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# Self-Assembly, Structure and Solution Dynamics of Tetranuclear $Zn^{2+}$ Hydrazone [2×2] Grid-Type Complexes

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**Keywords:** Self-assembly / Grid-type complexes / Hydrazone ligands / Zinc / Supramolecular chemistry

We describe the self-assembly processes as well as the structural and physico-chemical properties of $[2\times2]Zn^{2+}_4$ grid complexes involving the bis-tridentate ligands **7**–**12**, based on bis(hydrazone)pyrimidine complexation subunits and octahedrally coordinated $Zn^{2+}$ ions. The NMR spectroscopic data and the X-ray crystal structure results indicate that in solution and in the solid state the complexes **13**–**18** adopt a very compact arrangement providing stable [2×2] hydrazone-grid arrays. The π–π stacking between the phenyl ring and the hydrazone units of the perpendicular ligands in the complexes induces a perfect orthogonal arrangement suitable for applications in self-organized metallosupramolecular systems. Zinc complexes provide an opportunity to study the acid–base chemistry without the added effects due to paramagnetism or redox chemistry. The intermediate protonated grids undergo relatively rapid proton exchange on the NMR timescale, the presence of a sharp pyrimidine proton resonance suggesting that there is significant delocalization of the negative charge along the backbone of the ligand. Rotation of the phenyl ring is observed. It involves probably a mechanism in which one of the ligands partially dissociates allowing the initially intercalated phenyl group to rotate, before recoordination of the terminal pyridine.



## Introduction

During the last decade, intense investigations have been carried out on the spontaneous generation of various types of supramolecular inorganic architectures, both as touchstone for the design of self-organization processes and as devices for nanotechnology.[1] The first complexes of [2×2] grid-type architecture employed bipyridine- and terpyridine-like binding subunits and respectively tetrahedrally ($Cu^+$ and $Ag^+$)[2a,2b,2f] and octahedrally ($Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$)[2c–2f] coordinated metal ions. The latter in particular present remarkable electronic,[2d,3] magnetic,[4] and photophysical[7a] properties. The success in the formation of the [2×2] grid-type complexes as well as their interesting physical properties stimulated us to extend our investigations towards grids based on ligands for octahedrally coordinating metal ions, that would be synthetically more accessible than the earlier pyridine–pyrimidine sequences.[5]

The hydrazone unit is a suitable isomorphic analog of a pyridine group and is easily generated by hydrazine–carbonyl condensation. It has been implemented as a useful and simple method for the formation of molecular strands presenting extended helical architectures.[6] The *transoid*,*transoid* form of the free ligand is converted into the *cisoid,cisoid* form, corresponding to a terpyridine-type complexation site, on metal–ion binding (Scheme 1).

Thus, hydrazone-containing ligands were shown to yield [2×2] grid complexes presenting novel physical (optical,[7a] electrochemical,[7b,7c] magnetic[7d]) properties.

Based on these premises, we report here a study of the generation of several tetranuclear $[2\times2]Zn^{2+}_4$ grid-type complexes using such bis(hydrazone)pyrimidine ligands. It confirms their value as a synthetic alternative to the previously used pyridine–pyrimidine sequence and markedly simplifies the methodology for the synthesis of grid complexes based on octahedrally coordinated transition-metal ions.

We describe the self-assembly processes as well as the structural and physico-chemical properties of $[2\times2]Zn^{2+}_4$ grid complexes involving bis-tridentate ligands **7**–**12**, based on bis-hydrazone-pyrimidine complexation subunits and octahedrally coordinated $Zn^{2+}$ ions.

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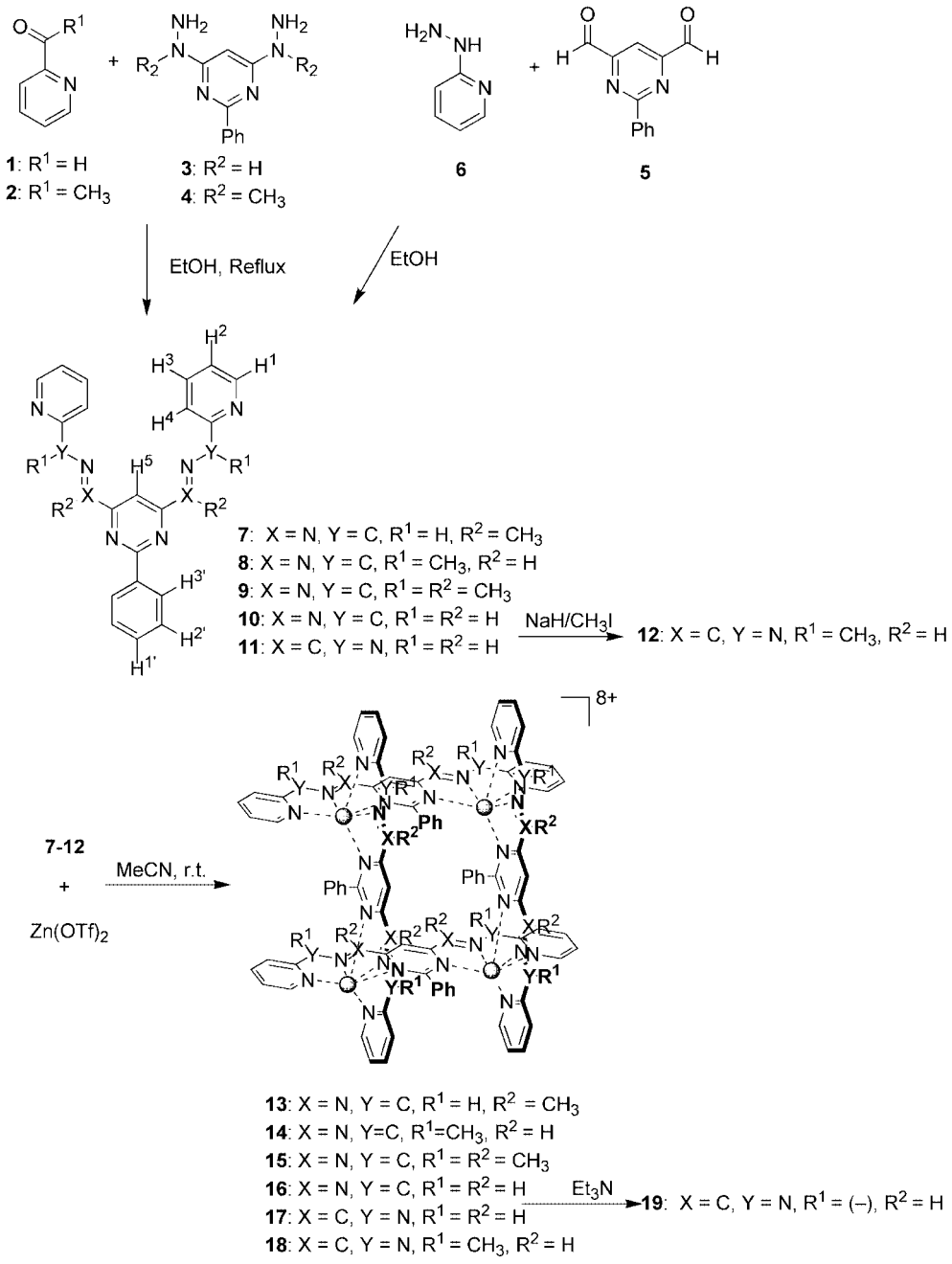


Scheme 1. Synthesis of the ligands **7**–**12** and of the $[2\times2]Zn^{2+}{}_4$ grid-type complexes **13**–**18**.

