogen bonds.

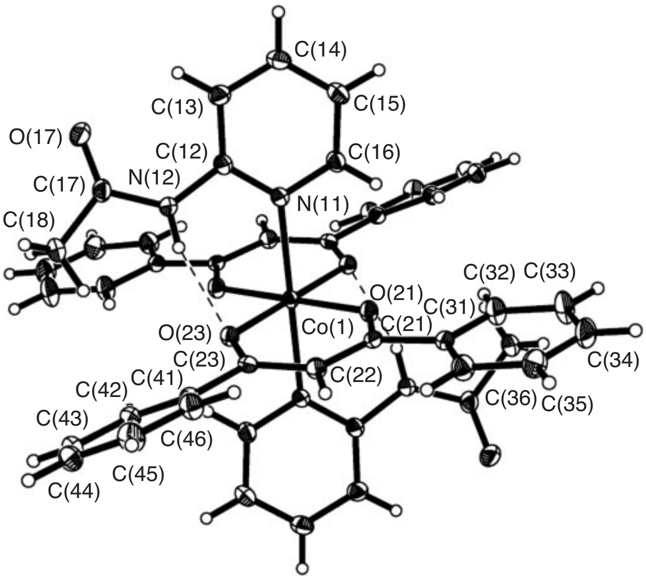

Fig. 11. Molecular geometry and thermal ellipsoids (50%) for the complex ion in **6**.

with hexane/ethyl acetate. The product was recrystallized as light yellow plates from ethyl acetate. Yield 64%. Mp 186–188°C. ν_{max}(KBr)/cm^{-1} 3254m (ν(NH)), 1687vs (ν(C=O)), 1532vs (ν(amide II)). δ_H (400 MHz, CDCl$_3$) 8.84 (d, J 1.56, 1H), 8.59 (dd, J 2, 1H), 7.85 (t, J 4, 1H), 7.88 (t, J 2.6, 1H), 7.63 (m, 2H), 7.56 (m, 2H), 7.52 (br s, 1H), 2.22 (s, 3H).

Synthesis of 4-(acetamidomethyl)pyridine **II**,[14] 3-acetamidopyridine **III**,[15] and 2-acetamidopyridine **IV** were carried out by previously reported methods.[8]

Synthesis of Metal Complexes

Synthesis of [Cu(4-(3-pyridyl)-1-acetamidobenzene)$_2$ (1,1,1,5,5,5-hexafluoro-2,4-pentanedione)$_2$] **1**

4-(3-Pyridyl)-1-acetamidobenzene (0.042 g, 0.20 mmol) was dissolved in hot methylene chloride (10 mL) and mixed with the hot solution of Cu(hfac)$_2$ (0.049 g, 0.10 mmol) in methylene chloride (15 mL). The resulting solution was boiled in a screw-cap vial several times and allowed to stand. The green prisms formed over a period of 7 days. ν_{max}(KBr)/cm^{-1} 3337m (ν(NH)), 1677vs (ν(C=O)), 1535, 1524vs (ν(amide II)). (Calc.: C 47.93, H 2.90, N 6.21%. Found: C 47.7, H 3.1, N 6.0.)

Synthesis of [Cu(4-(acetamidomethyl)pyridine)$_2$ (1,1,1,5,5,5-hexafluoro-2,4-pentanedione)$_2$]·2CH$_2$Cl$_2$ **2**

4-(Acetamidomethyl)pyridine (0.030 g, 0.20 mmol) was dissolved in cold methylene chloride (10 mL) and was added to the solution of Cu(hfac)$_2$(0.049 g, 0.10 mmol) in methylene chloride (15 mL). The resulting solution was transferred to a screw-cap vial and allowed to stand at room temperature. Green needles appeared over 3 days' time. ν_{max}(KBr)/cm^{-1} 3297m (ν(NH)), 1662vs (ν(C=O)), 1547, 1525vs (ν(amide II)). (Calc.: C 35.48, H 2.76, N 5.91%. Found: C 35.3, H 2.8, N 5.7.)

Synthesis of [Cu(3-acetamidopyridine)$_2$(1,1,1,5,5,5-hexafluoro-2,4-pentanedione)$_2$] **3**

A hot solution of Cu(hfac)$_2$ (0.049 g, 0.10 mmol) in methylene chloride (10 mL) was added to a solution of 3-acetamidopyridine (0.027 g, 0.20 mmol) also in methylene chloride (15 mL). The resulting solution was brought to the boil and then left to cool overnight. The following day, green crystals had formed. ν_{max}(KBr)/cm^{-1} 3268m (ν(NH)), 1684vs (ν(C=O)), 1546, 1525vs (ν(amide II)). (Calc.: C 38.44, H 2.42, N 7.47%. Found: C 38.7, H 2.5, N 7.3.)

