FULL PAPER

Generation of [2×2] Grid Metallosupramolecular Architectures from Preformed Ditopic Bis(acylhydrazone) Ligands and through Component Self-Assembly

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Dedicated to Professor Neil Bartlett on the occasion of his 75th birthday

Ditopic bis(acylhydrazone) ligands, derived from the reactions of carbohydrazides with 2-phenylpyrimidine-4,6-dicarbaldehyde and designed for grid formation with octahedrally coordinating transition-metal ions, exhibit a varied coordination chemistry depending upon the degree of their deprotonation. The neutral acylhydrazones are relatively poor ligands and are seemingly involved in multiple, labile complexation equilibria varying with the solvent and the particular metal salt in solution; nevertheless, grid complexes of different forms can be isolated in the solid state. Although only limited study has been made of the singly deprotonated ligands, grid species appear to be much more readily isolated. With the doubly deprotonated ligands, grid formation is strongly favoured in both the solution and solid states. As a consequence, the grid structures form spontaneously in the presence of a base by self-assembly from their components without need to preform the ditopic ligands. Extensive structural studies have been carried out both to establish the grid structures and to analyse the nature of the supramolecular interactions possible for neutral and charged grid species.
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Introduction

Metallosupramolecular chemistry has developed a wide range of fascinating multicomponent coordination architectures generated by self-assembly from suitably designed ligands and specific metal ions.[1–12] The structure of the ligand bears the molecular information, as a message in molecules, that is processed through the coordination algorithm of the metal ion. Grid-type metallosupramolecular entities are of special interest, as they represent regularly positioned arrays of metal ions that may display novel optical, electronic and magnetic properties.[8,12,13] In particu-

lar, [2×2] tetranuclear grids have been extensively studied by our group.[8] We describe here developments towards classes of [2×2] grids presenting novel structural and functional characteristics.

Design Features

The "parent" [2×2] grid architectures incorporate ditopic ligands based on pyridine (py) and pyrimidine (pym) groups in a py-py-pym-py-py sequence amounting to two tridentate terpyridine-type coordination centres (structure **L**).[8] Replacement of a py group by an isosteric hydrazone unit presents considerable synthetic advantages as well as other novel properties. It may be achieved by condensation of a central pyrimidine-4,6-dicarbaldehyde with either a pyridine-2-hydrazine or a hydrazide (Figure 1, routes leading to products **A** and **B**, respectively), thus generating ditopic ligands incorporating two hydrazone functions as central groups of two tridentate metal coordination centres. Ligands containing two unsubstituted hydrazone units (Figure 1) possess two ionisable sites[12,14–19] that may serve to modulate (i) the coordination properties of the ligands, (ii)

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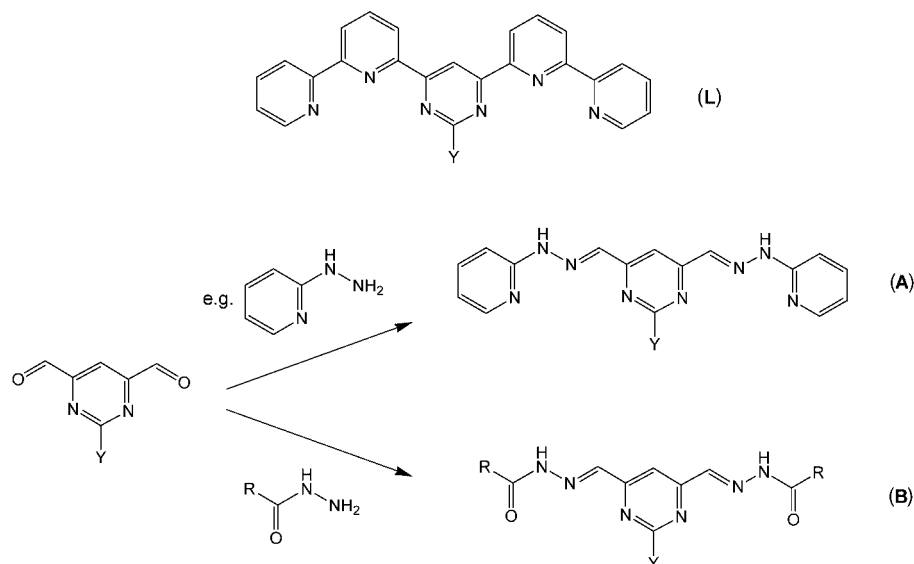
Figure 1. The parent [2×2] grid-forming bis(bipyridyl)pyrimidine ligand **L** and synthetic pathways to isosteric hydrazone (**A**) and acyl-hydrazone (**B**) analogues. Note that the bis(tridentate) form shown is but one of the configurations possible for such ligands.

the optical electronic and magnetic properties of the grid complexes, as well as (iii) the communication between external effectors and the metal centres.

In addition, the py-hydrazone ligands (**A** in Figure 1) may be fitted with side chains that will extend along the axis perpendicular to the mean plane of the four metal cations in the grid,[20] whereas for the grids formed from acylhydrazone ligands (**B** in Figure 1), the R side chains extend laterally. Thus, grid formation from these two types of ligands results in multiple "axial" and "lateral" functionalisation. Furthermore, the acylhydrazone groups may also bear axial side chains, resulting in grids presenting a total of sixteen substituents that can be of two different types.

Finally, the hydrazone-based ligands need not to be preformed, as they may form directly from their components and the metal ions in a single overall process in the course of the self-organisation of the grid architecture (Figure 2). Component self-assembly has a long history in coordination chemistry involving carbonyl condensation reactions.[21] Multicomponent/multinuclear self-assembly has been shown to take place in the spontaneous build-up of another type of [2×2] grid[22] and has been further exploited recently.[11]

Grid-type complexes formed from hydrazone-containing ligands display several features of great interest: (i) easy synthetic access from preformed ligands or by component
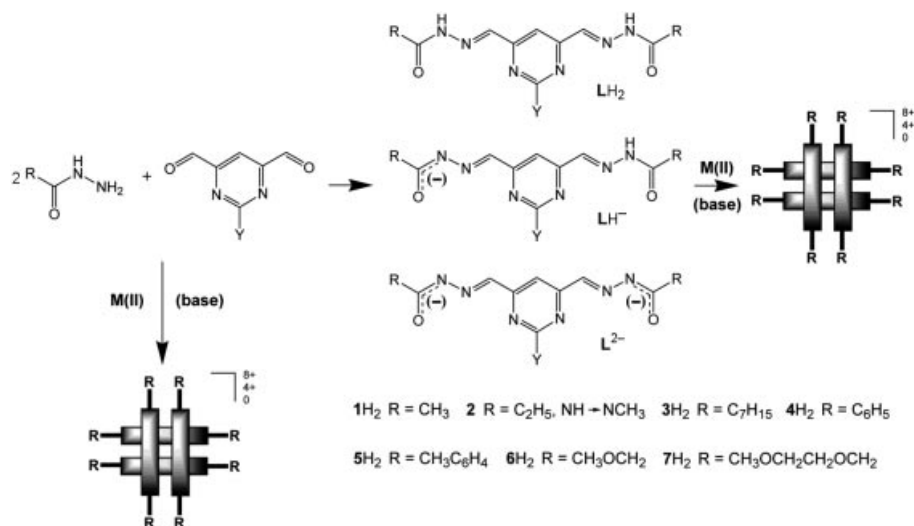

Figure 2. Formation and ionisation of a bis(acylhydrazone) derived from a pyrimidinedicarbaldehyde, with an idealised representation of the laterally functionalised grid, which may be formed by complexation either from the preformed ligand or by reaction with its constituents. Only the bis(tridentate) form of the ligand is shown. The seven particular acylhydrazones studied in the present work are listed (Y = phenyl in all cases).

self-assembly; (ii) multiple functionalisation; (iii) response to external effectors. We have undertaken studies towards the exploration and the exploitation of these different aspects of the potentialities offered by such grid complexes of the [2×2] type as well as of other types.

The readily ionised ligands of type **B** (Figure 2) provide functionalised grid complexes, giving rise to quartets of pairs of "lateral" functional groups. Crystal structure determinations on a range of these complexes with M^{II} transition-metal ions give indications of a variety of labile interactions possible in grid systems, which might be exploited in supramolecular chemistry.

Results and Discussion

1. Bis(acylhydrazone) Ligand Synthesis and Characterisation

The neutral, protonated forms of the bis(acylhydrazone) ligands presently described have all been obtained by double-condensation reactions of 2-phenylpyrimidine-4,6-dicarbaldehyde with carbohydrazides (designated henceforth as acylhydrazines). It is possible to conduct these reactions with a much greater variety of acylhydrazines, work which will be the subject of other publications,[23] and, of course, to vary the nature of the dicarbaldehyde. Characterisation of the reactions between the phenylpyrimidinedicarbaldehyde and acylhydrazines in homogeneous solution is complicated by the low solubility of the products in most solvents, as well as by changes in the form of the dicarbaldehyde in different solvents (Figure 3). The dicarbaldehyde, as obtained directly from the partially aqueous final synthetic medium,[24] is hydrated to a degree and thus present as a mixture of forms, even though it does crystallise well from diethyl ether. In aprotic solvents such as chloroform or acetonitrile, the ^1H NMR spectrum shows predominantly peaks attributable to the true aldehyde only (even in the presence of low concentrations of water present in the

undried solvents), whereas in methanol only an extremely weak –CHO signal of the aldehyde species can be discerned, and the bulk (99%) of the compound appears to be present as its bis(hemiacetal), giving rise to a CH resonance at $\delta = 5.54$ ppm, a similar weak resonance at $\delta = 5.53$ ppm along with the aldehyde peak at $\delta = 10.09$ ppm, consistent with the presence of ca. 1% mono(hemiacetal)monoaldehyde. We presume that, in the absence of an acid catalyst, further reactions to give acetal species must be very slow.

Fortunately, the hemiacetals are labile, since addition of an acylhydrazine to a methanol solution of the dicarbaldehyde results in the appearance of new peaks corresponding to hydrazide-N addition products within the time required for mixing the reagents and recording the spectrum. Typically after a period of some tens of minutes at room temperature for 2:1 molar mixtures of acylhydrazine and dicarbaldehyde, the bis(acylhydrazone) derivatives of the dicarbaldehyde begin to precipitate from such solutions, indicating that elimination reactions of the addition intermediates are also relatively rapid. The insolubility of the bis-(acylhydrazone) is commonly such that it is the material precipitated even from solutions in which the molar ratio of reactants is 1:1. Consistent with an inhibition of the reaction by acetal formation in methanol, product precipitation occurs much sooner (within a few minutes) in acetonitrile. In the particular case of benzoylhydrazine, the initial precipitate obtained from acetonitrile solvent appears to be amorphous and even oily but slowly (over days) transforms largely into clusters of pale yellow needles, indicating that the immediate product could be a mixture of stereoisomers.[25,26] A further indication of this is that, in the presence of some M^{II} ions (M = Mn, Zn), the precipitate, which still does not contain the metal ions, deposits more slowly and appears to be entirely crystalline. Perhaps this is because the precipitation of one form is retarded by complexation, even though complexation by both stereoisomers is well-established for simple acylhydrazones,[26,27] and (see below) at least two forms are still present in the precipitate. Up to the point of precipitation in solutions not containing
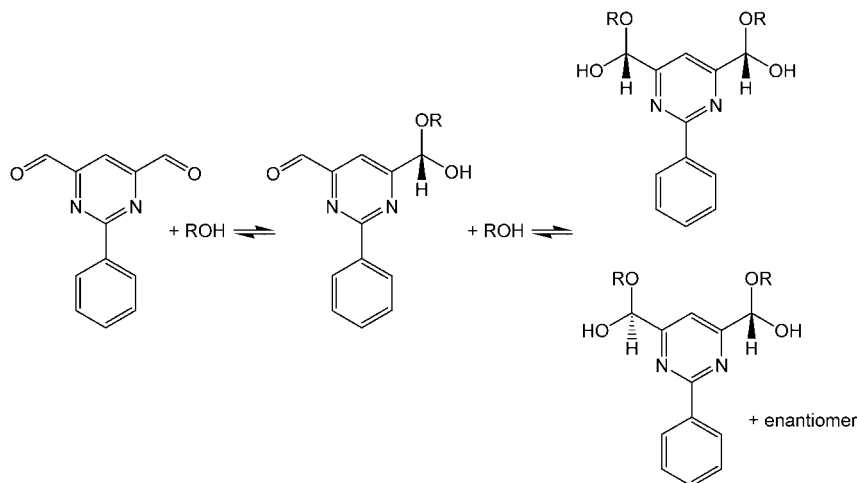

Figure 3. Hydrate (R = H) and hemiacetal (R = alkyl) formation reactions of 2-phenylpyrimidine-4,6-dicarbaldehyde.

metal ions, strong signals near $\delta = 5.7$ ppm are consistent with the fact that addition intermediates are the dominant solution species, at least two being apparent.

For the hydrazides derived from methoxy- and methoxyethoxyacetic acid, solvents can be found in which all components stay soluble up to the point of homogeneous equilibrium. Here, at concentrations of ca. 5×10^{-3} mol L^{-1}, NMR spectroscopy shows that small but detectable concentrations of species containing a tetrahedral methine centre are present even after several days at room temperature in acetonitrile, and over relatively short time periods (at least 1 h) in this solvent, the methoxyacetyl system seems simply to be involved in an addition equilibrium where a significant fraction of dicarbaldehyde is present. The addition of a metal ion such as Zn^{II} to a mixture of acylhydrazine and dicarbaldehyde has multiple effects, including an initial release of dicarbaldehyde, presumably as a consequence of coordination of the acylhydrazine reactant, though ultimately there is a modest acceleration of the formation of the acylhydrazone. The situation is simpler in dimethyl sulfoxide solvent, where an addition equilibrium appears to be very rapidly established and is then very slowly displaced towards the elimination products (hydrazones) unless Zn^{II} is added, in which case, for the addition of one molar equivalent, the spectrum changes over a period of minutes at ambient temperature towards that of the "free" bis(acylhydrazone) in this solvent. If Ga^{III} is used as catalyst, the reaction seems to be complete within the time of mixing of the reagents. Thus, it can be deduced that there is efficient Lewis acid catalysis of acylhydrazone formation in dmso.

The solids that precipitate commonly from preparative mixtures can be dissolved in solvents such as dmso and do not show ^{1}H spectral resonances near $\delta = 5.7$ ppm, nor do they appear to react with the low concentrations of water present in such solvents. In most cases, however, at least two NH resonances of different intensity are detectable, indicating that stereoisomers are present (Figure 4). For related grid-forming ligands derived from thiocarbonodihydrazide,[19b] it has been established by a crystallographic study that the most readily crystallised isomer is not that ultimately found in the grid complexes, intramolecular hydrogen bonding being suggested as a factor favouring the form observed. That the proton complex of the anionic ligand has coordination characteristics very different from those of its transition-metal complexes is hardly surprising and has, of course, a great number of precedents.