## Results and Discussions

### Synthesis and Characterization of Ligands 7–12 and of the $[2\times2]Zn^{2+}{}_4$ Grid-Type Complexes 13–18

The synthesis of the ligands **7**–**12** is outlined in Scheme 1.

The ligands **7**–**10** were obtained by the condensation of two equivalents of 2-pyridinecarboxaldehyde (**1**), or of 2-acetylpyridine (**2**), with one equivalent of dihydrazinopyrimidine (**3**) or of (dimethylhydrazino)pyrimidine (**4**) in ethanol. These ligands precipitate from the reaction mixture in ca. 90% yield as pure compounds. The NMR and ESI-MS spectra were in agreement with the proposed formula. Ligand **11** was obtained by the analogous condensation of the pyrimidinedicarbaldehyde **5** with 2-hydrazinopyridine (**6**). Ligand **12** was obtained through methylation of **11** in THF with $NaH/CH_3I$.

The grid-type complexes **13**–**18** resulted from spontaneous self-assembly of the ligands **7**–**12** with $Zn(CF_3SO_3)_2$ in acetonitrile (Scheme 1) at room temperature, followed by crystallization with diisopropyl ether or diethyl ether. The compounds **13**–**18** were characterized by NMR spectroscopy, positive ESI mass spectrometry, elemental analysis and in the case of **13**–**15** by single-crystal X-ray diffraction.

  

### Crystal Structure of the Complexes 13–15

Layering a 1:1 solution of the ligands **7**–**10** and $Zn(CF_3SO_3)_2$ in acetonitrile onto benzene resulted in the development of light-yellow prismatic crystals of grid-type Zn complexes **13**–**15**, which were investigated by X-ray crystallography.

In all these structures the complexes present a $[2\times2]Zn^{2+}{}_4$ grid-type architecture in which four metal ions form a square and lie close to an average common plane (Figure 1). In the case of complex **16** the overall quality of the crystal structure data is too low, and crystals of better quality are required for improving the structural data.

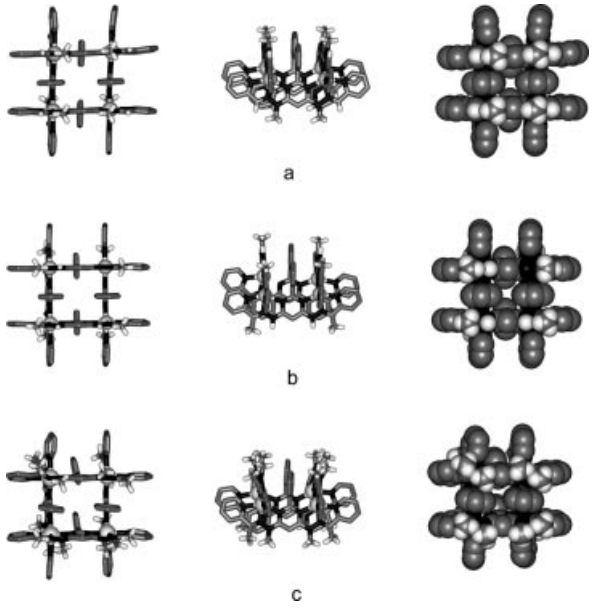


Figure 1. Crystal structure of the [2×2] $Zn_4^{2+}$ grid complexes: a) **13**, b) **14**, c) **15**: top view (left), side view in stick representation (center) and space-filling representation (right) The $Zn^{2+}$ ions are shown as spheres.

In the complexes **13**–**15** the $Zn^{2+}$ ions display a distorted octahedral coordination. The Zn–Zn distances lie in the range of 6.37–6.60 Å and the average inner angle between three Zn atoms of about 90°. The average Zn–N bonds are 2.17 Å for the pyridine nitrogen atoms, 2.20 Å for the pyrimidine nitrogen atoms and 2.14 Å for the hydrazone nitrogen atoms.

The average distance between two parallel ligands is 6.50 Å, and the average distance between the $–R^1C=N–NR^2–$ moiety of one ligand and the phenyl ring of the orthogonal one is 3.25 Å, indicating van der Waals contact and a strong π–π stacking. The almost parallel insertion of the phenyl substituent between two ligands, leads to an overall geometry of the $[2\times2]Zn^{2+}{}_4$ grid complexes **13** (Figure 1, a) and **14** (Figure 1, b) close to regular square. In the case of **15** (Figure 1, c) the steric interactions due to the close contacts (C–C distance of 2.95 Å) of the methyl substituents of the hydrazone moiety, are found to cause a distorted geometry, bending the planes of the ligands. The pinching angle provides information about the shape of complexes, smaller values being correlated with increased linearity of the ligand in the complex. It is smaller for **13**–**15** (16.5°) than for the analogous terpyridine grid-type[2e] (19.3°) and rack-type[8] (19.6°) $Zn^{2+}$ complexes.

### $^1$H NMR Spectra

The $^1$H NMR spectra of the ligands **7**–**12** are consistent with the presence of a *transoid*,*transoid* conformation along the connecting NC–CN bonds in both hydrazone pyridine functionalities. This conformation was further confirmed by intermolecular NOE interactions between the $H^4$ protons of external pyridines and the $H^5$ proton of internal pyrimidine, and between the protons of the $R^1$ (H or Me) and $R^2$ (H or Me) substituents of the hydrazone units.

The metal complexation leads to changes in $^1$H NMR spectra with large modifications in the chemical shifts of the protons of the ligands **7**–**12**. The metal–ion binding converts the wrapped *transoid*,*transoid* form of the free ligand to the linear *cisoid*,*cisoid* form, corresponding to a terpyridine-type complexation site (Scheme 1). This has been confirmed by a ROESY NMR experiment, where NOE interactions between $H^4$ and $R^1$ = H or Me as well as between $H^5$ and $R^2$ = H or Me are observed for the complexes **13**–**18**. The major changes observed in the NMR spectra on complexation reside in the strong shielding ($\Delta\delta$ = –1.66–3.34) of the phenyl protons when the zinc complexes **13**–**18** are formed (Table 1). Moreover, the *o*,*o′* and *m*,*m′* protons of the phenyl ring, which are equivalent in the ligands **7**–**12**, become non-equivalent in the complexes **13**–**17**, suggesting that in solution the grid-type-Zn complexes adopt a very compact structure where the phenyl rings of the two ligands on one face of the grid structure insert between the two ligands on the other face, blocking the rotation around the phenyl–pyrimidine C–C bonds, as seen in the parent grids.[2c] The phenyl insertion has been confirmed by a ROESY NMR experiment, where NOE interactions between $R^1$ and $H^{2'o}$, between $R^2$ and $H^{3'}$ and between $H^5$ and $H^{2'i}$ are observed for the complexes **9**–**12**.

The well-resolved NMR spectra of these species provide an opportunity to investigate the deprotonation of the hydrazone NH protons in these molecules. The hydrazones in the analogous complex $Zn(papy)_2$ are significantly more acidic as a result of metal complexation;[9] similar effects, with accompanying optical changes, have been reported for grids containing a hydrazone N–H group.[7a] Addition of eight equivalents of triethylamine to acetonitrile solutions of **18** results in the precipitation of the neutral complex **19** as gold-colored crystals. This deprotonation reaction can be monitored by titration with triethylamine and monitoring with $^1$H NMR spectroscopy (Figure 2).