Synthesis of [Ni(3-acetamidopyridine)$_2$(1,3-diphenyl-1,3-propanedione)$_2$]·2CH$_2$Cl$_2$ **4**

A solution of 3-acetamidopyridine (0.027 g, 0.20 mmol) in methylene chloride (15 mL) was added to a solution of nickel(II) DBM (0.048 g, 0.10 mmol) in 10 mL of methylene chloride. The mixture was heated for 5 min to reduce the volume to 7 mL and then allowed to stand in a screw-cap vial at room temperature until green crystals appeared. ν_{max}(KBr)/cm^{-1} 3301m (ν(NH)), 1673vs (ν(C=O)), 1550, 1520vs (ν(amide II)). (Calc.: C 58.32, H 4.47, N 5.91%. Found: C 58.5, H 4.6, N 5.6.)

Synthesis of [Ni(3-acetamidopyridine)$_2$(1,3-diphenyl-1,3-propanedione)$_2$] **5**

3-Acetamidopyridine (0.03 g, 0.22 mmol) was dissolved in acetonitrile (5 mL) and mixed with a solution of Ni^{II} DBM (0.049 g, 0.10 mmol) in acetonitrile (5 mL). The solution was heated for 10 min and then allowed to stand in a screw-cap vial at

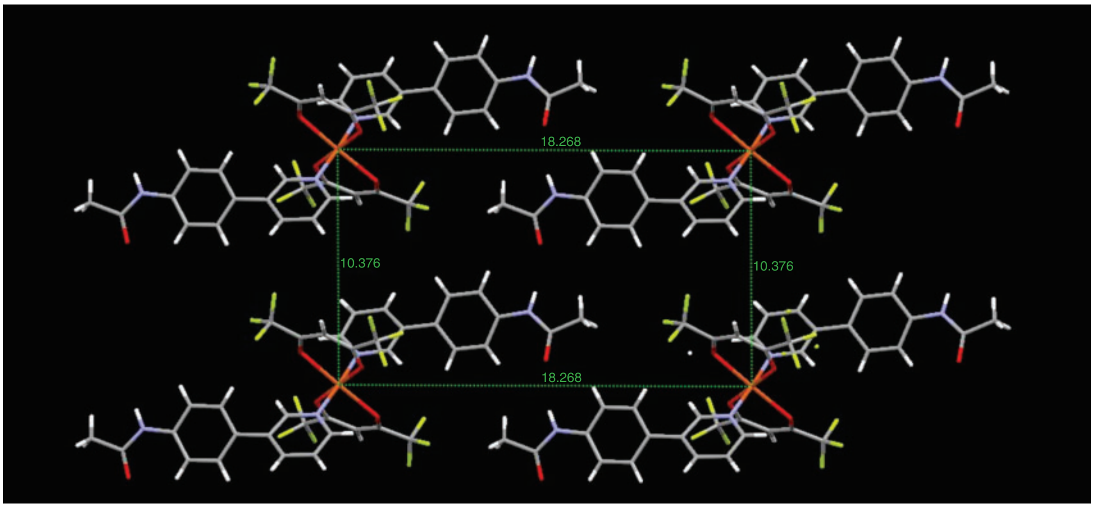

Fig. 12. Metal· · ·metal distances within the layer in the crystal structure of **1**. The metal ions are separated by 10.4 Å along the amide link, and by over 18 Å in the plane but perpendicular to this direction.

room temperature. The green plates were formed over 4 weeks' time. ν_{max}(KBr)/cm^{-1} 3306m (ν(NH)), 1684(ν(C=O)), 1548, 1525vs (ν(amide II)). (Calc.: C 67.97, H 4.93, N 7.21%. Found: C 67.8, H 5.1, N 7.2.)

Synthesis of [Co(2-acetamidopyridine)$_2$(1,3-diphenyl-1,3-propanedione)$_2$]·2CH_2Cl_2 **6**

2-Acetamidopyridine (0.027 g, 0.20 mmol) was dissolved in methylene chloride (10 mL) and mixed with a solution of cobalt(II) DBM (0.048 g, 0.10 mmol) in methylene chloride (12 mL). The solution was boiled and stored at room temperature in a screw-cap vial. The dark orange prisms were formed over 3 weeks. ν_{max}(KBr)/cm^{-1} 3295m (ν(NH)), 1704vs (ν(C=O)), 1545, 1521vs (ν(amide II)). (Calc.: C 58.31, H 4.47, N 5.91%. Found: C 58.2, H 4.6, N 5.8.)