While isomerism of acylhydrazones is usually considered to be associated with configuration about the hydrazone C=N bond, restricted rotation about the acyl-C–N bond is also possible; furthermore, there is evidence that intermolecular hydrogen bonding can give rise to multiple species in solution.[28] For bis(acylhydrazone)s, E/Z isomerisation about the hydrazone bond could give rise to at least three isomeric forms, and in several of the present hydrazones (e.g. **1**H$_2$, R = CH$_3$) the ^{1}H NMR spectra show multiple NH (and other) resonances consistent with the presence of at least two forms. For the ligand **6**H$_2$ (R = CH$_3$OCH$_2$), one NH resonance is strongly dominant, but there are pairs of methyl and methylene peaks of similar intensity, indicating that this molecule is largely in the (E,Z) form. This may also apply for the ligand **5**H$_2$ (R = CH$_3$C$_6$H$_4$), for which the spectrum shows two sets of resonances of very different intensity, although for the closely related benzoylhydrazine derivative **4**H$_2$ (R = C$_6$H$_5$), the ^{1}H NMR spectrum in [D$_6$]-
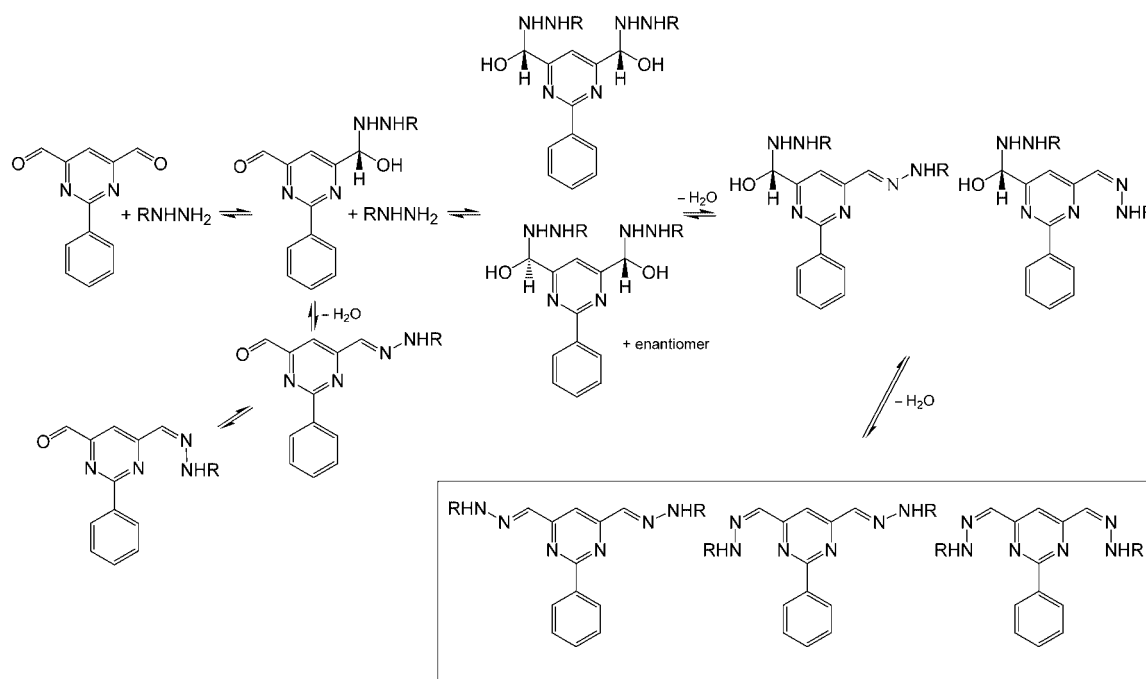

Figure 4. Species possibly present in reaction mixtures formed from 2-phenylpyrimidine-4,6-dicarbaldehyde and acylhydrazines in nonnucleophilic solvents; each stereoisomer may, of course, have other conformations than those shown.

dmso shows a single, relatively sharp NH resonance (δ = 12.40 ppm), and the NOESY spectrum (Figure 5) can be interpreted in terms of a single conformation of the (E,E) isomer. Thus, the correlation between the NH protons, C, and the CH=N protons, B, establishes the (E) configuration of the hydrazone link, while the correlation of C with the
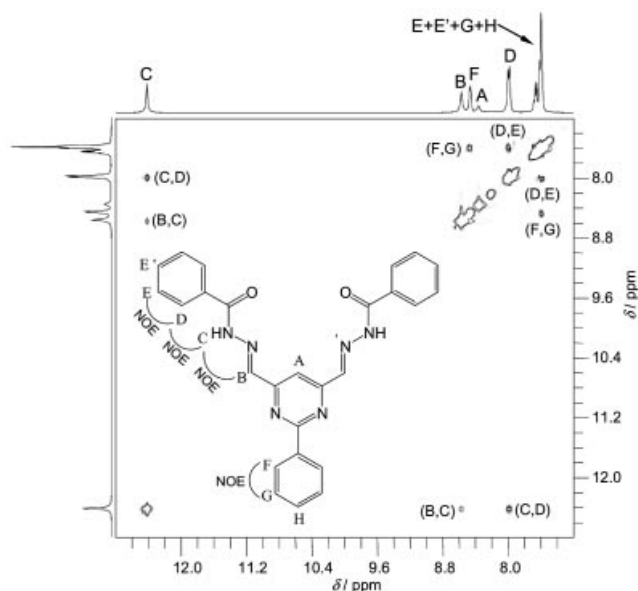

Figure 5. ^{1}H-NOESY spectrum (300 MHz, [D$_6$]dmso) for the compound **4H$_2$**; the observed correlations and the configuration deduced are shown in the inset.

aromatic protons, D, is consistent with the (E) configuration of the amide bond. Assuming that a *trans* conformation of the unsaturated-N substituents on the C(aromatic)–C(hydrazone) single bond would be favoured, the configuration deduced for this molecule is that shown in Figure 5.

This conclusion is supported by the NOESY spectrum of ligand **2** (Figure 6), which shows several important similarities to that of **4H$_2$**. A crystal structure determination for ligand **2** (Figure 7) has established not only proton locations consistent with the spectrum, but has also shown the anticipated arrangement about the C(aromatic)–C(hydrazone) single bonds. The correlation (B,C) between the methyl protons, C, and the hydrazone proton, B, is in agreement with the (E) configuration of the C=N hydrazone bond and with an *s-trans* conformation of the N–N bond substituents. Moreover, a correlation (B,F) between the hydrazone proton, B, and the phenyl protons, F, on C2 and C2′ confirms the *s-trans* conformation of the bond connecting the hyz group to the pym ring. The correlation (A,D) between the pyrimidine proton, A, on C5 and the methylene protons, D, suggests the *s-cis* conformation of the amide bond, a difference from the conformation in **4H$_2$**, which may be attributable to both steric and electronic differences between phenyl and ethyl substituents. The weak correlation (A,B) between the pyrimidine proton, A, on C5 and the hydrazone, B, shows that, in solution, the *s-trans* conformation of the C(aromatic)–C(hydrazone) bond is partially twisted because of the steric hindrance between the two acyl arms of the ligand.
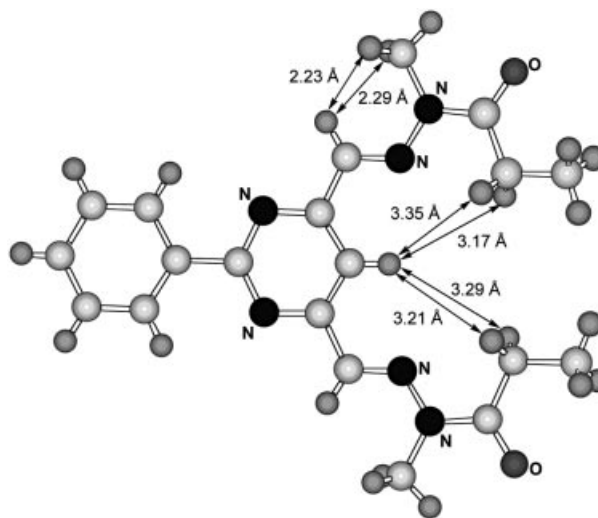
Figure 7. One molecule of **2** as found in the crystal lattice. Several intramolecular H···H separations are indicated.
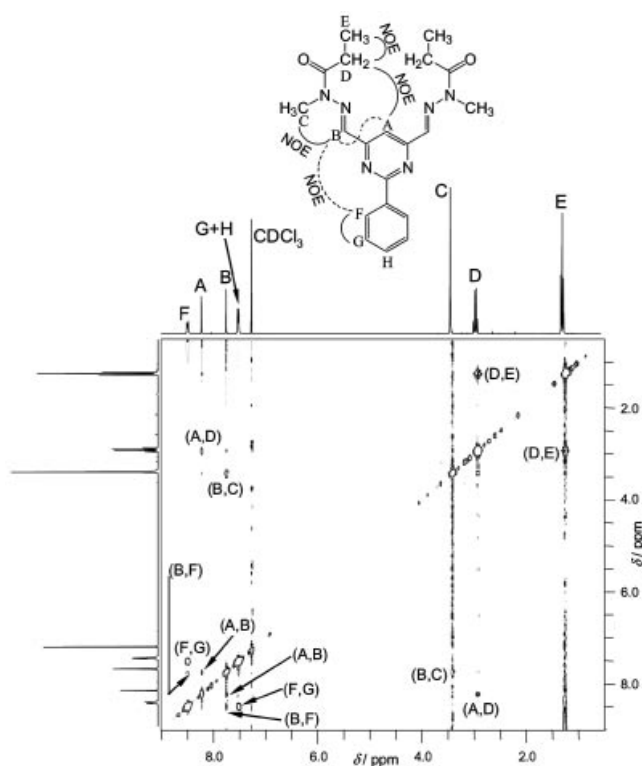

Figure 6. ^{1}H-NOESY spectrum (300 MHz, CDCl$_3$) of compound **2**; proton correlations and the deduced configuration of the molecule are shown in the inset.

2. Complexation of the Bis(acylhydrazone) Ligands

As the first transition-metal series provides a number of labile M^{II} species commonly showing octahedral coordination but with a variety of electronic properties, the most readily available members, viz. Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}

and Zn^{II}, were chosen for our initial investigations. Mn^{II} proved to be complicated to study, presumably because of both the relatively low stability of its complexes, as reflected by its position in the Irving–Williams series,[29] and its susceptibility to undergo multiple oxidation processes, even though mass spectra provided evidence that the expected grids were the initial products of synthesis. The present focus is therefore upon the remaining five metal ions, although Cu^{II} also provided some difficulties. In view of its diamagnetism, and hence the feasibility of recording high-resolution NMR spectra, Zn^{II} was generally chosen as the first metal ion to be investigated, though of course it was not expected to necessarily give the most stable complexes. As anticipated and confirmed by structural and spectroscopic studies, the bis(acylhydrazone) ligands do generate 2×2 grid complexes.

(a) Complex Formation from the Preformed Bis(acylhydrazone) Ligands

A limited degree of binding of the neutral ligands to M^{II} ions even in pure methanol or acetonitrile solvents is suggested by the fact that acylhydrazones dissolve quite readily in these solvents when, for example, the metal triflate is added, to give appreciably coloured solutions. In the case of ligand $7H_2$ (R = $CH_3OCH_2CH_2OCH_2$), which shows some solubility in CH_3CN, addition of one equivalent Zn^{II} causes significant changes in the ^1H NMR spectrum, and in general the spectra of mixtures of the neutral ligands with Zn^{II} vary somewhat with the metal ion concentration. Nevertheless, the spectra are poorly resolved and complex, showing slow, minor changes over time, indicating that several species may be present, and evaporation of the solvent generally results in reprecipitation of the free ligand. If, however, the initial reaction mixture containing Zn^{II} (as its triflate) is immediately diluted with a poorly ligating solvent such as diethyl ether, the colour changes from pale yellow to red, presumably indicating some degree of metal complexation, and ultimately both yellow (ligand) and red crystalline materials deposit from the solution. If nitromethane is used as the solvent for the reaction, complexation of the acylhydrazone appears to be more favoured than in acetonitrile, in that the solution formed has a clear red colour, but at least for bis(benzoylhydrazone) it is still the free acylhydrazone which precipitates most readily from the solution. This precipitation can be inhibited by increasing the amount of $Zn(CF_3SO_3)_2$ present, ultimately enabling the deposition of a red 2:1 complex. In the ^1H NMR spectrum of this species in acetonitrile (in which the ligand itself is completely insoluble), the *ortho* protons of the central phenyl ring appear to have undergone strong shielding, which is consistent with the binding of metal ions and the resulting rotation of the phenyl group. More interesting is the observation that with tetrafluoroborate in place of triflate, a 1:1 complex precipitates, as it does in the case of Ni^{II} when perchlorate is the associated anion. Note, however, that Ni^{II} does not guarantee success in the isolation of a neutral ligand complex, as, while $Ni(BF_4)_2$ and ligand $3H_2$ (R = C_7H_{15}) dissolve in boiling methanol to give an orange

solution, it is the ligand which precipitates on cooling, and with $Ni(NO_3)_2$ and ligand $4H_2$, the red complex which precipitates contains partly deprotonated ligand.

Overall, these observations indicate that there is a delicate balance of various solvent- and anion-dependent equilibria, including acid dissociation, involved in the interactions of neutral acylhydrazones with M^{II} transition-metal ions, complications which of course are undesirable in relation to the ultimate goal of using the complexes in solution chemistry. Both of the 1:1 complexes referred to above have the form of grids in the solid state (see crystallographic discussion) but they are nonetheless quite different, the Ni species having only the (E,E) form of the ligand while the Zn species has a 1:1 mixture of (E,E) and (Z,Z) isomers.

In contrast to the behaviour in neutral media, when a base such as triethylamine is added to the reaction mixtures, rapid changes occur, and for the Zn^{II} systems, the ^1H NMR spectra indicate the presence of distinctly different species after the addition of one and two molar equivalents of the base. The effects of adding more than two equivalents are negligible, and the final spectra are in fact identical with those obtained on dissolving the structurally characterised neutral grid species (see below) obtained by precipitation from preparative mixtures of similar composition. It is thus assumed that the species present in solution are also tetranuclear grids. In the high-resolution spectra that can be obtained with the Zn^{II} complexes, those at room temperature reflect a higher symmetry than would be expected for a grid having exactly the same structure as in the solid but that this is a reflection of site-exchange processes is indicated by the fact that at –40° in $CHCl_3$, the acetylhydrazone dianion complex shows aromatic resonances consistent with restricted rotation of the central (pyrimidine) phenyl group, giving rise to a distinction between "inner" and "outer" *ortho* and *meta* proton sites.[30]

(b) Complex Formation by Component Self-Assembly

In the absence of any added base in moderately polar and ligating solvents such as methanol or acetonitrile, the reaction between the phenylpyrimidinedicarbaldehyde and acylhydrazines in the presence of one molar equivalent of various M^{II} ions as their triflates leads commonly, as noted above, to the precipitation of the metal-free acylhydrazone. Nonetheless, the colour of the reaction medium prior to precipitation is indicative of some degree of complexation, and although the development of this colour in methanol and acetonitrile occurs over a time period similar to that required for precipitation of the acylhydrazone in the absence of the metal, in dimethyl sulfoxide it is clear that there is an efficient metal ion catalysis of hydrazone formation. When a base such as triethylamine is incorporated in the reaction mixtures, metal ion catalysis (template effect) appears to be important in all solvents, as very rapid reactions (extensive within the time of mixing) occur to give the same neutral complex species as those obtained from reactions with the preformed ligand in basic media. An advantage of performing the syntheses in this "one pot" manner is that a good solvent for all components is much more readily

found than for the reactions involving preformed ligands, so that precipitation of the product from a homogeneous solution occurs easily.

3. General Chemistry of the Grid Systems

As many of the neutral (grid) complexes show appreciable solubility in solvents in which the parent bis(acylhydrazone)s are completely insoluble, it is possible to recover the ligand from neutral complexes by their protonation upon acidification in solution. When the complex $[Zn_4(\mathbf{1})_4]$, for example, is dissolved in methanol, in which it forms an orange solution, and acetic acid is added, the colour is instantly discharged, and the neutral ligand rapidly precipitates. Significantly, the ^{1}H NMR spectrum of this material is identical with that of the "preformed" ligand, indicating it to be a mixture of species and, since the crystal structure of the neutral grid shows the presence of a single isomer of the dianionic ligand, this suggests that isomerisation of the neutral ligand is very rapid. Support for this conclusion is offered by the fact that the water-soluble complex $[Zn_4(\mathbf{6})_4]$ (R = CH$_3$OCH$_2$), when dissolved in D$_2$O, shows two sharp singlet resonances for the methyl and methylene protons, each of which become at least three peaks when acetic acid is added.

We thus conclude that ligand isomerisation cannot constitute a kinetic barrier to the formation of complexes. (It may be noted here that attempts to separate E/Z isomers of acylhydrazones by flash chromatography have been unsuccessful.[31]) Also significant is the fact that the use of a strong acid such as HCl to protonate the neutral complexes does not lead to precipitation of the neutral ligand, but instead to its hydrolysis, indicating that it should be possible to find conditions where all components (acylhydrazine, dicarbaldehyde and metal ion complexes) are in labile equilibrium.

Although neutral grid complexes do not generally show high solubility in apolar solvents, most dissolve readily in pyridine or, to a lesser extent, both in methanol and in dimethyl sulfoxide. Interestingly, the grids are frequently more soluble in a mixed solvent (protic + aprotic) than in either of its components. Preferential solubility in particular solvents results from the appropriate choice of acyl group; for example, the heptanoylhydrazine derivatives are moderately soluble in dichloromethane, the benzoylhydrazine derivatives in acetone and the tolylhydrazine complexes in benzene (and in dichloromethane but not in toluene), while the methoxy- and methoxyethoxyacetylhydrazine derivatives show some solubility in water. Acetonitrile is a useful solvent for the syntheses, both of the ligands and of their complexes, since the reactants are generally quite soluble and the desired products insoluble (while byproducts such as triethylammonium triflate are soluble), but, as indicated in the Experimental Section, a variety of simple approaches can be used successfully, and wherever either of the solvents methanol or acetonitrile has been used, it may certainly be substituted by the other. The successful synthesis of the neutral grids depends on the facile deprotonation of the coordinated acylhydrazone, and although no direct measurements of the acidity constants of the coordinated acylhydrazones used here have been made, triethylamine, in various solvents including water, sufficed to completely deprotonate ligands $\mathbf{1}H_2$ and $\mathbf{3}H_2$–$\mathbf{7}H_2$ when bound to first-row transition-metal(II) ions, indicating that the bound ligands are significantly stronger acids than the triethylammonium ion. This deduction is supported by the fact that the use of ^{1}H NMR to monitor the titration of 1:1 mixtures of Zn^{II} and various ligands with triethylamine showed shifts of the triethylamine protons consistent with complete protonation up to the point of addition of a full two equivalents of the base. Independent measurements[32] on water-soluble grids formed by pyrimidinedicarbaldehyde bis(acylhydrazone) derivatives indicate that the first ligand proton is quite acidic, and that the second is removed at pH ≈ 7.