The chemical shift of the ethyl $CH_2$ group is consistent with the nearly complete protonation of the triethylamine throughout the titration, confirming the high acidity of these complexes. Early in the titration, the exchange coupling to the ammonium NH proton is clearly resolved, indicating that proton-exchange processes are confined to the grid complex; however, as the titration proceeds, loss of this

  

Table 1. Chemical shifts[a] and chemical shift differences for $^1H$ NMR signals of the ligands **7**–**12** (in $CDCl_3$) and Zn grid-type complexes (in $CD_3CN$).[b]

| Compound | $H^{1'i}$ | $H^{1'o}$ | $H^{2'i}$ | $H^{2'o}$ | $H^{3'}$ | $H^1$ | $H^2$ | $H^3$ | $H^4$ | $H^5$ | $R^1$ | $R^2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **7** | 8.48 | 8.48 | 7.48 | 7.48 | 7.5 | 8.63 | 7.32 | 7.82 | 8.21 | 7.84 | 7.99 | 3.84 |
| **13** | 5.44 | 6.49 | 7.18 | 7.78 | 8.01 | 7.6 | 7.25 | 7.87 | 7.65 | 6.84 | 7.98 | 3.67 |
| $\Delta\delta$ | –3.04 | –1.99 | –0.3 | 0.3 | 0.5 | –0.98 | –0.07 | 0.05 | –0.61 | –1 | –0.01 | –0.17 |
| **8** | 8.36 | 8.36 | 7.46 | 7.46 | 7.46 | 8.68 | 7.25 | 7.76 | 8.24 | 8.39 | 2.48 | 8.42 |
| **14** | 5.51 | 6.48 | 7.07 | 7.8 | 8.05 | 7.66 | 7.27 | 7.9 | 7.79 | 6.74 | 2.4 | 10.97 |
| $\Delta\delta$ | –2.85 | –1.88 | –0.39 | 0.34 | 0.59 | –1.02 | 0.02 | 0.14 | –0.45 | –1.65 | –0.08 | 2.55 |
| **9** | 8.52 | 8.52 | 7.48 | 7.48 | 7.51 | 8.63 | 7.3 | 7.58 | 8.17 | 6.35 | 2.52 | 3.6 |
| **15** | 5.18 | 6.56 | 7.03 | 7.72 | 7.96 | 7.37 | 7.06 | 7.88 | 7.6 | 6.6 | 2.57 | 3.8 |
| $\Delta\delta$ | –3.34 | –1.96 | –0.45 | 0.24 | 0.45 | –1.26 | –0.24 | 0.3 | –0.57 | 0.25 | 0.05 | 0.2 |
| **10** | 7.48 | 7.48 | 7.32 | 7.32 | 7.34 | 8.69 | 7.42 | 7.68 | 8.18 | 6.89 | 7.96 | 9.87 |
| **16** | 5.82 | 5.92 | 7.49 | 7.49 | 8.19 | 7.39 | 6.84 | 7.75 | 6.97 | 7.89 | 8.09 | 12.09 |
| $\Delta\delta$ | –1.66 | –1.56 | 0.17 | 0.17 | 0.85 | –1.3 | –0.58 | 0.07 | –1.21 | 1 | 0.13 | 2.22 |
| **11**[c] | 8.42 | 8.42 | 7.55 | 7.55 | 7.55 | 8.21 | 6.91 | 7.78 | 7.42 | 8.17 | 11.62 | 8.11 |
| **17** | 5.84 | 5.92 | 7.45 | 7.45 | 8.14 | 7.39 | 6.83 | 7.75 | 6.98 | 8.07 | 11.8 | 7.88 |
| $\Delta\delta$ | –2.58 | –2.5 | –0.1 | –0.1 | 0.59 | –0.82 | –0.08 | –0.03 | –0.44 | –0.1 | 0.18 | –0.23 |
| **12** | 8.50 | 8.50 | 7.49 | 7.49 | 7.49 | 8.28 | 6.89 | 7.65 | 7.85 | 8.33 | 3.74 | 7.72 |
| **18** | 5.81 | 5.89 | 7.34 | 7.53 | 8.16 | 7.34 | 6.93 | 7.86 | 7.29 | 8.14 | 3.51 | 7.86 |
| $\Delta\delta$ | –2.69 | –2.61 | –0.15 | 0.04 | 0.67 | –0.94 | 0.04 | 0.21 | –0.56 | –0.19 | –0.23 | 0.14 |

[a] Chemical shifts for ligands **7**–**10** and complexes **13**–**16** were recorded at 500 MHz, chemical shifts for ligands **11**–**12** and complexes **17**–**18** were recorded at 300 MHz. [b] *i* and *o* designate the inner and outer *ortho* and *meta* protons, respectively, on the phenyl substituent. [c] 1H NMR spectrum of **11** was recorded in $[D_6]$DMSO.

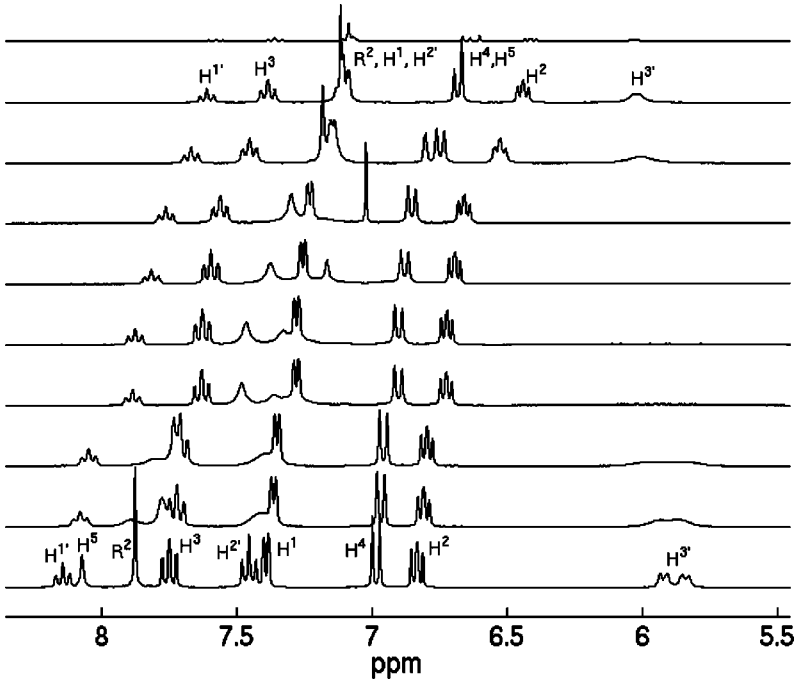


Figure 2. $^1H$ NMR of grid complex **17** with triethylamine in $[D_3]$acetonitrile. From bottom to top, the ratio $Et_3N$/**17** is 0.0, 0.7, 1.0, 2.5, 2.8, 3.5, 4.1, 5.0, 6.4, 7.9. The intensity of the last spectrum is reduced as a result of precipitation of the neutral complex.

resolution indicates rapid exchange of protons between the ammonium ion and the grid. During the titration, the $^1H$ NMR spectrum of the ligand undergoes a general upfield shift consistent with an increasing electron density on the ligand. The overall spectrum is remarkably simple indicating a rapid exchange of protons between sites on the grid, though significant broadening of some of the grid complex protons occurs. In particular, the imine and pyrimidine protons ($R^2$, $H^5$) show significant broadening consistent with deprotonation of the hydrazone N–H sites. Whereas the imine protons remain broadened until near the end of the titration, the pyrimidine proton appears as a sharp singlet around $Et_3N$/**18** ratios of 4:1 (i.e. deprotonation of half of the acidic NH sites). This is consistent with each ligand being deprotonated once before any are deprotonated a second time; with each ligand singly deprotonated, proton exchange does not significantly change the environment of the pyrimidine proton. More remarkable is the behavior of the phenyl *ortho* and *meta* protons, which rapidly broaden upon addition of traces of base. Halfway through the titration

  

these protons are barely visible as a broad rise in the baseline. The resonances only reappear toward the end of the titration but no longer show clear 'inner' and 'outer' peaks, which suggests a dynamic mechanism that allows rotation of the phenyl ring.