X-Ray Crystallography

X-ray data were collected on a Bruker SMART 1000 four-circle charge coupled device (CCD) diffractometer (**1**–**4**), Bruker Kappa APEX II (**5**), or Bruker SMART APEX CCD diffractometer (**6**) using, in each case, a fine-focus molybdenum Kα tube. Data were collected using *SMART* (**1**–**4**)[16] or *APEX2* (**5** and **6**)[17] software. Initial cell constants were found by small widely separated 'matrix' runs. Generally, an entire hemisphere of reciprocal space was collected regardless of Laué symmetry. Scan speed and scan width were chosen based on scattering power and peak rocking curves.

Unit cell constants and orientation matrix were improved by least-squares refinement of reflections thresholded from the entire dataset. Integration was performed with *SAINT*,[18] using this improved unit cell as a starting point. Precise unit cell constants were calculated in *SAINT* from the final merged dataset. Lorenz and polarization corrections were applied. Laué symmetry, space group, and unit cell contents were found with *XPREP*.

Data were reduced with *SHELXTL*.[19] The structures were solved in all cases by direct methods without incident. In general, hydrogen atoms were assigned to idealized positions and were allowed to ride. Where possible, the coordinates of the amide hydrogen atoms were allowed to be refined. Heavy atoms were refined with anisotropic thermal parameters. Absorption correction was performed with *SADABS* where possible.

Compound 1: Attempted absorption correction did not improve fit statistics and the uncorrected dataset was used for structure refinement. The complex sits on a general position. One of the four $-CF_3$ groups was disordered. All non-hydrogen atoms were given anisotropic thermal parameters. All hydrogen atoms were included in calculated positions and allowed to ride.

Compound 2: Data were corrected for absorption using *SADABS*. The asymmetric unit contains five species: a complete copper(II) complex on a general position, a half-complex (sitting on an inversion centre), and three ordered dichloromethane molecules. Five of the six $-CF_3$ groups were disordered. Four were modelled with two species, and the fifth was modelled with three species. Geometry of all $-CF_3$ fragments was restrained to be similar to the first fragment (C41A, F41A-F41C) by the SAME command. The geometry of the first fragment (C41A, etc.) was idealized to tetrahedral by using DFIX restraints on the C–F bond distances and F–F distances. Thermal parameters for the set of three fluorine atoms on each species having occupancy $<50\%$ were constrained with EADP commands. The fluorine atoms having occupancy $>60\%$ were given isotropic thermal parameters (anisotropic refinement of other fluorine atoms was unstable). All hydrogen atoms were included in calculated positions and were allowed to ride.

Compound 3: Data were corrected for absorption using *SADABS*. The complex sits on a crystallographic inversion centre. Both $-CF_3$ groups were disordered: they were both modelled as a triplet of species. For each triplet, site occupancy was restrained to 1.0 with individual occupancy free variables and a SUMP command; the major species ($>75\%$ occupancy) was refined with anisotropic fluorine atoms; the two minor species ($<15\%$ occupancy each) were refined with isotropic thermal parameters. Geometry of the six independent $-CF_3$ fragments was restrained using SAME commands. All hydrogen atoms were included in calculated positions and were allowed to ride.

Compound 4: Data were corrected for absorption using *SADABS*. The asymmetric unit contains three species: a nickel complex, an ordered dichloromethane solvent molecule, and a disordered dichloromethane solvent molecule. Geometry of all three dichloromethane fragments was restrained with SAME commands. All non-hydrogen atoms were given anisotropic thermal parameters. Thermal parameters for the two (closely located) disordered dichloromethane species were pairwise constrained