4. Crystal Structures of Acylhydrazone Complexes

Basic crystallographic data for all the complexes presently studied are summarised in Table 2, Table 3 and Table 4. Disorder associated with lattice solvent molecules, grid substituents and (in some cases) anions was a common problem, and not all the structures are of equivalent quality. In all cases, however, the nature of the metal aggregate has been established with certainty. Not all crystals obtained proved suitable for an X-ray structure determination, so that the following discussion is presented more in terms of identified grid types than in terms of the systematic variation of the ligands and metals, though certainly some ligand and metal effects are taken into consideration.

(a) Complexes of the Non-Deprotonated Ligands

(i) [Ni$_4$(4H$_2$)$_4$](ClO$_4$)$_8$

The reaction between acetonitrile-solvated Ni^{II} perchlorate and ligand $\mathbf{4}H_2$ (R = C$_6$H$_5$) in nitromethane provides a crystalline complex which may be formulated on the basis of its structure determination as $[Ni_4(\mathbf{4}H_2)_4](ClO_4)_8 \cdot 8H_2O \cdot 4CH_3NO_2$. (Elemental analysis of the dried bulk material is consistent with a formulation in which only one molecule of nitromethane of solvation is present.) The cation present in the lattice (Figure 8) is a 2×2 grid species of a form very similar to those formed with neutral hydrazone ligands[8,18,33] and remarkably similar to grids formed by the deprotonated acylhydrazones described below. It is thus a useful reference point for the whole of the present discussion.

As viewed perpendicular to the mean plane of the Ni$_4$ unit, it appears that this unit is very close to a square, but in fact there is a significant distortion towards a "butterfly" form reflected in the fact that the centroids of the two Ni···Ni diagonals are separated by 0.685 Å. This can be seen largely as a consequence of the fact that the metal–donor-atom array for a given ligand unit does not have the idealised geometry[34] shown in Figure 6, but instead is such
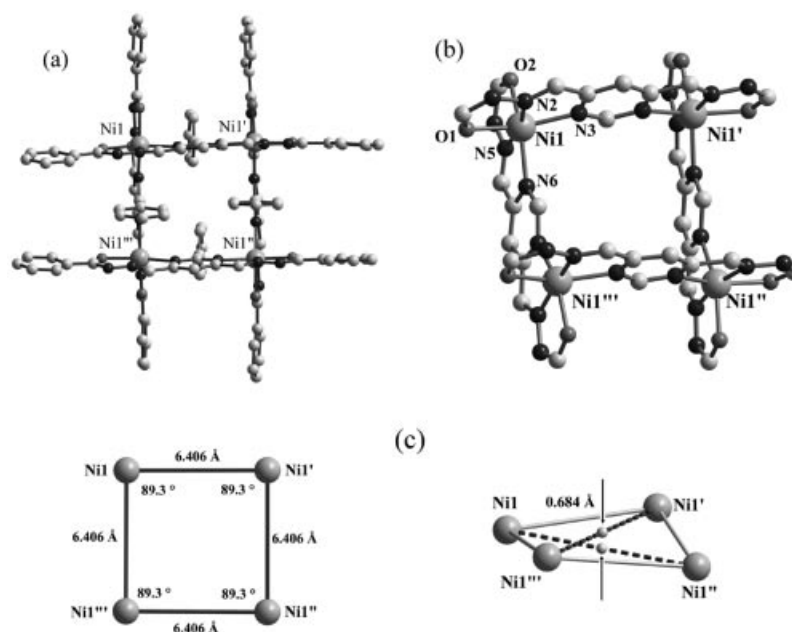
Figure 8. (a) A view of the full grid unit perpendicular to the Ni$_4$ plane and (b) a view of the grid in perspective, without phenyl substituents, to show the metal ion coordination; (c) aspects of the geometry of the Ni$_4$ unit.

that the Ni–N(hydrazide) vectors are slightly inclined to one another (here at 15°). This can be accommodated and allows six-coordination of the metal (by binding of a second ligand) by displacing two metal atoms in the same direction out of the idealised square which would be formed if the incline was 0°. As will be seen in considering other grids (see ahead), however, this is perhaps not the only factor of influence (Figure 9).
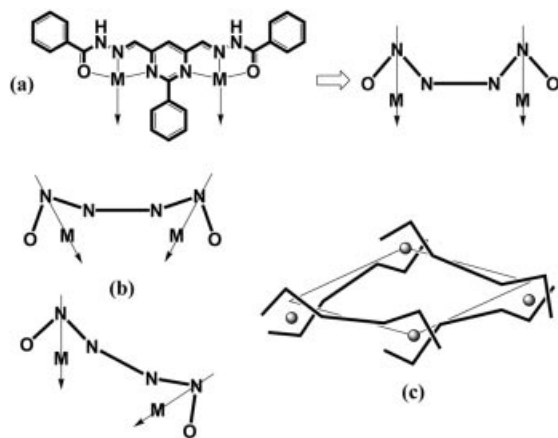

Figure 9. (a) An idealised structural representation of a metal-bound ditopic acylhydrazone and its schematic equivalent, showing parallel orientation of the M–N(hydrazide) vectors. (b) Schematic representations, with exaggerated inclination, of an actual metal-bound ditopic acylhydrazone, shown both in a form where the M···M vector is horizontal and where the O···N(inner) vector is horizontal. (c) Schematic representation of a grid formed by a real acylhydrazone, the metal atoms (grey spheres) located relative to a perfect square.

Ni^{II}-donor atom bond lengths (Table 1) reflect the expected weaker donor ability of the pyrimidine-N atom relative to the hydrazide-N atom, and C–N and C–O bond lengths within the hydrazide unit indicate significant delocalisation and hence an enhanced donor ability of the hydrazide-O atom relative to a simple carbonyl-O atom. While it is conceivable that the bound ligand is in fact deprotonated and that H$_3$O$^+$ and not H$_2$O is present in the lattice, each uncoordinated hydrazide-N atom has a short contact to oxygen (ca. 2.7–3.2 Å), suggesting that it is indeed protonated, nevertheless involved in strong hydrogen bonding. The oxygen atoms involved in these contacts, interestingly, are those of perchlorate anions and not of water molecules. Unfortunately, the quality of the structure (from a twinned crystal) and disorder of both perchlorate and water entities militate against a detailed analysis of the hydrogen bonding.

When viewed down a, for example, the lattice can be considered to be made up of layers of cations, water and some of the perchlorate anions, alternating with layers of perchlorate anions and water. Thus, direct interactions between grid units do not give rise to a three-dimensional array, but within the sheets of cations (parallel to the ab plane), there is an interlocking of grid units as a result of face-to-face interactions of the terminal phenyl rings (any edge-to-face contacts being very remote). Note that, as in several analogous hydrazone complexes, each phenyl group attached to a pyrimidine ring lies within the grid and is parallel to two flanking ligand units at a distance of ca. 3.5 Å, suggesting its involvement in intramolecular stacking. The phenyl group loses its plane of symmetry perpendicular to the ring plane, so that the two *ortho* and the two *meta* protons are nonequivalent, as also seen in the solution NMR spectra of certain other complexes.[30]

Though various Ni^{II} salts react with ligand **4H$_2$** to give isolable red complexes, not all of which prove to contain the undeprotonated ligand, with most of the other metal ions studied this is not so, and the free ligand is the material

Table 1. Metal–donor-atom bond lengths in acylhydrazone grids, $[M_4(LH_n)_4]^{4n+}$.

Metal	Ligand	M–N(hydrazide) /Å	M–N(pyrimidine) /Å	M–O /Å
Ni^{II}	$4H_2$	1.978(7), 2.006(5)	2.151(5), 2.167(6)	2.066(5), 2.092(5)
Zn^{II}	$4H_2$	2.122(5), 2.138(5)[a,b]	2.170(5), 2.169(5)[a,b]	2.147(4), 2.137(4)[a,b]
		2.105(5), 2.095(5)[b,d]	2.171(6), 2.169(6)[b,d]	2.134(5), 2.127(5)[b,d]
		2.183(5), 2.142(5)[a,c]		2.038(4), 2.024(4)[a,c]
		2.133(5), 2.133(5)[c,d]		2.099(4), 2.094(5)[c,d]
Co^{II}	$4H^-$	2.02(1), 2.07(1)	2.17(1), 2.21(1)	2.058(9), 2.14(1)
		2.02(1), 2.06(1)	2.19(1), 2.24(1)	2.05(1), 2.15(1)
		2.05(1), 2.07(1)	2.19(1), 2.21(1)	2.03(1), 2.16(1)
		2.05(1), 2.08(1)	2.16(1), 2.27(1)	2.06(1), 2.119(9)
Ni^{II}	$4H^-$	1.989(4), 1.980(4)	2.199(5), 2.171(5)	2.062(4), 2.082(4)
		2.018(4), 1.981(4)	2.168(4), 2.175(5)	2.039(4), 2.120(4)
		1.994(5), 1.993(4)	2.190(5), 2.172(4)	2.060(5), 2.077(4)
		1.977(4), 1.989(4)	2.169(5), 2.175(5)	2.063(5), 2.093(4)
Co^{II}	1^{2-}	2.037(4), 2.051(4)	2.186(4), 2.211(4)	2.083(4), 2.090(3)
Ni^{II}	1^{2-}	1.993(4), 1.997(4)	2.179(5), 2.182(5)	2.059(4), 2.072(4)
		1.991(4), 1.993(4)	2.182(5), 2.189(5)	2.067(4), 2.069(4)
Zn^{II}	1^{2-}	2.060(6), 2.064(6)	2.228(6), 2.249(6)	2.115(5), 2.127(6)
		2.072(6), 2.087(6)	2.245(6), 2.256(6)	2.108(6), 2.116(6)
Fe^{II}	3^{2-}	2.085(3), 2.103(3)	2.198(2), 2.271(3)	2.095(2), 2.113(2)
Co^{II}	3^{2-}	2.038(3), 2.041(3)	2.217(3), 2.238(3)	2.085(3), 2.090(3)
Ni^{II}	3^{2-}	1.990(5), 1.992(4)	2.191(5), 2.218(5)	2.067(4), 2.073(4)
Cu^{II}	3^{2-}	1.927(3), 1.969(3)	2.198(3), 2.591(4)	2.024(3), 2.211(3)
		1.933(4), 1.973(3)	2.220(3), 2.454(3)	2.028(3), 2.165(8)
Zn^{II}	3^{2-}	2.057(3), 2.059(3)	2.245(3), 2.334(3)	2.106(3), 2.138(3)
		2.030(3), 2.033(3)	2.268(3), 2.554(4)	2.064(3), 2.146(2)

[a] Terminal Zn atoms: Zn–N(CH$_3$CN) 2.0589(5), Zn–O(water) 2.052(4) Å. [b] (E,E) Ligand. [c] (Z,Z) Ligand. [d] Zn atoms bridged by $[BF_4]^-$: Zn–F 1.975(5), 1.980(5) Å.

preferentially precipitated from nearly all solutions containing equimolar amounts of Mn^{II}, Fe^{II}, Co^{II} and Zn^{II}. With Cu^{II}, there is obviously complexation, but the product appears to undergo slow decomposition and no crystals suitable for structure determination were isolated. With Zn^{II}, a method was finally found to isolate a crystalline complex, and its structure provides an intriguing contrast with that of the Ni^{II} complex described above.

(ii) Zn^{II} Complex of $4H_2$

The $Zn(BF_4)_2$ complex of $4H_2$ may be formulated as $[Zn_8(E,E-4H_2)_4(Z,Z-4H_2)_4(OH_2)_2(CH_3CN)_2(BF_4)_2](BF_4)_{14}\cdot 7C_6H_6\cdot 3CH_3CN\cdot 3H_2O$. The stoichiometric unit (Figure 10) is a double grid, tetrafluoroborate anions serving as the links between two identical Zn_4 grid units. The grids, however, are very different from those seen in the Ni^{II} complex, in that the Zn_4 are of a rectangular, and not square, shape each being very close to planar and involving pairs of $4H_2$ in their (E,E) and (Z,Z) forms. Each metal ion is thus bound to one site of an (E,E) ligand and one site of a (Z,Z) ligand, and it is because the latter site is only didentate that the Zn centres achieve six-coordination by binding either monodentate (H_2O, CH_3CN) or bridging didentate ($[BF_4]^-$) co-ligands. (This observation raises interesting prospects for rearrangements of complexes of the ligands by changes in the oxidation state of a metal, for example, Cu, where the different oxidation states have different preferred coordination geometry.) The combination of convergent, tridentate donor sites on one ligand (E,E) with divergent, didentate sites on the other (Z,Z) presumably explains the fact that the Zn_4 unit here is essentially planar. The

Zn^{II} centres bridged by the (Z,Z) ligand are quite remote (Figure 10), indicating that paramagnetic metal ions in the same structure would be unlikely to show significant magnetic interactions.

In its (Z,Z) form, the three phenyl groups of bound $4H_2$ are placed in proximity, with similar orientations away from the coordinated metal sites. In the double Zn_4 array of the Zn^{II} complex, this means that the upper and lower surfaces parallel to the Zn_4 planes consist essentially of arrays of phenyl groups, since it is the (Z,Z) ligands which form the exterior faces. Unsurprisingly, there is strong interpenetration of these arrays from different double-grid units, which is consistent with the fact that π-stacking plays a significant role in the lattice assembly. Though the (E,E) ligands appear less accessible for intermolecular contacts, the fact that, in this configuration, the terminal phenyl groups project laterally rather than axially allows significant "slipped" overlap between staggered arrays of one set of these ligands, while the other set has at most remote contacts between the terminal carbon atoms but is involved in stacking with the lattice benzene molecules. The lattice water and acetonitrile molecules, as well as the $[BF_4]^-$ anions, are involved also in various contacts between themselves and with aromatic rings, so that the full gamut of weak forces appearing to be operative is highly complicated.

Although its crystal structure has not been determined, it is worth noting that a 2:1 complex of $4H_2$, $Zn_2(4H_2)$-$(CF_3SO_3)_4\cdot 2H_2O\cdot CH_3CN$, is readily isolated. While it is perhaps surprising that the binding of two cations does not lead to facile acid dissociation of the ligand, it may be that repulsion between the cationic centres is relieved by adopt-
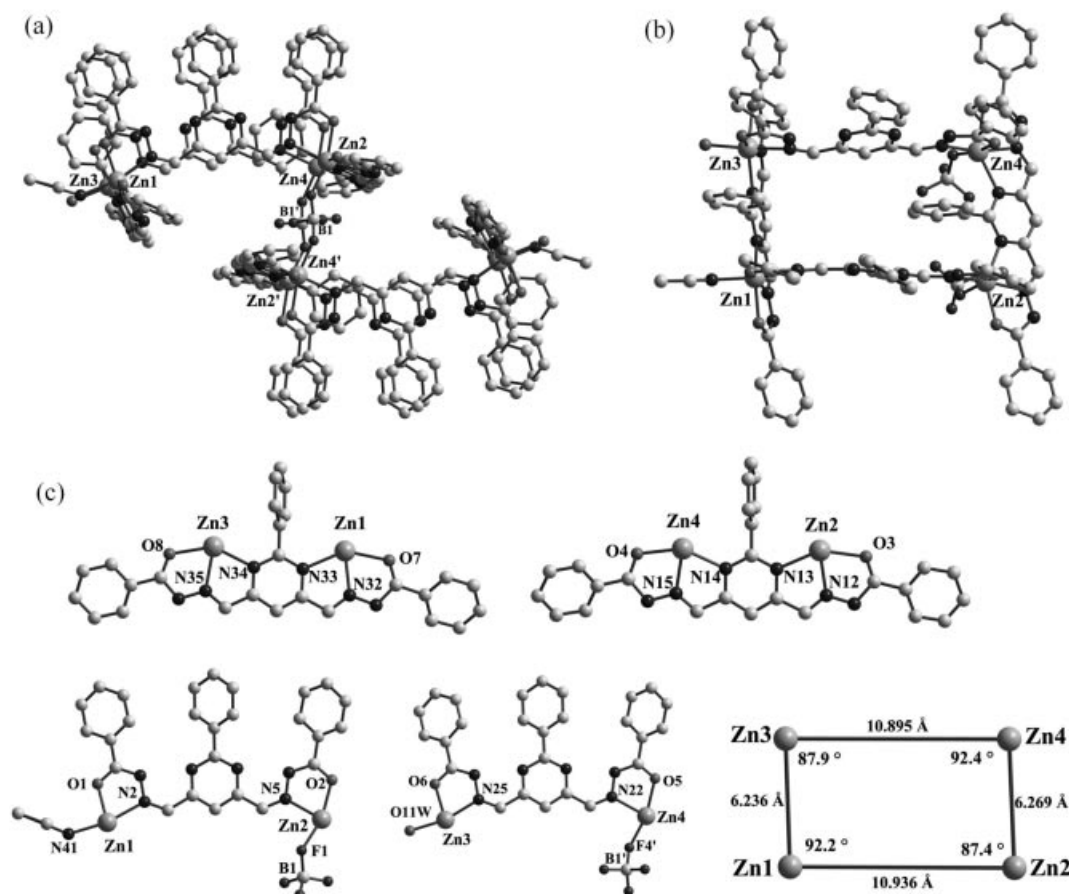
Figure 10. (a) A view of the "double-grid" unit and (b) an approximately orthogonal view of one rectangular grid; (c) geometry of the Zn_4 unit and views, perpendicular to the mean plane of the pyrimidine ring, of the two types of ligand unit [lower: (*Z,Z*); upper: (*E,E*)] found in each rectangle.

ing the (*E,E*) configuration seen in the 1:1 complex and which places the two metals at positions quite remote from one another, thus minimising the effect of the second metal on the hydrazide NH proton influenced more closely by the first metal.