This is further supported by variable-temperature NMR studies of the neutral complex **19** in chloroform (Figure 3). While at room temperature the inner and outer phenyl protons are equivalent, lowering the temperature results in broadening of this resonance. Resolved inner and outer phenyl proton resonances were not observed for this complex above the freezing point of the solvent.

Repeating the titration in [$D_6$]DMSO results in significantly different observations (Figure 4). Initially, NMR indicates that the grid complex **18** is completely dissociated in [$D_6$]DMSO; the $^1$H NMR spectrum indicates only free ligand. Addition of $Et_3N$, however, results in loss of the free ligand and eventual formation of the neutral grid **19** upon

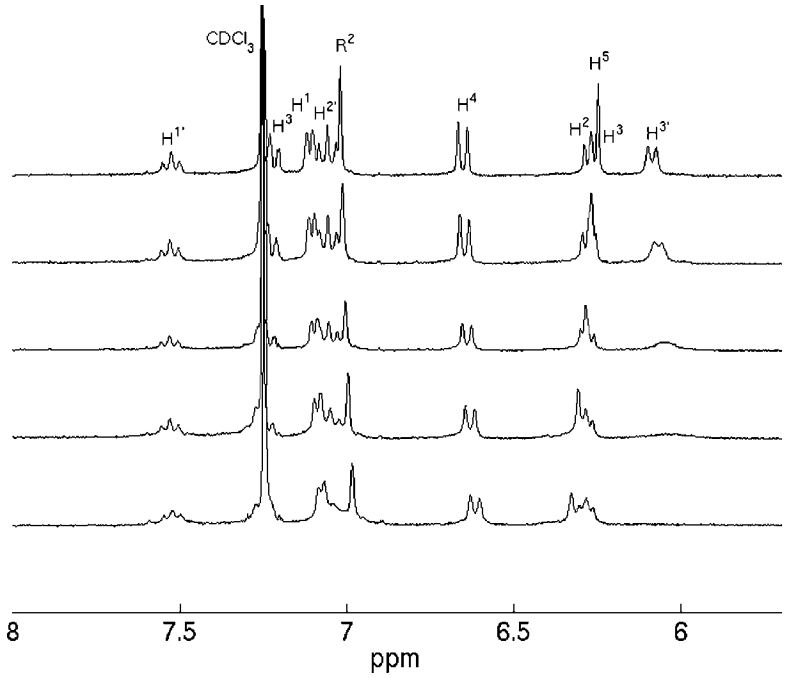


Figure 3. $^1$H NMR of neutral grid complex **19** in $CDCl_3$ at (top to bottom) 40 °C, 20 °C, 0 °C, –20 °C, –40 °C.

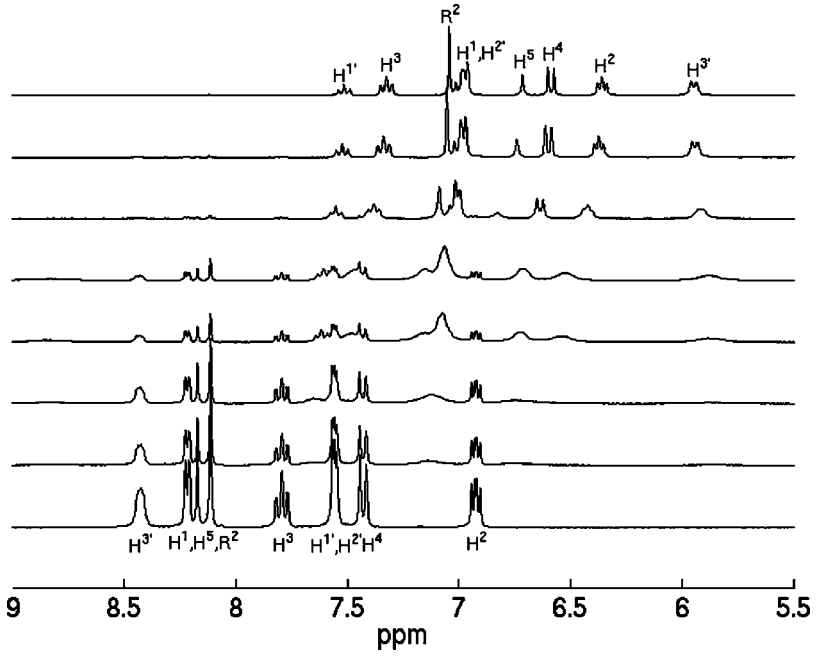


Figure 4. $^1$H NMR of grid complex **17** with triethylamine in [$D_6$]DMSO. From bottom to top, the ratio $Et_3N$/**17** is 0.0, 1.0, 2.0, 4.3, 5.0, 6.8, 9.3, 11.9.

  

addition of a full eight equivalents of base. That this is the only species in solution was confirmed by electrospray mass spectrometry. It is noteworthy that the coordinated ligand initially appears as very broad resonances in the $^1$H NMR spectrum, again indicative of dynamic processes, but upon completion of the titration a sharp spectrum is observed. Furthermore re-assembly of the grid is fast; the equilibration time allowed for collection of the data in Figure 4 was only that required to load and shim the sample and no further spectral changes were observed upon standing for 5–10 min.

## Discussion

The introduction of hydrazone links into the backbone of grid-forming ligands offers a means to modulate their properties and assembly through pH. The change in oxidation potential of protonated vs. unprotonated cobalt complexes has already been used to control the regioselective assembly of heterometallic cobalt grids.[7b] Zinc complexes provide an opportunity to study this acid–base chemistry without the added effects due to paramagnetism or redox chemistry. Any information on the pattern of deprotonation will give some information about the interactions within the grid complex. The quantitative protonation of triethylamine early in the titration clearly indicates the acidity of these complexes. Though the intermediate protonated grids undergo relatively rapid proton exchange on the NMR timescale, the presence of a sharp pyrimidine proton resonance at $Et_3N$/grid ratios of 4:1 indicates that not all of these are equally populated, and the ligands are all deprotonated once before they are further deprotonated. This suggests that there is significant delocalization of the negative charge along the backbone of the ligand. The intercalated phenyl ring could yield more information about the preferred tautomers; however, this is complicated by the presence of a dynamic process that allows interchange of inner and outer phenyl protons.