Table 1. X-ray crystallographic data for 1–6

	1	**2**	**3**	**4**	**5**	**6**
Systematic name	{*N*-[4-(3-pyridyl)phenyl] benzamide}$_2$Cu(F$_6$-acac)$_2$	*N*-(4-pyridylmethyl)acetamide, Cu(F$_6$-acac)$_2$(CH$_2$Cl$_2$)$_2$	[*N*-(3-pyridyl)acetamide]$_2$ Cu(F$_6$-acac)$_2$	[*N*-(3-pyridyl)acetamide]$_2$ Ni(Ph$_2$-acac)$_2$	[*N*-(3-pyridyl)acetamide]$_2$ Ni(Ph$_2$-acac)$_2$	[*N*-(3-pyridyl)acetamide]$_2$ Co(Ph$_2$-acac)$_2$ (CH$_2$Cl$_2$)
Formula moiety	$(C_{13}H_{12}N_2O)_2$ $Cu(C_5HF_6O_2)_2$	$(C_8H_{10}N_2O)_6Cu_3(C_5HO_2F_6)_6$ $(CH_2Cl_2)_6$	$(C_7H_8N_2O)_2Cu(C_5HO_2F_6)_2$	$(C_7H_8N_2O)_2Ni$ $(C_{15}H_{11}O_2)_2$ $(CH_2Cl_2)_2$	$(C_7H_8N_2O)_2Ni$ $(C_{15}H_{11}O_2)_2$	$(C_7H_8N_2O)_2(C_{15}H_{11}O_2)_2$ $Co(CH_2Cl_2)_2$
Emp. formu.	$C_{36}H_{26}CuF_{12}N_4O_6$	$C_{84}H_{78}Cl_{12}Cu_3F_{36}N_{12}O_{18}$	$C_{24}H_{18}CuF_{12}N_4O_6$	$C_{46}H_{42}Cl_4N_4NiO_6$	$C_{44}H_{38}N_4NiO_6$	$C_{46}H_{42}Cl_4CoN_4O_6$
Mol. weight	902.15	2843.60	749.96	947.35	777.49	947.57
Color, habit	Green prism	Green plate	Green prism	Green plate	Yellow plate	Orange block
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group, Z	P-1, 2	P2(1)/n, 2	P2(1)/c, 2	P2(1)/n, 4	P2(1)/c, 2	P2(1)/n, 2
a [Å]	10.3756(9)	8.7395(9)	8.510(2)	9.7146(6)	9.3654(6)	12.0885(5)
b [Å]	12.1480(9)	24.597(2)	20.290(6)	22.0514(15)	22.1464(15)	9.0020(4)
c [Å]	15.5456(12)	26.428(2)	9.635(3)	20.6655(14)	9.8255(6)	20.0771(9)
α [°]	81.548(4)	90.00	90.00	90.00	90.00	90.00
β [°]	76.475(5)	93.661(5)	114.450(6)	91.609(4)	112.103(2)	92.6610(10)
γ [°]	73.419(4)	90.00	90.00	90.00	90.00	90.00
V [Å^3]	1819.1(3)	5669.5(9)	1514.4(8)	4425.2(5)	1888.1(2)	2182.45(16)
Density [g cm^{-3}]	1.647	1.666	1.645	1.422	1.368	1.442
Temperature [K]	173(2)	153(2)	203(2)	173(2)	120(2)	100(2)
X-ray wavelength	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
μ [mm^{-1}]	0.715	0.965	0.840	0.733	0.569	0.692
Absorption corr.	None	Multi-scan	Multi-scan	Multi-scan	None	Multi-scan
Trans min/max	0.529/1.000	0.674/0.746	0.618/0.746		0.885/1.000	
θ_{min} [°]	1.35	1.13	2.01	1.35	2.35	2.48
θ_{max} [°]	27.93	27.91	28.20	28.23	33.14	30.04
Reflections						
Collected	13039	35851	13521	31082	57124	24434
Independent	7975	12747	3412	10086	7129	6344
Observed	6027	9274	2474	7011	6225	5895
Threshold expression	$>2\sigma(I)$	$>2\sigma(I)$	$>2\sigma(I)$	$>2\sigma(I)$	$>2\sigma(I)$	$>2\sigma(I)$
H atom treatment	Constrained	Constrained	Constrained	Mixed	Mixed	Mixed
$\Delta\rho$ max/min, e/Å^3	1.002/−0.761	1.235/−1.252	0.674/−1.095	0.359/−0.789	1.472/−0.804	0.519/−0.271
R_1 (observed)	0.0795	0.1190	0.0739	0.0513	0.0506	0.0323
wR_2 (all)	0.2147	0.2632	0.2333	0.1528	0.1535	0.0873

using EADP commands. The position of the two amide protons (H13 and H23) was allowed to be refined; all other hydrogen atoms were included in calculated positions and allowed to ride.

Compound 5: Data were corrected for absorption using *SADABS*. The position of the amide proton was allowed to be refined; all other hydrogen atoms were included in calculated positions and allowed to ride.

Compound 6: Data were corrected for absorption using *SADABS*. The position of the amide proton was allowed to be refined; all other hydrogen atoms were included in calculated positions and allowed to ride. Table 1 provides crystallographic data for **1**–**6**. CCDC-697901–697906 contain the supplementary crystallographic data for the present paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data-request/cif.

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