(b) Complexes Containing Partly Deprotonated Ligands

(i) [Co₄(4H)₄](BF₄)₄

While rational syntheses based on monodeprotonation of the acylhydrazones are presumably possible, the first complex of this type was isolated from a reaction medium (involving ligand $4H_2$) to which no base was deliberately added, a result which parallels those concerning several thioacylhydrazone analogues,[19] although it has proved difficult to reproduce. Under conditions of formally correct stoichiometry, it appears to be the complex [Co₄(**4**)₂(**4H**)₂](BF₄)₂ which precipitates. The crystal selected from the initial preparation was characterised by a single-crystal X-ray diffraction study, from which the composition [Co₄(4H)₄]-(BF₄)₄·7CH₃CN was deduced, as well as the presence of a quadruply charged [2×2]Co₄[II] grid species (Figure 11), very similar in form, including the "butterfly" nature of the M_4

unit, to that seen in the complex [Ni₄(**4H₂**)₄](ClO₄)₈· 8H₂O·4CH₃NO₂ (Figure 8). While the structure is somewhat more complicated to analyse than those of related neutral M^{II} complex species incorporating fully deprotonated ligands, there are some remarkable similarities between them all (see ahead). Assuming the residual proton of **4H⁻** to be localised on one N-centre, isomeric forms of the grid are possible, and thus it is unfortunate that NH protons were not located in the structure solution. However, a view of the cationic grid unit shows that each ligand unit is unsymmetrical, with a significant but different twisting distortion of one hydrazide entity on each, so that the idealised isomeric form is that of S_4 symmetry shown also in Figure 11. The actual symmetry of the lattice is such that the grid units have no symmetry and thus all four Co atoms are nonequivalent. In agreement with the fact that the bent ends of the ligands are the sites of protonation, the Co–O bond lengths (Table 1) are greater than those for the less distorted units, though comparison (ahead) with data for fully deprotonated complexes of Co[II] indicates that the overall effect of protonation/deprotonation on bond lengths is quite slight and may not be simply related to differences in the formal charge assigned to the donor atoms. Further-
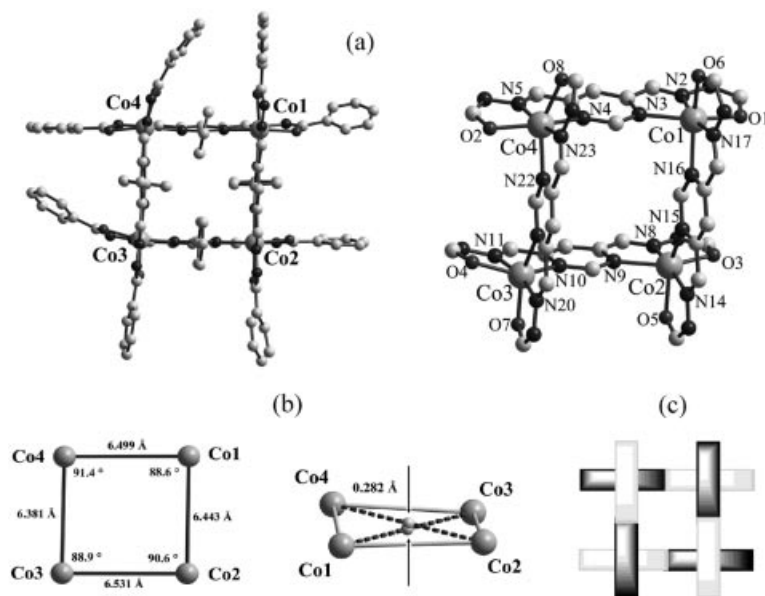
Figure 11. (a) Approximately orthogonal views of the grid unit present in $[Co_4(\mathbf{4H})_4](BF_4)_4\cdot 7CH_3CN$; (b) aspects of the geometry of the Co_4 unit and (c) the idealised representation of the grid in terms of ligand units that are unsymmetrical because of partial deprotonation.

more, given that force constants for bond stretching and bending for light elements considerably exceed those for transition-metal–donor-atom bonds,[33] it is reasonable that it is the ligand which imposes nearly a fixed coordination geometry on the metal.

A feature of the lattice of $[Co_4(\mathbf{4H})_4](BF_4)_4\cdot 7CH_3CN$, which is not found in that of $[Ni_4(\mathbf{4H_2})_4](ClO_4)_8\cdot 8H_2O\cdot 4CH_3NO_2$ presumably because of the need to accommodate a greater number of anions, is the three-dimensionality of the interactions between grids, a feature rather commonly observed in neutral grids. Every grid in the lattice of $[Co_4(\mathbf{4H})_4](BF_4)_4\cdot 7CH_3CN$ can be considered to be surrounded tetrahedrally by four others in a way which involves a kind of "slipped stacking" of pairs of hydrazone ligands from separate grids, so that every (grid)(grid)$_4$ unit has idealised S_4 symmetry (Figure 12). This extended tetra-

hedral interlocking of grids gives rise to a lattice which, when viewed down c, for example, appears to consist of columns composed of grids in alternating, inverted pairs separated by channels into which protrude the "bent" ends of the ligands and which contain partially disordered $[BF_4]^-$ anions and acetonitrile solvent as well. Some anions and solvents can also be considered to be located within the grid columns, and in both environments there are numerous contacts to aromatic entities.

(ii) $[Ni_4(\mathbf{4})_{2.5}(\mathbf{4H})_{1.5}](NO_3)_{1.5}\cdot CH_3OH\cdot 0.5(C_2H_5)_2O$

The isolation of a complex of a deprotonated thiohydrazone ligand by use of the metal nitrate in methanol has been suggested[19d] to be a consequence of the consumption of acid by a (metal-catalysed) reduction of nitrate by the solvent. Though this seems less likely for acetonitrile, the
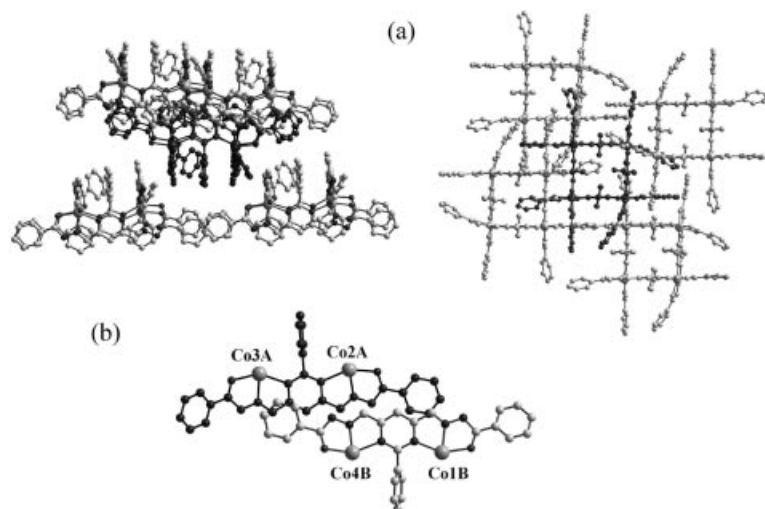

Figure 12. (a) Orthogonal views of a grid unit (atoms in black) and its environment of four other grids; (b) atom contacts within the proximal ligand units of separate grids.

presently isolated complex of ligand **4**H$_2$ with Ni(NO$_3$)$_2$ was recrystallised from methanol, and both needle and plate-like crystals were apparent in the product mass. As with the Co^{II} complex above, analysis of the bulk product corresponded to a composition, [Ni$_4$(**4**)(**4**H)$_3$](NO$_3$)$_3$, which is different from that deduced from solution of the crystal structure for a selected plate-like crystal. Perhaps the simplest explanation of all the present results, including the isolation of true complexes of the uncharged ligands from the most (Brønsted) acidic solvent, nitromethane, is that coordination of the ligand results in partial dissociation and the formation of multiple species related by proton loss in solution, and various species precipitate, depending upon subtle aspects of lattice interactions. The solid-state structure of the material, which was assigned the composition [Ni$_4$(**4**)$_{2.5}$(**4**H)$_{1.5}$](NO$_3$)$_{1.5}$·CH$_3$OH·0.5(C$_2$H$_5$)$_2$O (presumably indicating it to be a mixture of different protonated forms) on the basis of its structure solution, shows various similarities to that of [Co$_4$(**4**H)$_4$](BF$_4$)$_4$·7CH$_3$CN, including the bending of a terminal phenyl group unit (Figure 13) and the tetrahedral coordination of one grid unit by four others involving close contacts of atoms within parallel ligand planes of separate grids. Perhaps in reflection of the higher degree of ligand deprotonation, the Ni$_4$ unit is closer to a true square than that in the complex of the undeprotonated ligand.
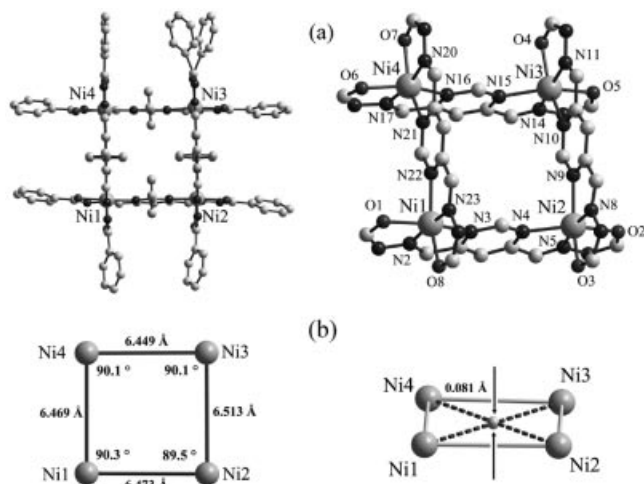

Figure 13. (a) Orthogonal views of the cationic grid unit in[Ni$_4$-(**4**)$_{2.5}$(**4**H)$_{1.5}$](NO$_3$)$_{1.5}$; (b) aspects of the geometry of the Ni$_4$ unit of the grid.

(c) Complexes of the Doubly Deprotonated Ligands

Structural studies within the group of ligands presently described have been limited to the Co^{II}, Ni^{II} and Zn^{II} complexes of ligand **1**H$_2$ and the Fe^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} complexes of ligand **3**H$_2$. All are confirmed to be [2×2] grids, but significant variations in both the grid core and the lattice interactions are seen.

Neutral Grids of Ligand 1^{2-}

A common feature of the Co, Ni and Zn complexes of **1**$^{2-}$ is the high degree of hydration of the solids.

(i) [Co$_4$(1)$_4$] Complex: From the structure determination, the Co^{II} complex is formulated as [Co$_4$(**1**)$_4$]·8CH$_3$OH·16H$_2$O and contains a familiar grid unit with a butterfly-form Co$_4$ aggregate and with Co–N and Co–O bond lengths all very similar on average to those of [Co$_4$(**4**H)$_4$](BF$_4$)$_4$·7CH$_3$CN. There is also a similarity to this complex in that the lattice can be regarded as involving tetrahedrally connected grid units, though the slipped stacking observed here is associated also with bridging of grids by water molecules forming hydrogen bonds to hydrazide-*N* and acetyl-*O* atoms of essentially orthogonal ligands of adjacent grids. Disorder in the solvent molecule array makes any detailed interpretation of its nature difficult, but it is clear that hydrogen bonding plays a major role in the assembly of the lattice.

(ii) [Ni$_4$(1)$_4$] Complex: The structure of [Ni$_4$(**1**)$_4$]·≈18H$_2$O (Figure 14) displays several significant differences from that of the Co complex, which may be to some extent dependent upon their differences in solvation, although the grid unit is overall very similar, despite the twofold and not fourfold symmetry associated with its different space group. The distortion of the Ni$_4$ unit from planarity, as measured by the distance between the centroids of the diagonals (0.216 Å vs. 0.925 Å for the Co species) is considerably smaller, and this is associated with a packing of the grid units which reflects their twofold symmetry in that although each grid is surrounded by four others in an essentially tetrahedral array (involving, once again, "slipped stacking" of parallel ligand units), two neighbours are slightly more remote than the others, so that the lattice, when viewed down *a*, has the appearance of being built up from staggered double-layers of grids. Despite its partial disorder, the water molecule array clearly involves hydrogen bonding to all the hydrazide-*N* and acetyl-*O* atoms of every grid as well as water–water interactions (Figure 15), forming chains that link the grids additionally to any stacking, and perhaps it is the importance of this extensive set of interactions that results in the distortion of the intergrid stacking (relative to that in the Co complex). Another possible consequence is
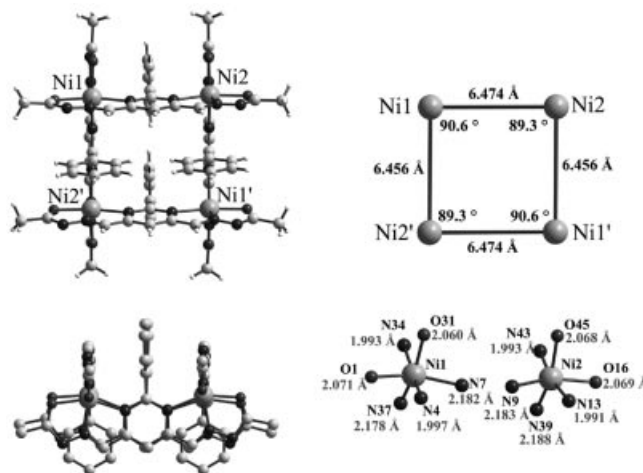

Figure 14. Structure and geometry of the grid unit present in [Ni$_4$(**1**)$_4$]·≈18H$_2$O.

the fact that grids lying along the columns seen end-on down *a* are now close enough for contacts to occur between the acetyl-*CH₃* groups and the acetyl-*O* atoms (C···O 3.66 Å). (For coplanar grid units of the Co structure, these atoms are >4 Å apart.) Other adjacent grids in the Ni complex have acetyl-*CH₃*/acetyl-*CH₃* and acetyl-*CH₃*/phenyl-*C* contacts of also ca. 3.7 Å.
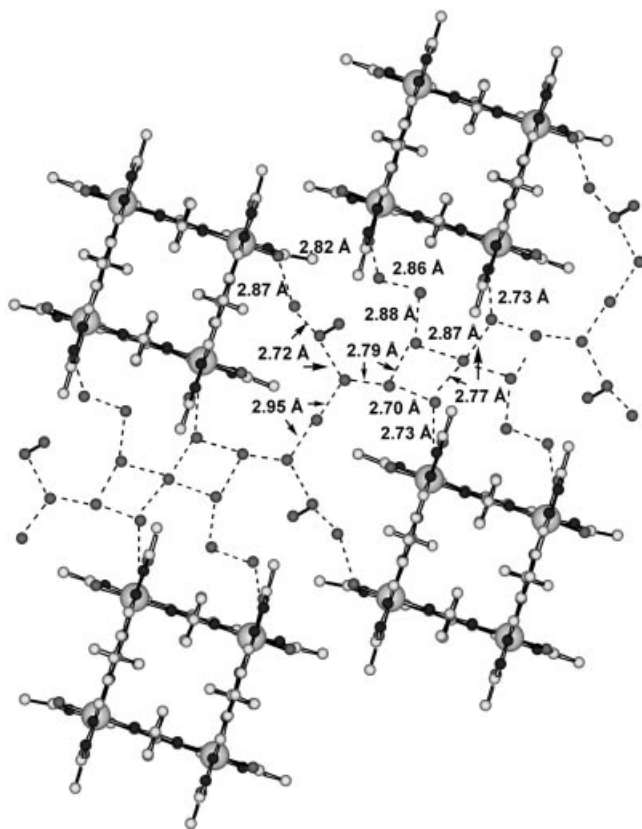

Figure 15. A partial view of the hydrogen bond network present in [Ni₄(**1**)₄]·≈18H₂O.

(iii) [Zn₄(1)₄] Complex: The structure of [Zn₄(**1**)₄]·≈18H₂O is practically isostructural with that of its Ni analogue. Metal–donor-atom bonds are slightly longer to Zn^{II} than to Ni^{II}, but the distortion of the Zn₄ unit from planarity (diagonal centroid separation 0.191 Å) is marginally smaller. Evidence for intergrid interactions is the same, so that again it appears that hydrogen bonding to the apolar grid is an important interaction.