Rotation of the phenyl ring in a pyridine-type grid complex is a phenomenon that has not been previously observed. Examination of models suggests that simple phenyl rotation is unlikely because the cavity is too constrained; more likely is a mechanism in which one of the ligands partially dissociates allowing the initially intercalated phenyl group to rotate. In such a mechanism, the enhanced donor strength of the hydrazone anion ligand would increase the electron density on the metal ion and allow dissociation of one of the terminal pyridyl nitrogen atoms. The flexibility of the resulting five-coordinate metal-ion center would allow rotation of the phenyl ring before recoordination of the pyridine. The effect of the increased ligand donor strength accounts for the initially paradoxical observation of greater complex stability combined with greater flexibility observed in DMSO.

The NMR spectroscopic data and the X-ray crystal structure results suggest that in solution and in the solid state the complexes **13**–**18** adopt a very compact arrangement providing stable [2×2] hydrazone-grid arrays. The π–π stacking between the phenyl ring and the hydrazone units of the perpendicular ligands in the complexes induces a perfect orthogonal arrangement suitable for applications in self-organized metallosupramolecular systems.

## Experimental Section

**General:** Compounds **1** and **2** were obtained from commercial suppliers and used without purification. Compounds **3**, **4** and **5** were prepared according to the procedures described in the literature.[10] $^1$H NMR, COSY and ROESY correlation measurements were recorded with an ARX 500 MHz Bruker spectrometer or a JEOL Eclipse+ 300 MHz spectrometer in $CDCl_3$, [$D_6$]DMSO and $CD_3CN$, with the use of the residual solvent peak as reference. Mass spectrometric studies were performed in the positive ion mode with a quadrupole mass spectrometer (Micromass, Platform II) or an ion trap mass spectrometer (Agilent 1100 series). Samples were dissolved in acetonitrile and were continuously introduced into the mass spectrometer at a flow rate of 10 mL/min by using either a Waters 616HPLC pump or a syringe pump. The temperature (60 °C), and the extraction cone voltage ($V_c$ = 5–10 V) was usually set to avoid fragmentations. The microanalyses were carried out at Service de Microanalyses, Institut Charles Sadron, Strasbourg.

**General Procedure for the Synthesis of the Ligands 7–12:** Two equivalents of 2-pyridinecarboxaldehyde **1** or of 2-acetylpyridine **2** with one equivalent of dihydrazinopyrimidine **3** or of di-methylhydrazinopyrimidine **4** were refluxed in ethanol for 3 h. The resulting precipitates were filtered and washed with ethanol to give **7**–**12** as analytically pure compounds.

**4,6-Bis{[*N*-methyl-*N*′-(pyridin-2-yl)methylidene]hydrazino}-2-phenylpyrimidine (7):** $^1$H NMR ($CDCl_3$, ppm): $\delta$ = 8.63 (d, $J$ = 3.6 Hz, 2 H, $H^1$), 8.49 (m, 4 H, $H^{2'}$), 8.21 (d, $J$ = 3.6 Hz, 2 H, $H^4$), 7.99 (s, 2 H, $R^1$ = H), 7.84 (s, 1 H, $H^5$), 7.82 (dt, $J$ = 7.6 Hz, 2 H, $H^3$), 7.50 (m, 2 H, $H^{4'}$), 7.48 (m, 4 H, $H^{3'}$), 7.32 (dt, $J$ = 7.6 Hz, 2 H, $H^2$), 3.84 (s, 6 H, $R^2$ = $CH_3$); assignments made on the basis of the COSY and the ROESY spectra. $^{13}$C NMR ($CDCl_3$, ppm): $\delta$ = 42.4, 88.9, 124.1, 125.9, 127.0, 128.5, 129.0, 135.8, 149.9, 152.5, 154.7 163.8, 170.7. ES-MS: $m/z$ (%) = 423.5 (100) $[M + H]^+$. $C_{24}H_{22}N_8$ (422.5): calcd. C 68.23, H 5.26, N, 26.52; found C 66.49, H 5.36, N 27.10.

**2-Phenyl-4,6-bis{[1-(pyridin-2-yl)ethylidene]hydrazino}pyrimidine (8):** $^1$H NMR ($CDCl_3$, ppm): $\delta$ = 8.68 (d, $J$ = 3.6 Hz, 2 H, $H^1$), 8.42 (s, 2 H, $R^1$ = H), 8.39 (s, 1 H, $H^5$), 8.36 (m, 4 H, $H^{1'}$), 8.24 (d, $J$ = 3.6 Hz, 2 H, $H^4$), 7.76 (dt, $J$ = 7.6 Hz, 2 H, $H^3$), 7.46 (m, 6 H, $H^{2'}$, $H^{3'}$), 7.25 (dt, $J$ = 7.6 Hz, 2 H, $H^2$), 2.48 (s, 6 H, $R^1$ = $CH_3$); assignments made on the basis of the COSY and the ROESY spectra. $^{13}$C NMR ($CDCl_3$, ppm): $\delta$ = 12.4, 88.9, 124.1, 126.4, 127.0, 128.5, 129.3, 134.8, 149.9, 152.5, 155.6, 164.6, 170.2. ES-MS: $m/z$ (%) = 423.5 (100) $[M + H]^+$. $C_{24}H_{22}N_8$ (422.5): calcd. C 68.23, H 5.26, N, 26.52; found C 66.45, H 5.56, N 26.53.

**4,6-Bis{[*N*-methyl-*N*′-[1-(pyridin-2-yl)ethylidene]hydrazino}-2-phenylpyrimidine (9):** $^1$H NMR ($CDCl_3$, ppm): $\delta$ = 8.63 (d, $J$ = 3.6 Hz, 2 H, $H^1$), 8.52 (m, 4 H, $H^{1'}$), 8.17 (d, $J$ = 3.6 Hz, 2 H, $H^4$), 7.58 (dt, $J$ = 3.6 Hz, 2 H, $H^3$), 7.51 (m, 2 H), 7.48 (m, 4 H), 7.30 (dt, $J$ = 7.6 Hz, 2 H, $H^2$), 6.35 (s, 1 H, $H^5$), 3.60 (s, 6 H, $R^2$ = $CH_3$), 2.52 (s, 6 H, $R^1$ = $CH_3$); assignments made on the basis of the COSY and the ROESY spectra. $^{13}$C NMR ($CDCl_3$, ppm): $\delta$ = 12.8, 42.4, 88.9, 124.1, 125.9, 127.0, 128.5, 129.0, 135.8, 149.9, 152.5, 155.6 163.8, 170.7. ES-MS: $m/z$ (%) = 451.5 (100) $[M + H]^+$. $C_{26}H_{26}N_8$

  

(450.3): calcd. C 69.31, H 5.82, N, 24.87; found C 70.48, H 5.63, N 29.35.

**2-Phenyl-4,6-bis{[(pyridin-2-yl)methylidene]hydrazino}pyrimidine (10):** $^1$H NMR ($CDCl_3$, ppm): $\delta$ = 9.87 (s, 2 H, $R^2$ = H), 8.69 (d, $J$ = 3.6 Hz, 2 H, $H^1$), 8.18 (d, $J$ = 3.6 Hz, 2 H, $H^4$), 7.96 (s, 2 H, $R^1$ = H), 7.68 (dt, $J$ = 7.6 Hz, 2 H, $H^3$), 7.48 (m, 4 H, $H^{1'}$), 7.42 (dt, $J$ = 7.6 Hz, 2 H, $H^2$), 7.32–7.34 (m, 6 H), 6.89 (s, 1 H, $H^5$); assignments made on the basis of the COSY and the ROESY spectra. $^{13}$C NMR ($CDCl_3$, ppm): $\delta$ = 12.8, 42.4, 88.9, 124.1, 125.9, 127.0, 128.5, 129.0, 135.8, 149.9, 152.5, 155.6 163.8, 170.7. ES-MS: $m/z$ (%) = 395.5 (100) $[M + H]^+$. $C_{22}H_{18}N_8$ (394.5): calcd. C 66.99, H 4.60, N, 28.41; found C 67.34, H 4.89, N 27.86.

**2-Phenylpyrimidine-4,6-dicarbaldehyde Bis[(pyridin-2-yl)hydrazone] (11):** To a solution of 2-phenylpyrimidine-4,6-dicarbaldehyde (0.201 g, 0.95 mmol) in ethanol (15 mL) was added a solution of 2-hydrazinopyridine (0.206 g) in ethanol (2 mL). A yellow precipitate of **11** formed after about 30 s. The solution was allowed to stand overnight after which the precipitate was removed by filtration, recrystallized from tetrahydrofuran and dried in air to give 0.370 g of the product (99%).$^1$H NMR ([D$_6$]DMSO, ppm): $\delta$ = 11.62(s, 1 H, NH, exchanges w $D_2O$, $R^1$ = H), 8.42 (m, 2 H, $H^{1'}$), 8.21 (d, $J$ = 4.11 Hz, 2 H, $H^1$) 8.17 (s, 1 H, $H^5$), 8.11 (s, 2 H, $R^2$ = H), 7.78 (dd, $J$ = 7.4 Hz, $J$ = 8.2 Hz, 2 H, $H^3$), 7.55 (m, 3 H, $H^{2'}$, $H^{3'}$) 7.42 (d, $J$ = 8.2 Hz, 2 H, $H^4$), 6.91 (dd, $J$ = 7.4 Hz, $J$ = 4.1 Hz, 2 H, $H^2$). $^{13}$C NMR ([D$_6$]DMSO, ppm): $\delta$ = 107.5, 107.6, 117.1, 128.4, 129.2, 131.5, 137.6, 137.7, 139.0, 148.5, 156.7, 161.9, 164.2. IR (NaCl plate): $\tilde{\nu}$ = 1640, 1561, 1439, 751 cm$^{-1}$. ES-MS: $m/z$ (%) = 395 (100) $[M - H]^+$. $C_{22}H_{18}N_8$ (394.5): calcd. C 66.99, H 4.60, N, 28.41; found C 66.12, H 4.71, N 27.50.

**2-Phenylpyrimidine-4,6-dicarbaldehyde Bis[*N*-methyl-*N*-(pyridin-2-yl)hydrazone] (12):** Excess sodium hydride (60% dispersion in mineral oil) was added to a solution of **11** (419 mg) in tetrahydrofuran. The yellow solution rapidly turned dark blue-purple. To this solution was added excess methyl iodide, and the solution was stirred for 30 minutes during which the color dispersed to give a yellow solution. The solution was filtered and evaporated, and the residue washed with hexane to give 435 mg (97%) of **12**. $^1$H NMR ($CDCl_3$, ppm): $\delta$ = 3.74 (s, 6 H, $R^1$ = $CH_3$) 6.89 (ddd, $J$ = 1.0, $J$ = 5.0, $J$ = 7.0 Hz, 2 H, $H^2$), 7.49 (m, 3 H, phenyl) 7.65 (ddd, $J$ = 1.8, $J$ = 7.0, $J$ = 8.6 Hz, 2 H, $H^3$), 7.72 (s, 2 H, $R^2$) 7.85(d, $J$ = 8.6 Hz, 2 H, $H^4$), 8.28 (ddd, $J$ = 1.0, $J$ = 1.8, $J$ = 1.8 Hz, 2 H, $H^1$), 8.33 (s, 1 H, $H^5$), 8.5 (m, phenyl). $^{13}$C NMR ($CDCl_3$, ppm): $\delta$ = 30.03, 107.75, 110.44, 128.26, 128.61, 130.57, 132.98, 137.62, 138.01, 147.23, 157.21, 162.19. IR (NaCl plate): $\tilde{\nu}$ = 1624 cm$^{-1}$ (C=N). ES-MS: $m/z$ (%) = 423 (50) $[M + H]^+$, 421 (100), 242 (100). $C_{24}H_{22}N_8$ (422.5): calcd. C 68.23, H 5.25, N, 26.52; found C 67.04, H 5.35, N 25.57.

**General Procedure for the Formation of the [2×2]$Zn^{2+}_4$ Grid-Type Complexes 13–18:** An equimolar mixture of $Zn(CF_3SO_3)_2$ and of the ligands **7**–**12** in acetonitrile was stirred at room temperature for 5 h. The complexes were obtained by crystallization with diisopropyl ether or diethyl ether.

**Complex [$7_4Zn_4$]$(CF_3SO_3)_8$ (13):** $^1$H NMR ($CDCl_3$, ppm): $\delta$ = 8.01 (t, $J$ = 7.6, 2 H, $H^{3'}$), 7.98 (s, 2 H, $R^1$ = H), 7.87 (dt, $J$ = 7.6 Hz, 2 H, $H^3$), 7.78 (dt, $J$ = 7.6 Hz, 2 H, $H^{2'o}$), 7.65 (d, $J$ = 3.6 Hz, 2 H, $H^1$), 7.60 (d, $J$ = 3.6 Hz, 2 H, $H^4$), 7.25 (dt, $J$ = 7.6 Hz, 2 H, $H^2$), 7.18 (dt, $J$ = 7.6 Hz, 2 H, $H^{2'i}$), 6.84 (s, 1 H, $H^5$), 6.49 (d, $J$ = 7.3 Hz, 2 H, $H^{1'o}$), 5.44 (d, $J$ = 7.3 Hz, 2 H, $H^{1'i}$), 3.67 (s, 6 H, $R^2$ = $CH_3$); assignments made on the basis of the COSY and the ROESY spectra. ES-MS: $m/z$ (%) = 637 (100) [(**7**$_4$Zn$_4$)$(CF_3SO_3)_4]^{4+}$.

**Complex [$8_4Zn_4$]$(CF_3SO_3)_8$ (14):** $^1$H NMR ($CDCl_3$, ppm): $\delta$ = 10.97 (s, 2 H, $R^2$ = H), 8.05 (t, $J$ = 7.6 Hz, 2 H, $H^{3'}$), 7.76 (dt, $J$ = 7.6 Hz, 2 H, $H^3$), 7.80 (dt, $J$ = 7.6 Hz, 2 H, $H^{2'o}$), 7.79 (d, $J$ = 3.6 Hz, 2 H, $H^4$), 7.66 (d, $J$ = 3.6 Hz, 2 H, $H^1$), 7.27 (dt, $J$ = 7.6 Hz, 2 H, $H^2$), 7.07 (dt, $J$ = 7.6 Hz, 2 H, $H^{2'i}$), 6.74 (s, 1 H, $H^5$), 6.48 (d, $J$ = 7.3 Hz, 2 H, $H^{1'o}$), 5.51 (d, $J$ = 7.3 Hz, 2 H, $H^{1'i}$), 2.40 (s, 6 H, $R^1$ = $CH_3$); assignments made on the basis of the COSY and the ROESY spectra. ES-MS: $m/z$ (%) = 637 (100) [(**8**$_4$Zn$_4$)$(CF_3SO_3)_4]^{4+}$.