Neutral Grids of Ligand 3²⁻

Complexes of the ligand **3²⁻** make up the most nearly complete series of metallogrid complexes structurally characterised. All five metals (Fe, Co, Ni, Cu, Zn) studied form the expected [2×2]M₄^{II} grids, but with some significant differences in structure both within the series and between their analogues in the series formed by **1²⁻**. Introduction of a C₇H₁₅ "tail" in **3²⁻** in place of the methyl group of **1²⁻** leads to a much lower degree of hydration of the [M₄(**3**)₄] series, where either tetra- (Fe, Co, Ni) or di- (Cu, Zn) hy-

drates are formed. The retained water molecules act in isolation to form bridges, again involving hydrazide-*N* and acyl-*O* acceptors, between grids. Across the [M₄(**3**)₄] series, there is remarkably little variation in M–O and M–N(pyrimidine) distances (Cu^{II} excepted – see below) and only the M–N(hydrazide) bond lengths show the variations expected on the basis of changes in effective nuclear charge across the transition-metal group. For the Co, Ni and Zn complexes of **3²⁻** and **1²⁻**, there are no significant differences in analogous M–O and M–N bond lengths, but considerable differences are found in the distortions of the M₄ units from planarity. Thus, in all [M₄(**3**)₄] complexes, the diagonal–centroid separations are ca. 1 Å and do not diminish dramatically across the series, as seems to be the case for the **1²⁻** complexes. The origins of this difference are obscure, especially given that despite such an "internal" difference, "externally" all the grids (from both ligands) display similar properties in that they form very similar lattices (space group differences accommodated). A particular common feature is the tetrahedral coordination of any one grid by four others, associated in all cases with a seeming stacking of ligand units and, given its persistence, indicating that, whatever the nature of the interactions giving rise to these contacts, they are an important means of association of acylhydrazone grids.

The Fe^{II}, Co^{II} and Ni^{II} complexes of ligand **3²⁻** are isostructural, while the analogous Zn^{II} complex crystallises in a cell of lower symmetry associated with a lower degree of hydration. Useful for more detailed consideration of the [M₄(**3**)₄] structures is the form of [Cu₄(**3**)₄]·2H₂O, which, although unique as a structurally characterised grid, provides a lattice that may be considered to be the "Rosetta Stone" for the interpretation of all the present structures. In the molecular grid unit [Cu₄**3**₄] (Figure 16), several features of the geometry differ markedly from those of the Co, Ni and Zn grids. One that does not is the geometry of the binding portion of the ligand, indicating that bond lengths and bond angles about the metals must be the primary means of adapting to any degree of metal–ligand misfit. Thus, for a ligand intended to generate grids with octahedral units by coordinating metal ions, it is unsurprising, given the well-known tendency of Cu^{II} to adopt strongly tetragonally distorted octahedral geometry (and generally to readily lose one or two of its six ligands), to find that the Cu^{II} coordination geometry in the present complex is very irregular (Figure 17), involving in particular considerable variation (up to ca. 0.4 Å) in the Cu–N(pyrimidine) distances.

As discussed earlier, the outer donor atoms of a given tritopic site cannot generally lie at the same distance from the metal as the central donor while also giving bond angles of π/2. Thus, distortion of some kind is inherent in grid formation, and it is certainly well-known that it can become very marked in grids larger than the [2×2] type.[8,33,35] Hence, the form of the Cu grid here may express the way in which any grid must tend to distort in order to achieve the most efficient coordination of the ligand. While all the
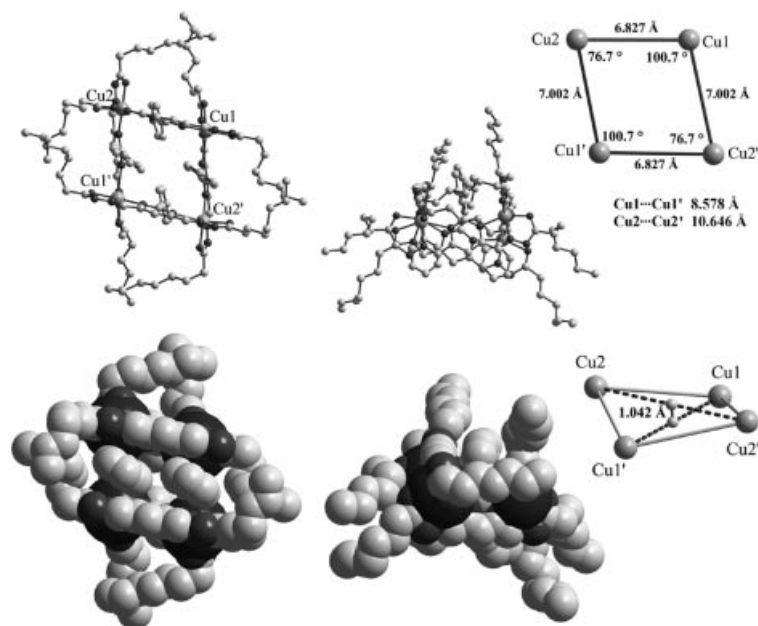
Figure 16. Views and various features of the geometry of the grid unit present in the lattice of [Cu$_4$**3**$_4$]·2H$_2$O. The projection of the Cu$_4$ unit is given with Cu(1)···Cu(1′) along x and Cu(2)···Cu(2′) along y, although the two axes are not coplanar.
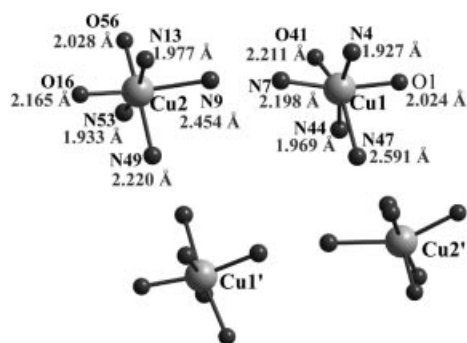

Figure 17. Donor atom distribution about the Cu^{II} centres of a grid unit.

grids formed by the C$_7$-functionalised ligand involve a "butterfly" form of the M$_4$ unit, with Cu^{II} this is associated also with a marked "extrusion" (Figure 16), which results in very different diagonal Cu···Cu distances (possibly influenc-

ing magnetic properties, for example). Significantly, however, even with Cu^{II}, there is no change in the system which is great enough to result in an apparent change in the form of the metal–ligand aggregate formed.

Thus, outside the grid units, the lattice of [Cu$_4$**3**$_4$]·2H$_2$O is of very similar appearance (Figure 18) to those of the other metal complexes; kinked C$_7$ substituents occupy the space between grids, each of which is surrounded tetrahedrally by four other grids. (The alkyl chain conformations differ, but this presumably corresponds to a very small energy difference.) The specific location and quantity of the lattice water in the Cu^{II} complex, however, may be associated with the distorted form of the Cu$_4$ grid. It is apparent (Figure 19) that the water molecules lie essentially within the columns of grids which run parallel to c and they are in fact not in positions where they can bridge grids lying in separate columns, as is the case in the Co compound lattice, for example. Thus, hydrogen bond bridging of grids (Figure 20) occurs in one dimension only (i.e. along c), where it
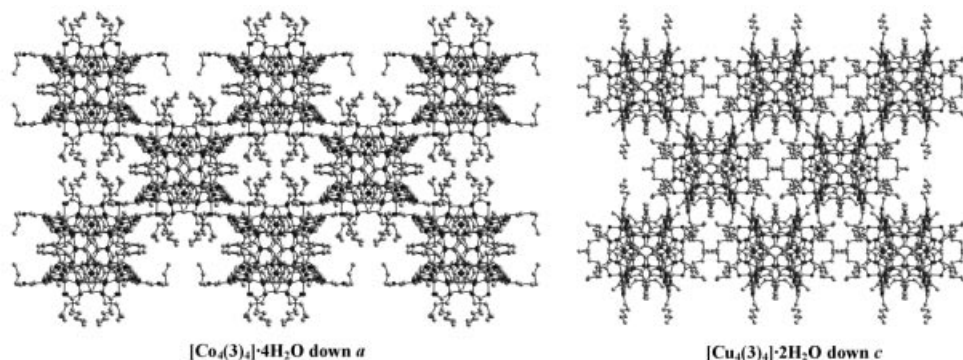

Figure 18. Comparison illustrating the grossly similar forms of the lattices of the Co and Cu complexes.
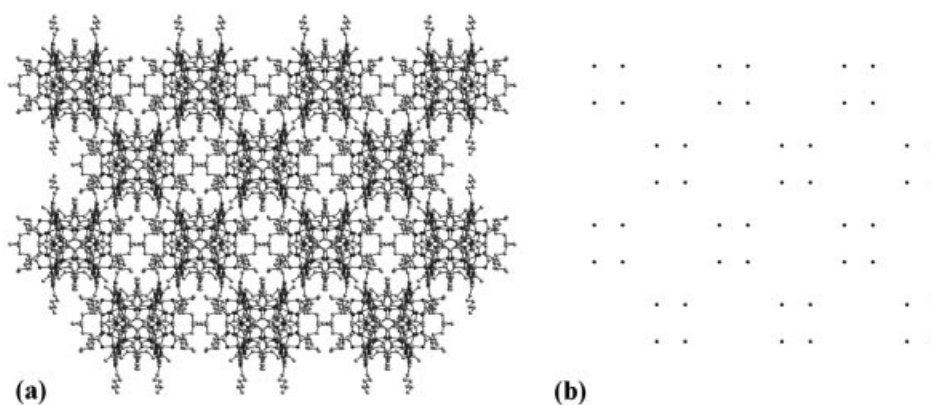
Figure 19. Partial views of the lattice of [Cu$_4$**3**$_4$]·2H$_2$O (down *c*) showing (a) all atoms and (b) water molecule oxygen atoms only.
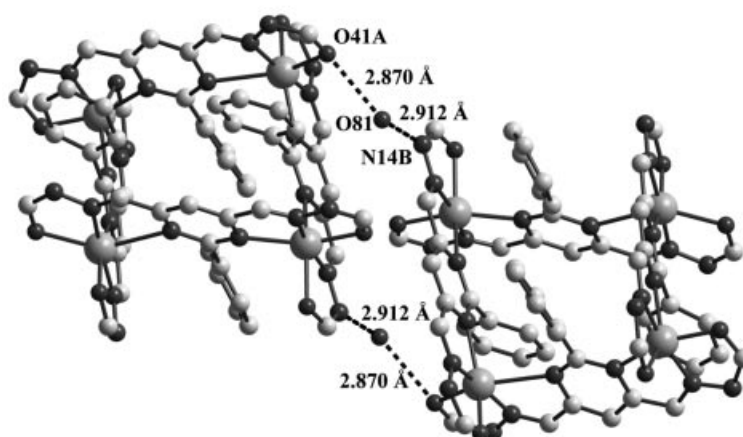

Figure 20. Adjacent Cu$_4$ grids with their shorter edges at the closest position, showing water molecules that form bridges between the two grids.

brings the shorter edges of the grid units into proximity. Longer edge pairs are also present, but their proximity does not seem to be directly assisted by hydrogen bonding. Perhaps the length of the edges keeps hydrogen-bond-acceptor sites too remote to be efficiently bridged by a single water molecule, while "aromatic–aromatic" contacts are maintained (Figure 21), which is perhaps again consistent with their provision of a more important contribution to the lattice energy and structure.
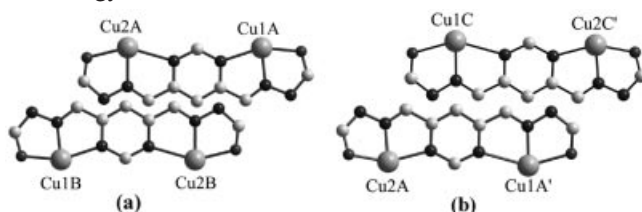
Figure 21. Atom contacts of 3.6 Å or less between ligand atoms in (a) the shorter edges of two adjacent grids and (b) the longer edges of two adjacent grids.

(d) Properties of the Grid Complexes

Crucial to the extension of the chemistry of bis(acyl-hydrazone) ligands presently studied is the knowledge of the exact conditions under which metallogrid species are stable. Clearly, the several crystal structures obtained here inspire confidence in the belief that in the solid state, certainly with doubly deprotonated ligands, grid species are present. In solution, the situation is less certain in general, although NMR spectroscopy of Zn^{II} complexes again indicates the presence of grids (at [Zn^{II}] ≈ 10^{-3} mol L^{-1}) only when the ligands are doubly deprotonated. Nonetheless, most of the neutral grid complexes can be subjected to adsorption (silica) chromatography without decomposition, indicating that all of them retain at least the grid stoichiometry in solution (in solvents such as dichloromethane containing ca. 10% methanol). The most direct evidence of the form of paramagnetic species in solution, particularly that of those for which crystal structures have not been obtained, is provided by MALDI-TOF mass spectrometry, though of course this establishes most directly the stoichiometry and not the structure. Here, in a relatively strongly coordinating solvent like tetrahydrofuran, there is evidence that the grids begin to undergo extensive dissociation at concentrations below 10^{-4} mol L^{-1}.

In regard to possible applications, the properties of grid complexes of importance include not only their redox, elec-

tronic and magnetic behaviour,[8] but also the supramolecular chemistry which may be mediated by their substituents. The crystal structures reported here show that, despite their symmetrical and thus apolar nature, neutral grids derived from acylhydrazones are good hydrogen bond acceptors, in view of the presence of charged sites in the deprotonated ligands, and are prone to stacking interactions involving the delocalised ligand entities. Differing substituents derived from the acid hydrazide moieties have a marked influence on the interactions of the grids with the medium, viz. upon their solubility, and in the particular case of the grid derived from methoxyethoxyacetohydrazide, the detection of Na^+ adducts by mass spectrometry indicates that metal ion coordination by appropriate side chains is possible.

Different transition-metal ions must endow their grids with different redox, spectroscopic and magnetic properties, and while detailed studies of the magnetism of the complexes are still in progress, ^1H NMR spectroscopy shows that the Fe^{II} complexes are in mixed-spin states at room temperature (in solution). Fluorescence apparent for the Zn^{II} grids is quenched in all the open-shell transition-metal ion grids, though the exact mechanism of deactivation is yet to be established. All the grids show strong absorption in the visible region, with features that vary not only with the metal, but also with the acyl-unit substituents. That the acylhydrazone-derived grids may show very different redox behaviour from the grids derived from pyridylhydrazones is indicated by the difficulty experienced in obtaining a Co^{III} complex of the benzoylhydrazone $\mathbf{4}H_2$. While Co^{II} complexes of pyridylhydrazones are very sensitive to atmospheric oxygen under basic conditions and readily give tetra-Co^{III} grids,[8] the Co^{II} complex of $\mathbf{4}^{2-}$ is insensitive to oxygen or hydrogen peroxide, and appears to undergo only partial oxidation by Ce^{IV} to give a mixed-valence Co^{III}-Co^{II} grid.

Conclusions

The grid complexes presently characterised are related to but differ significantly from those derived from both bis-(hydrazone)s of 2-phenylpyrimidine-4,6-dicarbaldehyde and thiocarbonylbis(hydrazone)s. Bis(acylhydrazone)s, as neutral ligands, appear to be poorer chelators than the analogous neutral bis(hydrazone)s, but they are more easily deprotonated, enhancing their donor properties and thus providing, with M^{II} ions, a family of neutral grids with lateral substituents which may be very readily varied over a wide range. Compared to thiocarbonylbis(hydrazone)s, their metal-chelating sites are considerably more widely separated [especially in their (Z,Z) form], so that different electronic and magnetic interactions within the metal ion quartet of the grids are expected.

The present structural studies show that some aspects of grid geometry, in particular the distortion of the M_4 unit from planarity, are remarkably sensitive to minor variations in the ligand structure. The geometry of the chelating sites of the ligands, in contrast, is insensitive to both its substitu-

ents and to the bound metal ion, and it is clear that accommodation of the requirements of a grid array is largely achieved through the flexibility of the metal ion coordination environment. A feature of nearly all the grid lattices presently studied is the association of grid units in pseudo-tetrahedral arrays, where ligands of different grids lie parallel and with numerous atom contacts < 3.5 Å, which is presumably indicative of a type of stacking interaction. Another common feature is hydration of the formally apolar grid units through hydrazide-N and acyl-O hydrogen bond acceptor sites. Finally, a remarkable feature resides in the efficient self-assembly of the grid structures in the presence of a base directly from their organic components and the metal ions (see also ref.[22]).

Experimental Section

Reagents and Equipment: Although a literature synthesis of 2-phenylpyrimidine-4,6-dicarbaldehyde exists,[24a] the compound was presently prepared by an adaptation of an alternative literature method for partial oxidation of azaaromatic methyl groups[24b] applied to 4,6-dimethyl-2-phenylpyrimidine[36] and developed by Dr. J.-L. Schmitt. The procedure is detailed below. 1-methyl-1-propionylhydrazine was obtained as described in the literature.[37] Acetohydrazide, benzohydrazide, 4-toluohydrazide and heptanohydrazide were obtained from Aldrich Chemicals and used as received. Methoxyacetyl- and methoxyethoxyacetyl chlorides were obtained commercially (Lancaster) and converted into the hydrazides by reaction with excess hydrazine. All solvents and chemicals used in the syntheses were reagent grade and were used without further purification or drying. Dimethyl sulfoxide (dmso) solvates of metal triflates and tetrafluoroborates used as reactants in various complex ion syntheses were prepared by precipitation (at least twice) of the (commercial) anhydrous or hydrated salts from dmso by the addition of ethanol/diethyl ether. For $[Cu(dmso)_6](CF_3SO_3)_2$, the presence of the hexakis(solvent) species in the solid was confirmed by a crystal structure determination.[38] $[Ni(CH_3CN)_6](ClO_4)_2$ was prepared as described in the literature.[39] Iron(II) ascorbate was purchased from Sigma Chemicals.