**Complex [$9_4Zn_4$]$(CF_3SO_3)_8$ (15):** $^1$H NMR ($CDCl_3$, ppm): $\delta$ = 7.96 (t, $J$ = 7.6 Hz, 2 H, $H^{3'}$), 7.88 (dt, $J$ = 7.6 Hz, 2 H, $H^3$), 7.72 (dt, $J$ = 7.6 Hz, 2 H, $H^{2'o}$), 7.60 (d, $J$ = 3.6 Hz, 2 H, $H^4$), 7.37 (d, $J$ = 3.6 Hz, 2 H, $H^1$), 7.06 (dt, $J$ = 7.6 Hz, 2 H, $H^2$), 7.03 (dt, $J$ = 7.6 Hz, 2 H, $H^{2'i}$), 6.60 (s, 1 H, $H^5$), 6.56 (d, $J$ = 7.3 Hz, 2 H, $H^{1'o}$), 5.18 (d, $J$ = 7.3 Hz, 2 H, $H^{1'i}$), 3.80 (s, 6 H, $R^2$ = $CH_3$) 2.57 (s, 6 H, $R^1$ = $CH_3$); assignments made on the basis of the COSY and the ROESY spectra. ES-MS: $m/z$ (%) = 669.5 (100) [(**9**$_4$Zn$_4$)-$(CF_3SO_3)_4]^{4+}$.

**Complex [$10_4Zn_4$]$(CF_3SO_3)_8$ (16):** $^1$H NMR ($CDCl_3$, ppm): $\delta$ = 12.09 (s, 6 H, $R^2$ = H) 8.19 (t, $J$ = 7.6 Hz, 2 H, $H^{3'}$), 8.09 (s, 6 H, $R^1$ = H), 7.89 (s, 1 H, $H^5$), 7.75 (dt, $J$ = 7.6 Hz, 2 H, $H^3$), 7.49 (dt, $J$ = 7.6 Hz, 2 H, $H^{2'}$), 7.39 (d, $J$ = 3.6 Hz, 2 H, $H^1$), 6.97 (d, $J$ = 3.6 Hz, 2 H, $H^4$), 6.84 (dt, $J$ = 7.6 Hz, 2 H, $H^2$), 5.92 (d, $J$ = 7.3 Hz, 2 H, $H^{1'o}$), 5.82 (d, $J$ = 7.3 Hz, 2 H, $H^{1'i}$); assignments made on the basis of the COSY and the ROESY spectra. ES-MS: $m/z$ (%) = 610 (100) [(**10**$_4$Zn$_4$)$(CF_3SO_3)_4]^{4+}$.

**Complex [$11_4Zn_4$]$(CF_3SO_3)_8$ (17):** Ligand **11** (38 mg, 0.1 mmol) and $Zn(OTf)_2$ (38 mg, 0.11 mmol) gave after recrystallization from acetonitrile/diethyl ether, 48 mg (63%) of greenish yellow crystals $^1$H NMR ($CD_3CN$, ppm): $\delta$ = 11.80 (s, 8 H, $R^2$ = H) 8.14 (t, $J$ = 7.6 Hz, 8 H, $H^{3'}$), 8.07 (s, 4 H, $H^5$), 7.88 (s, 8 H, $R^1$ = H), 7.75 (ddd, $J$ = 1.6, 7.4, 8.2, Hz 2 H, $H^3$), 7.45 (t, $J$ = 7.7 Hz, 2 H, $H^{2'}$), 7.39 (dd, $J$ = 0.8 Hz, 5.5, 2 H, $H^1$), 6.98 (d, $J$ = 8.5 Hz, 2 H, $H^4$), 6.83 (td, $J$ = 0.8 Hz, 1.6, 5.5, 2 H, $H^2$), 5.92 (d, $J$ = 7.1 Hz, 2 H, $H^{1'o}$), 5.84 (d, $J$ = 7.1 Hz, 2 H, $H^{1'i}$); assignments made on the basis of the COSY and the ROESY spectra. $^{13}$C NMR ([D$_3$]acetonitrile, ppm): $\delta$ = 166.1, 157.8, 148.9, 146.1, 142.8, 135.8, 134.0, 131.0, 129.0, 127.1, 123.1, 123.0, 121.0, 120.5, 111.9. ES-MS: $m/z$ (%) = 545 (100) 395 (45). **11**$_4$Zn$_4$$(CF_3SO_3)_8$ (3031.8): calcd. C 38.03, H 2.39, N, 14.78; found C 37.13, H 2.37, N 14.51.

**Complex [$12_4Zn_4$]$(CF_3SO_3)_8$ (18):** Ligand **12** (42 mg, 0.1 mmol) and $Zn(OTf)_2$ (38 mg, 0.1 mmol) gave after recrystallization from acetonitrile/diethyl ether, 55 mg (68%) of orange crystals with $^1$H NMR ($CD_3CN$, ppm): $\delta$ = 8.16 (t, $J$ = 7.6 Hz, 4 H, $H^{3'}$), 8.14 (s, 8 H, $H^5$), 7.86 (m, 16 H, $R^1$ = H, $H^3$), 7.53 (t, $J$ = 7.4 Hz, 4 H, $H^{2'o}$), 7.34 (m, 12 H, $H^1$,$H^{2'i}$), 7.29 (d, $J$ = 8.5 Hz, 8 H, $H^4$), 6.93 (dd, $J$ = 6.7 Hz, 5.4, 8 H, $H^2$), 5.89 (d, $J$ = 7.4 Hz, 4 H, $H^{1'o}$), 5.81 (d, $J$ = 7.7 Hz, 4 H, $H^{1'i}$), 3.51 (s, 24 H, $R^2$ = $CH_3$). $^{13}$C NMR (ppm): $\delta$ = 165.8, 157.9, 149.5, 146.8, 143.2, 135.1, 133.8, 130.2, 129.7, 129.0, 127.7, 123.8, 122.0, 121.1, 111.7, 34.0; assignments made on the basis of the COSY and the ROESY spectra. ES-MS: $m/z$ (%) mass envelope at 637 (100) [(**12**$_4$Zn$_4$)$(CF_3SO_3)_4]^{4+}$: calcd. C 39.73, H 2.82, N 14.26; found C 37.83 H 2.54 N 13.46

**Complex [$11^{2-}_4Zn_4$] (19) Method 1:** 2-Phenylpyrimidine-4,6-dicarbaldehyde bis[(pyridin-2-yl)hydrazone], (0.11 g, 0.28 mmol) was suspended in EtOH (20 mL), and a solution of anhydrous $ZnCl_2$ (0.04 g ) in EtOH (1 mL) was added. After stirring 5 min, the dark brown solution was made basic by the addition of 2 equiv. NaOH whereupon the mixture turned blue-purple. Evaporation left a dark purple-bronze solid that was purified by dissolution in THF, filtration and evaporation of the filtrate. The residue was recrystallized from water/EtOH to give small, golden, pyramidal crystals (85 mg, 66%)

**Method 2:** Complex **17** (20 mg) was dissolved in acetonitrile (2 mL) and excess triethylamine (10 μL) was added. The solution immedi-