Solution ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded with a Bruker Ultrashield Avance 400 instrument, using residual solvent proton resonances as internal references for the ^1H NMR spectra and the solvent ^{13}C peaks as references for the ^{13}C NMR spectra. The atom numbering used in assignments of the NMR peaks is shown in Figure 22. Mass spectra [MALDI-TOF and electrospray (ESMS)] were provided by the Service de Spectrometrie de Masse, Université Louis Pasteur. MALDI-TOF spectra of neutral grid species in all cases provided $[M + H]^+$ peaks. Elemental microanalyses (C,H,N) were provided by the Service d'Ana-
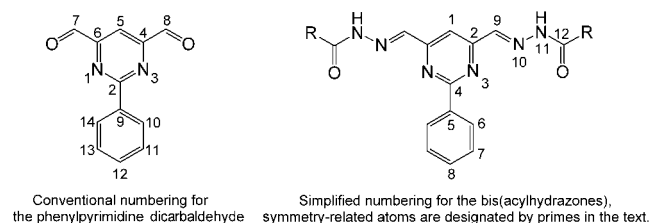

Figure 22. Atom numbering used in description of the NMR spectra.

lyses, Université Louis Pasteur, all samples being gently dried by storage in an unevacuated desiccator containing concentrated H_2SO_4 as desiccant for at least 3 d.

Synthesis

(a) 2-Phenylpyrimidine-4,6-dicarbaldehyde: A stirred solution of 4,6-dimethyl-2-phenylpyrimidine (5.08 g; 27.6 mmol), iodine (14.02 g; 53.2 mmol) and trifluoroacetic acid (8.0 mL; 103.8 mmol) in deoxygenated dmso (200 mL) was heated, under argon, at 150 °C for 135 min. After cooling to ambient temperature, further manipulations were conducted under the normal atmosphere. A solution of $Na_2S_2O_3\cdot5H_2O$ (31.6 g; 127.3 mmol) in water (100 mL) was added, causing discharge of the I_2 colour, after which the solution was neutralised by the addition of saturated $NaHCO_3$ solution. The product was extracted into CH_2Cl_2 (6×100 mL) and the combined extracts dried with $MgSO_4$ before being taken to dryness in vacuo. The dmso remaining in the orange residue was removed by high-vacuum distillation, and the product was then crystallised from diethyl ether as pale yellow needles. Yield: 4.06 g (19.2 mmol, 80%). M.p. 123.5 °C. ^1H NMR (CDCl$_3$): δ = 10.18 (s, 2 H, 7,8-H), 8.60 (d, ^3J = 7.9 Hz, 2 H, 10,14-H), 8.12 (s, 1 H, 5-H), 7.58 (m, 3 H, 11,12,13-H) ppm. ^{13}C NMR (CDCl$_3$): δ = 192.13 (C-7,8), 166.76 (C-2), 160.25 (C-4,6), 135.50 (C-9), 128.60, 128.93 (C-10,14, C-11,13), 132.17 (C-12), 109.97 (C-5) ppm.

(b) Bis(acylhydrazone)s of 2-Phenylpyrimidine-4,6-dicarbaldehyde, $RCONR'N=CHC_{10}H_6N_2CH=NNR'COR$

(i) R = CH$_3$, R′ = H (1H$_2$): Solutions of 2-phenylpyrimidine-4,6-dicarbaldehyde (250 mg) in CH$_3$CN (10 mL) and acetohydrazide (190 mg) in CH$_3$CN (10 mL) were mixed to give a pale yellow solution. Within 30 s, the solution became turbid, and after 5 min, formation of a granular but not obviously crystalline pale yellow precipitate was extensive. After 12 h, the well-settled precipitate was separated from the colourless supernatant, washed with CH$_3$CN and diethyl ether, and dried in vacuo. Yield: 280 mg (80%). $C_{16}H_{16}N_6O_2\cdot^1/_4H_2O$ (327.85): calcd. C 58.51, H 4.99, N 25.63; found C 58.7, H 4.85, N 25.2%. M.p. > 310 °C (decomp.). ^1H NMR ([D$_6$]dmso): δ = 11.93, 11.91, 11.83 (NH), 8.41 (m, br), 8.24, 8.20, 8.17, 8.10, 8.09, 8.07, 8.05, 7.57, 2.28, 2.27, 2.04 ppm. ^{13}C NMR ([D$_6$]dmso): δ = 172.5, 172.4, 166.3, 166.2, 163.8, 161.2, 160.8, 143.9, 143.4, 141.1, 140.6, 136.4, 131.1, 128.7, 127.8, 108.1, 107.8, 54.8, 21.7, 20.2, 19.9 ppm. ESMS: m/z (%) = 325.24 (100) [M + H]$^+$.

(ii) R = C$_2$H$_5$, R′ CH$_3$ (2): 2-Phenylpyrimidine-4,6-dicarbaldehyde (421 mg) and 1-methyl-1-propionylhydrazine (405 mg) were dissolved in ethanol (35 mL), and the solution was stirred at room temperature for 24 h as a yellow precipitate formed. The precipitate was collected, washed with ethanol and dried under vacuum. Yield: 443 mg (59%). The compound was recrystallised from CHCl$_3$ by addition of CH$_3$CN. M.p. 231–232 °C. ^1H NMR (CDCl$_3$): δ = 8.49–8.46 (m, 2 H), 8.24 (s, 1 H), 7.77 (s, 2 H), 7.51–7.50 (m, 3 H), 2.93 (q, J = 7.6 Hz, 4 H), 1.25 (t, J = 7.6 Hz, 6 H) ppm. ^{13}C NMR (CDCl$_3$): δ = 176.2, 165.3, 161.7, 137.2, 137.1, 131.3, 128.9, 128.5, 108.3, 28.5, 27.2, 9.6 ppm. ESMS: m/z (%) = 381.30 (100) {[M + H]$^+$ = $[C_{20}H_{24}N_6O_2 + H]^+$}.

(iii) R = C$_7$H$_{15}$, R′ = H (3H$_2$): Essentially the same procedure as described for the synthesis of **1**H$_2$ was followed, except that ethanol (20 mL) was used as solvent in the reaction of 2-phenylpyrimidine-4,6-dicarbaldehyde (273 mg) and heptanohydrazide (469 mg), the acylhydrazone precipitating as an almost white solid. Yield: 478 mg (75%). The compound was recrystallised from boiling acetonitrile (or methanol) by cooling on ice. $C_{28}H_{40}N_6O_2$ (492.66): calcd. C 68.26, H 8.18, N 17.06; found C 68.6, H 8.10, N 17.1%. M.p. 225–

227 °C. ^1H NMR ([D$_6$]dmso): δ = 11.85 (br., 2 H), 8.43 (m, 2 H), 8.25 (m, 1 H), 8.09 (m, 2 H), 7.58 (br. m, 3 H), 2.68 (m, 2 H), 2.31 (m, 2 H), 1.63 (m, 4 H), 1.32 (m, 16 H), 0.86 (m, 6 H) ppm. ^{13}C NMR (CDCl$_3$): δ = 174.8, 169.3, 163.9, 161.3, 160.9, 143.9, 143.6, 141.0, 140.5, 136.5, 131.2 128.7, 127.8, 108.2, 107.3, 34.3, 31.8, 31.2, 28.8, 28.7, 28.5, 28.4, 24.8, 24.2, 24.0, 22.1, 13.9$_2$,13.8$_8$ ppm. ESMS: m/z (%) = 492.30 (100) [M + H]$^+$.

(iv) R = C$_6$H$_5$, R′ = H (4H$_2$): Solutions of 2-phenylpyrimidine-4,6-dicarbaldehyde (50 mg) in CH$_3$CN (3 mL) and benzohydrazide (64 mg) in CH$_3$CN (2 mL) were mixed to give a pale yellow solution. Within 2 min, deposition of pale yellow, globular material commenced, and, on continued standing, this material transformed into clusters of pale yellow needles. After 12 h, the solid was collected, washed with CH$_3$CN and dried in air. Yield: 98 mg (93%). Use of methanol as a solvent gave essentially the same result, though initiation of the precipitation was slower (ca. 30 min). The compound was recrystallised from pyridine by addition of acetonitrile. $C_{26}H_{20}N_6O_2\cdot^1/_2H_2O$ (457.49): calcd. C 68.26, H 4.63, N 18.37; found C 68.4, H 4.74, N 18.1%. M.p. 286–287 °C. ^1H NMR ([D$_6$]dmso): δ = 12.40 (s, 2 H), 8.56 (s, 2 H), 8.45 (t, ^3J = 3.6 Hz, 2 H), 8.35 (s, 1 H), 7.98 (d, ^3J = 7.2 Hz, 4 H) 7.67–7.62 (m, 3 H), 7.62–7.53 (m, 6 H) ppm. ^{13}C NMR ([D$_6$]dmso): δ = 164.0, 163.6, 161.3, 145.7, 136.5, 132.8, 132.3, 131.2, 128.8, 128.6, 127.9, 108.9 ppm. ESMS: m/z (%) = 449.10 (100) [M + H]$^+$.

(v) R = 4-CH$_3$C$_6$H$_4$, R′ = H (5H$_2$): The procedure used for ligand **3**H$_2$ was followed for the reaction of 2-phenylpyrimidine-4,6-dicarbaldehyde (223 mg) and toluohydrazide (331 mg), the acylhydrazone again precipitating as an almost white solid which was recrystallised from pyridine by addition of acetonitrile. Yield: 364 mg (73%). $C_{28}H_{24}N_6O_2$ (476.53): calcd. C 70.57, H 5.08, N 17.64; found C 70.5, H 4.69, N 17.6%. M.p. 287–288 °C. ^1H NMR ([D$_6$]dmso): δ = 14.59 (w), 12.39 (w), 12.34, 8.56, 8.46, 8.34, 8.22 (w), 8.21 (w), 7.90, 7.89, 7.81 (w), 7.79 (w), 7.59, 7.40, 7.38, 7.33 (w), 7.31 (w), 2.44 (w), 2.41 ppm. ^{13}C NMR ([D$_6$]dmso): δ = 164.0, 163.4, 161.3, 158.2, 145.4, 142.5, 136.5, 136.1, 131.6, 131.2, 129.9, 129.8, 129.4, 129.2, 128.8, 128.2, 127.9, 127.7, 114.9, 108.8, 104.5, 104.4, 21.1$_3$, 21.0$_9$ ppm. ESMS: m/z (%) = 477.2 (100) [M + H]$^+$.

(vi) R = CH$_3$OCH$_2$, R′ = H (6H$_2$): $CH_3OCH_2CONHNH_2$ (21 mg) in CH$_3$CN (1 mL) and 2-phenylpyrimidine-4,6-dicarbaldehyde (22 mg) in CH$_3$CN (1 mL) were mixed to give a slightly cloudy, pale yellow solution, which was filtered (the cloudiness appearing to be due to traces of acid impurity in the hydrazide) before being mixed with a solution of [Ga(dmso)$_6$](CF$_3$SO$_3$)$_3$ (5 mg; ca. 0.1 molar equivalent) in CH$_3$CN (1 mL). The colour of the mixture changed to a deeper yellow, and within 5 min, deposition of the product commenced. (In the absence of Ga^{III}, no precipitate forms within at least 2 h.) After 1 h, the solid was collected and washed with CH$_3$CN and diethyl ether. Yield: 30 mg (75%). The compound was recrystallised from hot thf by addition of an equal volume of diethyl ether after cooling. $C_{18}H_{20}N_6O_4\cdot^1/_2H_2O$ (393.40): calcd. C 54.96, H 5.38, N 21.36; found C 54.9, H 5.1, N 21.8%. M.p. 238–239 °C. ^1H NMR ([D$_6$]dmso): δ = 11.93 (NH) (two very weak peaks at δ = 13.86 and 12.00 ppm may also be NH resonances), 8.43 (s, br.), 8.39 (m, br.), 8.20, 8.01 (t, ^3J = 15 Hz), 7.55 (s, br.), 4.49, 4.08, 3.39, 3.35 ppm. ^{13}C NMR ([D$_6$]dmso): δ = 171.6, 166.9, 164.4, 161.7, 161.1, 146.3, 146.0, 142.3, 141.6, 136.8, 131.7, 129.2, 128.3, 109.4, 108.9, 108.7, 71.5, 69.4, 59.3, 59.0 ppm. ESMS: m/z (%) = 385.29 (100) [M + H]$^+$.

(vii) R = CH$_3$OCH$_2$CH$_2$OCH$_2$, R′ = H (7H$_2$): The relatively high solubility of the product in most organic solvents made its direct precipitation from the volume of solvent required to dissolve the reactants rather inefficient. Hence, 2-phenylpyrimidine-4,6-dicarb-

aldehyde (40 mg) and methoxyethoxyacetohydrazide (82 mg) were allowed react in acetonitrile (5 mL) for 2 h before the solvent was removed under vacuum. The pale yellow residue was then dissolved in the minimum volume of boiling acetonitrile and the solution cooled on ice to provide clusters of pale yellow needles. These were recrystallised similarly. Yield: 57 mg (64%). $C_{22}H_{28}N_6O_6\cdot1/2H_2O$ (481.51): calcd. C 54.88, H 6.07, N 17.45; found C 54.8, H 6.2, N 17.6%. M.p. 165–166 °C. ^{1}H NMR (CD$_3$CN): δ = 10.66, 9.82, 8.50, 8.24, 8.15, 7.92, 7.56, 4.62, 4.17, 3.74, 3.60, 3.55, 3.43, 3.33 ppm. ^{13}C NMR (CDCl$_3$): δ = 168.4, 167.9, 166.9, 164.7, 162.9, 161.0, 158.1, 147.4, 146.0, 137.7, 136.9, 136.2, 131.7, 131.1, 129.1, 128.8$_3$, 128.7$_7$, 128.6, 128.3, 124.6, 115.0, 111.3, 71.6, 71.5, 71.4, 71.1, 71.0, 70.1, 70.0, 59.1, 58.8 ppm. ESMS: m/z (%) = 473.36 (100) [M + H]$^+$.

(c) Metal Ion Complexes of the Bis(acylhydrazone) Ligands

(i) R = CH$_3$, R′ = H (1H$_2$)

Zn^{II} Complex (Zn/L 1:1) of the Doubly Deprotonated Ligand, [Zn$_4$(1)$_4$]·23H$_2$O: Solutions of [Zn(dmso)$_6$](BF$_4$)$_2$ (730 mg) and CH$_3$CONHNH$_2$ (180 mg) in CH$_3$CN (5 mL) and of 2-phenylpyrimidine-4,6-dicarbaldehyde (215 mg) in CH$_3$CN (5 mL) were mixed to give a clear yellow solution from which no precipitate formed (cf. ligand synthesis). Addition of triethylamine (0.3 mL) caused immediate precipitation of a canary yellow solid which, after 12 h, was collected by filtration, washed with CH$_3$CN and diethyl ether and dried in air. Yield: 424 mg (85%). The crude product was dissolved in methanol (40 mL), filtered to remove a small amount of gelatinous material and reprecipitated by the addition of diethyl ether. [Zn$_4$(1)$_4$]·23H$_2$O·CH$_3$OH = $C_{65}H_{106}N_{24}O_{32}Zn_4$ (1997.3): calcd. C 39.09, H 5.35, N 16.83; found C 39.3, H 4.4, N 16.9%. M.p. > 250 °C (decomp.). ^{1}H NMR ([D$_6$]dmso): δ = 7.60 (t, ^3J = 7.7 Hz, 1 H, 8-H), 7.52 (s, 1 H, 1-H), 7.51 (s, 2 H, 9,9′-H), 7.09 (t, ^3J = 7.7 Hz, 2 H, 7,7′-H), 6.28 (d, ^3J = 7.3 Hz, 2 H, 6,6′-H), 1.82 (s, 6 H, CH$_3$) ppm. (A large water peak was also observed, as expected from the high degree of hydration of the solid.) ^{13}C NMR ([D$_6$]dmso): δ = 181.7, 165.1, 158.4, 136.1, 133.4, 130.0, 128.0, 125.2, 117.8, 22.5 (CH$_3$) ppm. MS (MALDI-TOF): m/z (%) = 1551.1 (100) [M + H]$^+$.

Other M^{II} Complexes (M/L 1:1) of the Doubly Deprotonated Ligand, [M$_4$(1)$_4$]·nH$_2$O: The following synthesis illustrates an alternative to the above, in which the preformed diacylhydrazone is used as a reactant. A solution of KOtBu (71 mg) in dry methanol (5 mL) was slowly added to a stirred slurry of 1H$_2$ (99 mg) in dry CH$_2$Cl$_2$ (20 mL) to give a yellow solution. This was mixed with a solution of [M(dmso)$_6$](CF$_3$SO$_3$)$_2$ (254 mg for M = Zn, with the appropriate slightly different amounts for M = Co and Ni) in dry methanol (5 mL), causing a marked intensification of the colour (dark red-brown for Co, deep yellow-brown for Ni and orange for Zn) and some precipitation. After stirring the mixture for 1 h, the solvents were removed under vacuum and the residues crystallised from methanol as above. Yields were essentially quantitative.

M = Co^{II}: [Co$_4$(1)$_4$]·23H$_2$O = $C_{64}H_{102}Co_4N_{24}O_{31}$ (1939.4): C 39.64, H 5.30, N 17.33; found C 39.6, H 4.95, N 17.4%. M.p. >250 °C (decomp.). MS (MALDI-TOF) m/z (%) = 1526.3 (100).

M = Ni^{II}: [Ni$_4$(1)$_4$]·22H$_2$O = $C_{64}H_{100}N_{24}Ni_4O_{30}$ (1920.4): calcd. C 40.02, H 5.25, N 17.50; found C 40.1, H 5.01, N 17.8%. M.p. >250 °C (decomp.). MS (MALDI-TOF): m/z (%) = 1523.2 (100).

(ii) R = C$_2$H$_5$, R′ = CH$_3$ (2): This acylhydrazone appears to be a rather poor ligand, and no solid transition-metal complexes were readily obtained from it.

(iii) R = C$_7$H$_{15}$, R′ = H (3H$_2$): All complexes (M/L 1:1) containing the doubly deprotonated ligand were obtained as described above

(for ligand 1H$_2$) by using KOtBu to deprotonate the preformed ligand. Again, yields appeared to be essentially quantitative. [Fe(dmso)$_6$](CF$_3$SO$_3$)$_2$ was used as the reactant for the synthesis of the Fe^{II} complex.

Fe^{II} Complex [Fe$_4$(3)$_4$]·3H$_2$O: $C_{112}H_{158}Fe_4N_{24}O_{11}$ (2240.0): calcd. C 60.05, H 7.11, N 15.00; found C 59.7, H 7.21, N 14.9%. M.p. >250° (decomp.). MS (MALDI-TOF): m/z (%) = 2187.0 (100).

Co^{II} Complex [Co$_4$(3)$_4$]·11H$_2$O: $C_{112}H_{174}Co_4N_{24}O_{19}$ (2396.5): calcd. C 56.13, H 7.32, N 14.03; found C 56.0, H 7.03, N 13.7%. M.p. >250 °C (decomp.). MS (MALDI-TOF): m/z (%) = 2199.8 (100).

Ni^{II} Complex [Ni$_4$(3)$_4$]·11H$_2$O·2CH$_2$Cl$_2$: $C_{114}H_{178}Cl_2N_{24}Ni_4O_{19}$ (2565.4): calcd. C 53.37, H 6.99, N 13.10; found C 53.4, H 7.33, N 13.1%. M.p. >250 °C (decomp.). MS (MALDI-TOF): m/z (%) = 2198.9 (100).

Cu^{II} Complex [Cu$_4$(3)$_4$]·2H$_2$O: $C_{112}H_{156}Cu_4N_{24}O_{10}$ (2252.9): calcd. C 59.71, H 6.98, N 14.92; found C 60.0, H 7.04, N 15.1%. M.p. >250 °C (decomp.). MS (MALDI-TOF): m/z (%) = 2217.4 (100).

Zn^{II} Complex [Zn$_4$(3)$_4$]·4.5H$_2$O: $C_{112}H_{161}N_{24}O_{12.5}Zn_4$ (2323.2): calcd. C 57.90, H 6.99, N 14.47; found C 57.9, H 7.07, N 14.8%. M.p. >250 °C (decomp.). ^{1}H NMR (CDCl$_3$): δ = 7.62 (t, ^3J = 7.5 Hz, 1 H, 8-H), 7.37 (s, 2 H, 9-H), 7.13 (t, ^3J = 7.5 Hz, 2 H, 7,7′-H), 6.80 (s, 1 H, 1-H), 6.50 (d, ^3J = 6.9 Hz, 2 H, 6,6′-H), 2.19 (m, 4 H), 1.50 (m, 4 H), 1.20 (m, 16 H), 0.82 (t, ^3J = 6.6 Hz, 6 H, CH$_3$) ppm. ^{13}C NMR (CDCl$_3$): δ = 186.4, 165.9, 159.1, 137.2, 132.6, 130.5, 128.3, 126.3, 116.5, 37.2, 31.9, 29.8, 29.2, 26.9, 22.7, 14.2 ppm. MS (MALDI/TOF): m/z (%) = 2225.8 (100) [M + H]$^+$.

(iv) R = C$_6$H$_5$, R′ = H (4H$_2$)

Attempted Synthesis of the Co^{II} Complex (Co/L 1:1) of the Singly Deprotonated Ligand: Triethylamine (10 mg, viz. 1 mL of a solution of 0.1 g of the amine in 10 mL of CH$_3$CN) was added to a yellow solution of 2-phenylpyrimidine-4,6-dicarbaldehyde (22 mg) in CH$_3$CN (1 mL), causing the colour to become brownish, though immediate addition of a solution of benzohydrazide (27 mg) in CH$_3$CN (1 mL) caused a return to pale yellow. Without delay, a solution of [Co(dmso)$_6$](BF$_4$)$_2$ (70 mg) in CH$_3$CN (1 mL) was added, producing a deep brown-red solution from which small, dark red crystals began to deposit within 30 s. After 12 h, the precipitate was collected and washed on the filter with CH$_3$CN and then diethyl ether. Yield: 18 mg (33%). The complex was recrystallised from chloroform (in which it is only moderately soluble) by the addition of acetonitrile. [Co$_4$(4)$_2$(4H)$_2$](BF$_4$)$_2$ = $C_{104}H_{74}B_2Co_4F_8N_{24}O_8$ (2197.3): calcd. C 56.85, H 3.39, N 15.30; found C 56.8, H 3.9, N 15.4%. Note that a single crystal drawn from the initial reaction product was found, as a result of the solution of its structure by X-ray crystallography, to have the composition [Co$_4$(4H)$_4$](BF$_4$)$_4$·7CH$_3$CN.

Co^{II} Complex (Co/L 1:1) of the Doubly Deprotonated Ligand: The procedure above was repeated except that the quantity of triethylamine added (20 mg) was doubled. Here, copious precipitation of a dark red solid occurred immediately, though again 12 h was allowed for equilibration. The final precipitate was collected and washed with acetonitrile followed by diethyl ether on the filter. Yield: 48 mg (89%). The complex was recrystallised from chloroform by the addition of acetonitrile. [Co$_4$(4)$_4$]·7H$_2$O = $C_{104}H_{86}Co_4N_{24}O_{15}$ (2147.77): calcd. C 58.16, H 4.04, N 15.65; found C 58.2, H 4.2, N 15.0%. MS (MALDI/TOF): m/z (%) = 2022.2 (100) [M + H]$^+$.

Ni^{II} Complexes (Ni/L 1:1) of the Undeprotonated and Partly Deprotonated Ligand: (a) Ligand 4H$_2$ (42.4 mg) and [Ni(CH$_3$CN)$_6$]-

(ClO$_4$)$_2$ (47.7 mg) were stirred at room temperature with anhydrous CH$_3$NO$_2$ (8 mL) until a clear red solution was obtained. Stirring was continued for another 3 h before diisopropyl ether was added to cause precipitation of the red complex. [Ni$_4$(**4**H$_2$)$_4$](ClO$_4$)$_8$·CH$_3$NO$_2$ = C$_{105}$H$_{83}$Cl$_8$N$_{25}$Ni$_4$O$_{42}$ (2885.3): calcd. C 43.70, H 2.90, N 12.13; found C 43.9, H 3.6, N 12.2%. Note that a single crystal drawn from the reaction mixture was assigned the composition [Ni$_4$(**4**H$_2$)$_4$](ClO$_4$)$_8$·8H$_2$O·4CH$_3$NO$_2$ on the basis of the solution of its X-ray structure determination. (b) [Ni(OH$_2$)$_6$](NO$_3$)$_2$ (29 mg) and 2-phenylpyrimidine-4,6-dicarbaldehyde (23 mg) were dissolved in CH$_3$CN (2 mL), giving a yellow-green solution. C$_6$H$_5$CONHNH$_2$ (27 mg) in CH$_3$CN (1 mL) was then added, an initial pale violet precipitate dissolving readily on agitation of the mixture. Within 30 s, a yellow precipitate commenced to form from the yellow solution, but on continued agitation, the solution became dark red, and the precipitate transformed into a red-brown solid. After 2 h, the solid was collected by filtration and washed with CH$_3$CN and diethyl ether. Yield: 28 mg (48%). The complex was recrystallised from methanol by the addition of diethyl ether. Slow crystallisation by vapour diffusion of diisopropyl ether into a methanol solution provided a mixture of plate- and needle-like crystals. The synthesis can equally well be conducted in methanol, in which case no precipitates form, but a reaction time of at least 3 h is required at room temperature before the product can be precipitated by the addition of ether. Elemental analyses indicated that the complex in fact contains the ligand in both its doubly and singly deprotonated forms. [Ni$_4$(**4**)(**4**H)$_3$](NO$_3$)$_3$·4CH$_3$OH = C$_{108}$H$_{93}$N$_{27}$Ni$_4$O$_{21}$ (2339.9): calcd. C 55.44, H 4.01, N 16.16; found C 55.7, H 4.2, N 16.7%.

Zn^{II} Complex (Zn/L 1:1) of the Undeprotonated Ligand: 2-Phenyl-pyrimidine-4,6-dicarbaldehyde (23 mg), C$_6$H$_5$CONHNH$_2$ (27 mg) and Zn(BF$_4$)$_2$ (23 mg) were dissolved in CH$_3$CN (5 mL) to give a red solution, which was then taken to dryness under vacuum. The residue was dissolved in a mixture of CH$_3$CN (1 mL) and CH$_3$NO$_2$ (2 mL), giving a deep red solution which was then diluted with benzene (10 mL). On keeping the mixture in a sealed flask, small red plates slowly deposited within a few hours, to be followed over a period of several days by yellow crystals of free ligand. One of the red crystals was selected for a crystal structure determination, from which it was assigned the composition [Zn$_8$(*E,E*-**4**H$_2$)$_4$(*Z,Z*-**4**H$_2$)$_4$(OH$_2$)$_2$(CH$_3$CN)$_2$(BF$_4$)$_2$](BF$_4$)$_{14}$·7C$_6$H$_6$·3CH$_3$CN·3H$_2$O.

Zn^{II} Complex (Zn/L 2:1) of the Undeprotonated Ligand: A filtered solution of C$_6$H$_5$CONHNH$_2$ (27 mg) and Zn(CF$_3$SO$_3$)$_2$ (75 mg) in CH$_3$NO$_2$ (3 mL) was mixed with a filtered solution of 2-phenylpyrimidine-4,6-dicarbaldehyde (22 mg) in CH$_3$NO$_2$ (2 mL), giving a bright yellow solution which developed a red-orange colour within 5 min. Slow deposition of small, red-orange crystals commenced shortly thereafter. After 48 h, the crystals were collected, washed with diethyl ether and dried in air. Yield: 65 mg (52%). The complex was recrystallised from acetonitrile by vapour diffusion of diethyl ether, forming clusters of fine, red needles. Zn$_2$(**4**H$_2$)(CF$_3$SO$_3$)$_2$·2H$_2$O·CH$_3$CN = C$_{31}$H$_{27}$F$_{12}$N$_7$O$_{16}$S$_4$Zn$_2$ (1241.7): calcd. C 30.68, H 2.17, N 7.83; found C 30.7, H 3.1, N 7.8%. ^{1}H NMR (CD$_3$CN): δ = 12.58 (s, br., 2 H, NH), 8.61 (s, 2 H, 9,9′-H), 8.45 (s, 1 H, 1-H), 8.01 (d, ^3J = 8 Hz, 4 H), 7.76 (m, 3 H), 7.62 (t, ^3J = 8 Hz, 4 H), 7.49 (t, ^3J = 8 Hz, 2 H), 7.42 (s, br., 2 H) ppm.

Attempted Formation of the Zn^{II} Complex (Zn/L 1:1) of the Singly Deprotonated Ligand: The procedure described above for preparation of the Co^{II} analogue was repeated with [Zn(dmso)$_6$](CF$_3$SO$_3$)$_2$ (83 mg) substituted for [Co(dmso)$_6$](BF$_4$)$_2$. A copious, dark-red, seemingly crystalline precipitate formed immediately and 12 h at room temperature was then allowed for equilibration before

the solid was collected and washed with acetonitrile and diethyl ether. Yield: 34 mg. Microscopic examination indicated contamination of this crude product with a few crystals of the bis(acylhydrazone). The complex was recrystallised from CHCl$_3$ by addition of CH$_3$CN, microanalysis then indicating that it was in fact the complex of the doubly deprotonated ligand. [Zn$_4$(**4**)$_4$]·4H$_2$O = C$_{104}$H$_{80}$N$_{24}$O$_{12}$Zn$_4$ (2119.5): calcd. C 58.94, H 3.80, N 15.86; found C 59.3, H 3.9, N 15.9%. M.p. >250 °C (decomp.).

Zn^{II} Complex (Zn/L 1:1) of the Doubly Deprotonated Ligand: The procedure described above for preparation of the Co^{II} analogue was repeated with [Zn(dmso)$_6$](CF$_3$SO$_3$)$_2$ (83 mg) substituted for [Co(dmso)$_6$](BF$_4$)$_2$. A bright red precipitate formed immediately, though again 12 h was allowed for full equilibration. The solid was collected and washed with acetonitrile and diethyl ether. Yield: 45 mg (84%). The complex was recrystallised from CHCl$_3$ by addition of CH$_3$CN. [Zn$_4$(**4**)$_4$]·5H$_2$O = C$_{104}$H$_{82}$N$_{24}$O$_{13}$Zn$_4$ (2137.5): calcd. C 58.44, H 3.87, N 15.73; found C 58.3, H 3.5, N 15.3%. M.p. >250 °C (decomp.). ^{1}H NMR (CD$_3$OD/CD$_2$Cl$_2$ 1:4): δ = 7.80 (m, 5 H, phenyl 2-protons superimposed on H-8); 7.73 (s, 2 H, 9-H); 7.43 (s, 1 H, 1-H); 7.40 (t, ^3J = 8 Hz, 2 H, phenyl 4-protons); 7.27 (t, ^3J = 8 Hz, 4 H, phenyl 3-protons); 7.14 (t, 2 H, 7,7′-H); 6.42 (d, ^3J = 8 Hz, 2 H, 6,6′-H) ppm. ^{13}C NMR (C$_2$D$_5$OD/CD$_2$Cl$_2$ 1:4): δ = 175.0, 156.8, 132.9, 132.5, 129.6, 128.4, 127.3, 126.7, 126.5, 126.4, 126.3, 123.9, 115.7 ppm. MS (MALDI-TOF): *m*/*z* (%) = 2048.3 (100) [M + H]$^+$.

Other M^{II} Complexes (M/L 1:1) of the Doubly Deprotonated Ligand

M = Fe: Fe^{II} ascorbate (43 mg, 5% excess) was dissolved in water (0.5 mL) and added to a solution of benzohydrazide (27 mg) in CH$_3$CN (3 mL) to give a deep violet solution. 2-phenylpyrimidine-4,6-dicarbaldehyde (22 mg) in CH$_3$CN (1 mL) was added and the mixture allowed stand for 5 min. The oily, violet precipitate which formed was redissolved by the addition of water (2 mL) before triethylamine (20 mg) was added, causing the solution to gain a deep yellow-brown colour and brown crystals to commence depositing. After 2 h, the crystals were collected and washed with water, acetonitrile and diethyl ether, then air dried. Yield: 39 mg (74%). The complex was recrystallised from ethanol/CH$_2$Cl$_2$ (1:10) by adding an equal volume of ethanol and allowing the CH$_2$Cl$_2$ to evaporate out. [Fe$_4$(**4**)$_4$]·6H$_2$O = C$_{104}$H$_{84}$Fe$_4$N$_{24}$O$_{14}$ (2117.4): calcd. C 59.00, H 4.00, N 15.88; found C 59.2, H 3.7, N 16.2%. MS (MALDI-TOF): *m*/*z* (%) = 2010.4 (100) [M + H]$^+$.

M = Ni: Benzohydrazide (54 mg) and [Ni(dmso)$_6$](CF$_3$SO$_3$)$_2$ (164 mg) were dissolved in CH$_3$CN (2 mL), forming a blue solution. Triethylamine (40 mg) was added, followed by a solution of 2-phenylpyrimidine-4,6-dicarbaldehyde (43 mg) in CH$_3$CN (2 mL). An amorphous, deep yellow-brown precipitate formed immediately. After 12 h, by which time the precipitate was obviously crystalline, this was collected and washed with a little acetonitrile (slightly soluble) and then ether. Yield: 82 mg (73%). The complex was recrystallised from boiling ethanol (20 mL) by cooling to room temperature, very slow deposition of small, brown, rod-like crystals ensuing. [Ni$_4$(**4**)$_4$]·2CH$_3$CN·9H$_2$O = C$_{108}$H$_{96}$N$_{26}$Ni$_4$O$_{17}$ (2265.0): calcd. C 57.27, H 4.27, N 16.08; found C 57.1, H 4.0, N 16.1%. MS (MALDI-TOF): *m*/*z* (%) = 2021.3 (80) [M + H]$^+$.