  

ately turned dark blue and small golden crystals of complex **19** began to precipitate. After standing for 15 h, these were removed by filtration and dried to give 3.9 mg (33%). Spectral properties of both products were identical. $^1$H NMR ([D$_6$]DMSO, ppm): $\delta$ = 5.96 (d, $J$ = 7.7 Hz, 8 H), 6.32 (t, $J$ = 5.8 Hz, 8 H), 6.56 (d, $J$ = 8.2 Hz, 8 H), 6.64 (s, 4 H), ≈ 6.95 (m, 16 H), 7.02 (s, 8 H), 7.29 (ddd, 8 H, $J$ = 8.2, 7.1, 2.0 Hz), 7.49 (t, $J$ = 7.3 Hz, 4 H). $^1$H NMR ($CDCl_3$, 40 °C, ppm) d 6.09 (d, $J$ = 7.2 Hz, 8 H), 6.246 (s, 4 H), 6.27 (t, $J$ = 6.3 Hz, 8 H), 6.65 (d, $J$ = 8.3 Hz, 8 H), 7.02 (s, 8 H), 7.06 (t, 8 H, $J$ = 7.2 Hz), 7.11 (d, $J$ = 5.2 Hz, 8 H), 7.23 (m, 8 H), 7.52 (t, $J$ = 7.4 Hz, 4 H). $^{13}$C NMR (25 °C, [D$_6$]DMSO, ppm): $\delta$ = 165.13, 162.04, 156.88, 143.83, 139.28, 138.02, 129.04 (broad), 128.48 (broad), 128.16, 125.36, 123.79, 117.16, 115.51. $^{13}$C NMR ($CDCl_3$, 40 °C, ppm): $\delta$ = 165.48, 161.74, 156.92, 144.00, 138.51, 138.21, 128.67, 128.05, 125.64, 123.35, 117.06, 115.45, 110.40. IR (NaCl plate): $\tilde{\nu}$ = 1587, 1548, 1513, 1476, 1458, 1412, 1334, 1295, 1269, 1236, 1113, 1093, 984 cm$^{-1}$; ES-MS (solution in DMSO/NaCl): $m/z$(%) = 1831 [(**11**$^{2-}{}_4$Zn$_4$)H]$^+$, 1855 [(**11**$^{2-}{}_4$Zn$_4$)Na]$^+$. (**11**$^{2-}{}_4$Zn$_4$)·10H$_2$O: calcd. C 52.55, H 4.21, N 22.28; found C 52.86, H 4.02, N 21.88.

**Crystal Structure Determinations:** X-ray diffraction data for compounds **13**–**15** were collected with a Nonius Kappa charge-coupled device (CCD) diffractometer with a graphite-monochromatized Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å). $\varphi$ scans at 173 K, at the Laboratoire de Cristallochimie, Université Louis Pasteur, Strasbourg. The structures of the compounds **13**–**15** were determined using direct methods and refined (based on $F_2$ using all independent data) by full-matrix least-square methods (SHELXTL 97). Data were reduced by using the Bruker SAINT software. Hydrogen atoms were included at calculated positions by using a riding model. Single crystals of **13**–**15** were grown from acetonitrile/benzene. Crystals were placed in oil and a single crystal was selected, mounted on a glass fiber and placed in a low-temperature $N_2$ stream. The structure of **2-H** and **2-DH** were determined using direct methods and refined (based on $F_2$ using all independent data) by full-matrix least-square methods (SHELXTL 97). Hydrogen atoms were included at calculated positions by using a riding model.

**Complex [5$_4$Zn$_4$](CF$_3$SO$_3$)$_8$ (13):** Yellow single crystal of (**7**$_4$Zn$_4$)(CF$_3$SO$_3$)$_8$ (**13**), ($C_{120}H_{112}F_{24}N_{40}O_{24}S_8Zn_4$) of dimension 0.18×0.16×0.14 mm. The structure contains four grid complexes together with thirty two triflate anions and thirty two acetonitrile molecules. The unit cell was monoclinic with a space group of $C2/c$. Cell dimensions: $a$ = 27.5875(4) Å, $b$ = 26.9243(4) Å, $c$ = 20.1356(3) Å, $\alpha = \gamma$ = 90°, $\beta$ = 92.759(5)°, $V$ = 14938.9(4) Å$^3$ and $Z$ = 8 (FW is 7072, $\rho$ = 1.54 g cm$^{-3}$). Reflections were collected from 2.5° ≤ $\theta$ ≤ 27.48° for a total of 17483 of which 9423 were unique having $I > 3\sigma(I)$; number of parameters is 931. Final $R$ factors were $R_1$ = 0.103 (based on observed data), $wR_2$ = 0.121 (based on all data), GOF = 1.303, maximum residual electron density is 1.406 e·Å$^{-3}$.

**Complex [6$_4$Zn$_4$](CF$_3$SO$_3$)$_8$ (14):** Single yellow crystals of (**8**$_4$Zn$_4$)(CF$_3$SO$_3$)$_8$ (**14**), ($C_{120}H_{112}F_{24}N_{40}O_{24}S_8Zn_4$) of dimension 0.08×0.08×0.08 mm. The structure contains eight grid complexes together with sixty four triflate anions, thirty two acetonitrile molecules and thirty two water molecules. The unit cell was tetragonal with a space group of $P42/n$. Cell dimensions: $a$ = 17.9114(3) Å, $b$ = 17.9114(3) Å, $c$ = 22.7093(4) Å, $\alpha = \gamma = \beta$ = 90°, $V$ = 7285.6(2) Å$^3$ and $Z$ = 8 (FW is 3440, $\rho$ = 1.54 g cm$^{-3}$). Reflections were collected from 2.5° ≤ $\theta$ ≤ 27.48° for a total of 15477 of which 3415 were unique having $I > 3\sigma(I)$; number of parameters is 428. Final $R$ factors were $R_1$ = 0.087 (based on observed data), $wR_2$ = 0.107 (based on all data), GOF = 1.280, maximum residual electron density is 1.269 e·Å$^{-3}$.

**Complex [7$_4$Zn$_4$](CF$_3$SO$_3$)$_8$ (15):** Single yellow crystals of (**9**$_4$Zn$_4$)(CF$_3$SO$_3$)$_8$ (**15**), ($C_{136}H_{145}F_{24}N_{38}O_{28}S_8Zn_4$) of dimension 0.16×0.13×0.10 mm. The structure contains two grid complexes together with sixteen triflate anions, twelve acetonitrile molecules, three benzene molecules, two ethanol molecules and four water molecules. The unit cell was triclinic with a space group of $P\bar{1}$. Cell dimensions: $a$ = 18.212(2) Å, $b$ = 20.4537(2) Å, $c$ = 23.5718(4) Å, $\alpha$ = 99.242(5)°, $\beta$ = 1000.793(5)°, $\gamma$ = 103.058(5)°, $V$ = 82112(2) Å$^3$ and $Z$ = 2 (FW is 3830, $\rho$ = 1.51 g cm$^{-3}$). Reflections were collected from 2.5° ≤ $\theta$ ≤ 27.48° for a total of 64440 of which 14197 were unique having $I > 3\sigma(I)$; number of parameters is 1987. Final $R$ factors were $R_1$ = 0.072 (based on observed data), $wR_2$ = 0.097 (based on all data), GOF = 1.598, maximum residual electron density is 1.558 e·Å$^{-3}$.

CCDC-288070 to -288072 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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