M = Cu: Benzohydrazide (54 mg) and [Cu(dmso)$_6$](CF$_3$SO$_3$)$_2$ (164 mg) were dissolved in CH$_3$CN (2 mL), forming a blue solution. Triethylamine (40 mg) was added (causing a colour change to brownish-green), followed by a solution of 2-phenylpyrimidine-4,6-dicarbaldehyde (43 mg) in CH$_3$CN (2 mL). An amorphous, dark brown precipitate formed immediately. Again, the mixture was allowed stand for 12 h before the precipitate was collected and washed with acetonitrile (slightly soluble) and ether. Yield: 88 mg

(82%). The complex was recrystallised from ethanol/CH_2Cl_2 (1:10) by slow evaporation of the filtered solution. $[Cu_4(\mathbf{4})_4]\cdot 6H_2O$ = $C_{104}H_{84}Cu_4N_{24}O_{14}$ (2148.1): calcd. C 58.15, H 3.94, N 15.65; found C 58.1, H 3.7, N 15.2%. MS (MALDI-TOF): m/z (%) = 2041.3 (5) $[M + H]^+$.

(v) R = $4\text{-}CH_3C_6H_4$, R′ = H ($5H_2$)

Cu^{II} Complex (Cu/L 1:1) of the Doubly Deprotonated Ligand: $[Cu(dmso)_6](CF_3SO_3)_2$ (166 mg), 2-phenylpyrimidine-4,6-dicarbaldehyde (44 mg) and $4\text{-}CH_3C_6H_4CONHNH_2$ (60 mg) were dissolved together in CH_3CN (5 mL), the initially green solution developing a deep red colour within 60 s. Precipitation of a red-brown solid with a metallic sheen rapidly ensued but, before this was extensive, triethylamine (50 mg) was added, causing the precipitate to become a darker red and to become more voluminous. After 15 min, the precipitate was well-settled and the supernatant retained only a pale yellow colour. The precipitate was collected, washed with CH_3CN then diethyl ether, and air-dried. Yield: 86 mg (75%). It was recrystallised from the minimum volume (ca. 20 mL) of EtOH/ CH_2Cl_2 (1:10) by adding EtOH (10 mL) after filtration and allowing the CH_2Cl_2 to evaporate out. $[Cu_4(\mathbf{5})_4]\cdot 7H_2O$ = $C_{112}H_{102}Cu_4N_{24}O_{15}$ (2278.3): calcd. C 59.04, H 4.51, N 14.75; found C 59.1, H 4.4, N 14.8%. MS (MALDI-TOF): m/z (%) = 2153.5 (10) $[M + H]^+$.

Zn^{II} Complex (Zn/L 1:1) of the Doubly Deprotonated Ligand: The method using the preformed ligand deprotonated by KOtBu was used to provide the orange complex, which was recrystallised from a 1:1 mixture of CH_3OH and CH_2Cl_2 by adding an equal volume of CH_3CN and then allowing the CH_2Cl_2 to evaporate out. $C_{112}H_{152}N_{24}O_8Zn_4\cdot 12H_2O$ (2375.8): calcd. C 56.62, H 4.75, N 14.15; found C 56.3, H 4.09, N 14.2%. M.p. >250 °C (decomp.). ^1H NMR ($CDCl_3$ + CD_3OD, 1:1): δ = 7.67 (t, ^3J = 7.3 Hz, 1 H, 8-H), 7.64 (d, ^3J = 8.0 Hz, 4 H, tolyl-2-protons), 7.59 (s, 2 H, 9,9′-H), 7.23 (s, 1 H, 1-H), 7.03 (t, ^3J = 7.7 Hz, 2 H, 7,7′-H), 7.01 (d, ^3J = 8.0 Hz, 4 H, tolyl-3-protons), 6.34 (d, ^3J = 7.3 Hz, 2 H, 6,6′-H), 2.26 (s, 6 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 177.1, 166.3,

158.9, 152.8, 142.1, 137.6, 132.9, 131.0, 129.7, 128.2, 126.6, 116.1, 107.9, 73.5, 69.3, 32.1, 30.6, 29.9_5, 29.9_2, 29.8_7, 29.8, 29.7, 29.6_4, 29.5_6, 29.5, 26.3_3, 26.3_0, 22.86, 22.9, 14.2_7, 14.2_5 ppm. MS (MALDI-TOF): m/z (%) = 2161.3 (100) $[M + H]^+$.

As an alternative synthesis, solutions of $Zn(BF_4)_2\cdot 6dmso$ (70 mg) and $4\text{-}CH_3C_6H_4CONHNH_2$ (30 mg) in CH_3CN (1 mL) and of 2-phenylpyrimidine-4,6-dicarbaldehyde (22 mg) in CH_3CN (1 mL) were mixed to give an initially pale yellow solution, which developed a deep orange colour over 2 min. Triethylamine (30 mg) was then added to give immediately a red precipitate, which was collected by filtration and washed with acetonitrile and diethyl ether. Yield: 43 mg (59%). This was recrystallised by dissolution in the minimum volume (ca. 20 mL) of 1:1 ethanol/CH_2Cl_2, filtration and slow evaporation of the filtrate.

(vi) R = CH_3OCH_2, R′ = H ($6H_2$)

Zn^{II} Complex (Zn/L 1:1) of the Doubly Deprotonated Ligand: $CH_3OCH_2CONHNH_2$ (42 mg) and $Zn(BF_4)_2\cdot 6dmso$ (120 mg) were dissolved in CH_3CN (2 mL) and added to a solution of 2-phenyl-pyrimidine-4,6-dicarbaldehyde (43 mg) in CH_3CN (2 mL) to give a clear, yellow solution. Triethylamine (50 mg, excess) was added to produce an immediate bright orange precipitate which settled within 5 min, leaving a pale yellow supernatant. After 1 h, the precipitate was collected, washed with CH_3CN and diethyl ether and dried in air. Yield: 65 mg (64%). The crude product was dissolved in boiling CH_3OH (10 mL), filtered to remove a small amount of brownish, gelatinous material, and the filtrate diluted with an equal volume of diethyl ether to produce small orange crystals. $C_{72}H_{72}N_{24}O_{16}Zn_4\cdot 11H_2O$ (1989.2): calcd. C 43.47, H 4.76, N 16.75; found C 43.5, H 4.4, N 16.8%. M.p. >255 °C (about this temperature, the sample shrinks and its colour lightens but there is no obvious melting). ^1H NMR (D_2O): δ = 7.78 (m, br.), 7.73 (s), 7.28 (m, br.), 3.91 (s, 2 H), 3.21 (s, 3 H) ppm. ^{13}C NMR (D_2O + ca. 10% CD_3OD): δ = 181.6, 166.6, 159.8, 138.9, 136.7, 132.9, 130.0, 121.2, 72.1, 59.5 ppm. MS (MALDI-TOF): no peaks above m/z 897 were detectable.

Table 2. Crystal and refinement data.

Compound	Ligand 2	$[Ni_4(\mathbf{4}H_2)_4](ClO_4)_8\cdot 12H_2O$	$[Zn_8(\mathbf{4}H_2)_8](BF_4)_{16}\cdot 7C_6H_6\cdot 5CH_3CN\cdot 5H_2O$	$[Co_4(\mathbf{4}H)_4](BF_4)_4\cdot 7CH_3CN$
Chemical formula	$C_{20}H_{24}N_6O_2$	$C_{104}H_{104}Cl_8N_{24}Ni_4O_{52}$	$C_{260}H_{227}B_{16}F_{64}N_{53}O_{23}Zn_8$	$C_{118}H_{97}B_4Co_4F_{16}N_{31}O_8$
M/g mol^{-1}	380.5	3184.4	6374.1	2660.2
Crystal system	triclinic	tetragonal	monoclinic	monoclinic
Space group	$P\bar{1}$	$I4_2d$	$P2_1/n$	$P2_1/c$
a /Å	7.7940(2)	17.835(3)	18.581(5)	22.0163(4)
b /Å	10.7990(3)	17.835(3)	22.001(5)	24.0465(4)
c /Å	23.9020(6)	52.461(11)	33.559(8)	22.9922(5)
α /°	88.312(2)	90	90	90
β /°	87.627(2)	90	95.163(12)	99.531(5)
γ /°	76.929(1)	90	90	90
V /Å^3	1957.6	16687(5)	13663(6)	12004.4(4)
Z	1	4	2	4
D_{calcd} /g cm^{-3}	1.291	1.268	1.545	1.470
λ /Å	0.71073 (Mo-K_α)	0.71073 (Mo-K_α)	0.38745 (Synchrotron)	0.71073 (Mo-K_α)
μ /mm^{-1}	0.087	0.65	0.432	0.639
$F(000)$	808	6112	6444	5432
T /K	173(2)	173(2)	120(2)	173(2)
R_{int}	0.027	0.051	0.064	0.08
R_1	0.057	0.109	0.089	0.103
wR_2	0.185	0.267	0.2395	0.129
GOF	0.813	1.028	1.042	1.167
$\Delta\rho_{min}$ /e Å^{-3}	−0.26	−0.55	−1.56	−0.17
$\Delta\rho_{max}$ /e Å^{-3}	0.23	0.81	1.03	1.42
CCDC #	637552	637553	637554	637555

(vii) R = CH₃OCH₂CH₂OCH₂, R′ = H (7H₂)

Zn^II Complex (Zn/L 1:1) of the Doubly Deprotonated Ligand: Again, this was prepared from the preformed ligand by using KO*t*Bu as base. The orange product was recrystallised from CH₃CN by addition of diethyl ether. C₈₈H₁₀₄N₂₄O₂₄Zn₄·13H₂O (2377.7): calcd. C 44.45, H 5.51, N 14.14; found C 44.3, H 5.03, N 14.4%. M.p. >250 °C (decomp.). ¹H NMR (CD₃CN): δ = 7.64 (t, ³*J* = 7.6 Hz, 1 H, 8-H); 7.51 (s, 2 H, 9-H); 7.25 (s, 1 H, 1-H); 7.17 (t, ³*J* = 7.6 Hz, 2 H, 7,7′-H); 6.39 (d, ³*J* = 7.2 Hz, 2 H, 6,6′-H); 3.95 (s, 4 H, COCH₂O); 3.46 (m, 4 H, CH₂CH₂); 3.39 (m, 4 H,

CH₂CH₂); 3.22 (s, 6 H, CH₃) ppm. ¹³C NMR (CD₃CN): δ = 182.6, 173.7, 166.7, 159.8, 137.5, 136.2, 131.6, 129.6, 126.7, 72.4, 71.8, 70.9, 58.7 ppm. MS (MALDI-TOF): *m/z* (%) = 2144.4 (100).

Crystallography

(a) Growth of Crystals for Structure Determination (formulae indicate the composition determined from the structure solutions): Bis(acylhydrazone) (**2**) crystals were obtained by liquid diffusion of CH₃CN into a solution of **2** in CHCl₃. [Ni₄(**4**H₂)₄](ClO₄)₈·8H₂O·4CH₃NO₂ crystals were obtained by vapour diffusion of di-

Table 3. Crystal and refinement data.

Compound	[Ni₄(**4**)₄](NO₃)₁.₅·CH₃OH·0.5Et₂O·4H₂O	[Co₄(**1**)₄]·8CH₃OH·16H₂O	[Ni₄(**1**)₄]·(≈18H₂O)	[Zn₄(**1**)₄]·(≈18H₂O)
Chemical formula	C₁₀₇H₉₀.₅N₂₅.₅Ni₄O₁₈	C₇₂H₁₂₀Co₄N₂₄O₃₂	C₆₄H₉₂N₂₄Ni₄O₂₆	C₆₄H₉₂N₂₄O₂₆Zn₄
M/g mol⁻¹	2248.83	2069.6	1840.0	1873.2
Crystal system	triclinic	tetragonal	monoclinic	monoclinic
Space group	P1̄	I4₁/a	C2/c	C2/c
a /Å	16.1617(4)	19.8830(7)	16.489(3)	16.669(3)
b /Å	18.0510(4)	19.8830(7)	25.581(5)	25.573(5)
c /Å	21.3102(5)	25.2440(7)	20.524(4)	20.493(4)
α /°	89.621(1)	90	90	90
β /°	73.838(1)	90	110.29(3)	109.96(3)
γ /°	72.380(2)	90	90	90
V /Å³	5670.6(3)	9979.8(6)	8120(3)	8226(3)
Z	2	4	4	4
*D*_calcd. /g cm⁻³	1.311	1.356	1.505	1.513
λ /Å	0.71073 (Mo-*K*α)	0.71073 (Mo-*K*α)	0.71073 (Mo-*K*α)	0.71073 (Mo-*K*α)
μ /mm⁻¹	0.728	0.741	1.004	1.242
F(000)	2297	4144	3837	3883
T /K	173(2)	173(2)	173(2)	173(2)
R_int	0.10	0.054	0.088	0.089
R₁	0.086	0.078	0.080	0.107
wR₂	0.2185	0.211	0.156	0.246
GOF	0.984	1.002	1.080	1.089
Δρ_min /e Å⁻³	–0.64	–0.37	–1.49	–0.82
Δρ_max /e Å⁻³	0.98	0.67	1.51	1.74
CCDC #	637556	637557	637558	637559

Table 4. Crystal and refinement data.

Compound	[Fe₄(**3**)₄]·4H₂O	[Co₄(**3**)₄]·4H₂O	[Ni₄(**3**)₄]·4H₂O	[Cu₄(**3**)₄]·2H₂O	[Zn₄(**3**)₄]·2H₂O
Chemical formula	C₁₁₂H₁₆₀Fe₄N₂₄O₁₂	C₁₁₂H₁₆₀Co₄N₂₄O₁₂	C₁₁₂H₁₆₀N₂₄Ni₄O₁₂	C₁₁₂H₁₅₆Cu₄N₂₄O₁₀	C₁₁₂H₁₅₆N₂₄O₁₀Zn₄
M/g mol⁻¹	2258.0	2270.4	2269.5	2252.8	2256.1
Crystal system	tetragonal	tetragonal	tetragonal	monoclinic	monoclinic
Space group	I4₁/a	I4₁/a	I4₁/a	I2/a	C2/c
a /Å	21.184(1)	21.215(3)	21.167(3)	19.949(4)	29.3560(6)
b /Å	21.184(1)	21.215(3)	21.167(3)	25.296(5)	25.4480(8)
c /Å	25.391(3)	25.231(5)	25.163(5)	22.233(4)	20.0720(5)
α /°	90	90	90	90	90
β /°	90	90	90	91.77(3)	130.919(2)
γ /°	90	90	90	90	90
V /Å³	11394.5(15)	11356(3)	11274(3)	11214(4)	11330.6(5)
Z	4	4	4	4	4
*D*_calcd. /g cm⁻³	1.312	1.328	1.337	1.334	1.323
λ /Å	0.31840 (Synchrotron)	0.71073 (Mo-*K*α)	0.71073 (Mo-*K*α)	0.71073 (Mo-*K*α)	0.71073 (Mo-*K*α)
μ /mm⁻¹	0.303	0.644	0.728	0.817	0.904
F(000)	4768	4816	4832	4768	4768
T /K	180(2)	173(2)	173(2)	173(2)	173(2)
R_int	0.159	0.055	0.103	0.095	0.066
R₁	0.0825	0.067	0.088	0.067	0.077
wR₂	0.212	0.169	0.181	0.138	0.157
GOF	1.055	1.095	1.095	1.051	1.017
Δρ_min /e Å⁻³	–1.12	–0.66	–0.68	–0.71	–0.74
Δρ_max /e Å⁻³	0.73	1.80	1.89	1.34	–0.70
CCDC #	637560	637561	637562	637563	637564

isopropyl ether into a CH_3NO_2 solution. A $[Zn_8(E,E\text{-}\mathbf{4}H_2)_4(Z,Z\text{-}\mathbf{4}H_2)_4(OH_2)_2(CH_3CN)_2(BF_4)_2](BF_4)_{14}\cdot7C_6H_6\cdot3CH_3CN\cdot3H_2O$ crystal was selected from the mixture of products obtained as described above. A $[Co_4(\mathbf{4}H)_4](BF_4)_4\cdot7CH_3CN$ single crystal was selected from the mass obtained on one occasion when the ligand and metal ion were subjected to reaction in the absence of any deliberately added base. $[Ni_4(\mathbf{4})_{2.5}(\mathbf{4}H)_{1.5}](NO_3)_{1.5}\cdot CH_3OH\cdot0.5(C_2H_5)_2O$ single crystals, as a mixture of needles and plates, were grown by vapour diffusion of diethyl ether into a methanol solution of the complex. All variously solvated complexes $[M_4(\mathbf{1})_4]$, M = Co^{II}, Ni^{II}, Zn^{II}, were crystallised by slow evaporation of methanol solutions in air. All variously hydrated complexes $[M_4(\mathbf{3})_4]$, M = Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, were crystallised by liquid-liquid diffusion of CH_3CN into $CHCl_3$ solutions.

(b) Structure Determination: The structures were determined under various conditions on various instruments in Jyväskälä, Strasbourg and Grenoble (European Synchrotron Radiation Facility). Basic information for each structure is given in Tables 2, 3 and 4.

CCDC-637552–637565 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.

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