Two-Level Self-Organisation of Arrays of [2×2] Grid-Type Tetranuclear Metal Complexes by Hydrogen Bonding

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Here we report on the synthesis and characterisation of four new complexes of the [2×2] M^{II}_4 grid-type (M = Co, Fe, Zn) with oligopyridine-derived ligands. The presence of aminopyrazine and aminopyrimidine moieties at the edge of the ligands potentially enables the formation of infinite hydrogen-bonded multi-grid networks. The ligands were synthesised by subsequent stannylations and Stille-type coupling reactions. The complexes were obtained by self-assembly of the ligand with the metal salt. The single-crystal X-ray structure was determined for the Co complex **7** containing aminopyrimidine as the hydrogen-bonding moiety [$P\bar{1}$; a = 15.4976(4), b = 18.2114(6), c = 31.9538(10) Å, α = 86.9809(13), β = 83.4137(18), γ = 67.2828(16)°]. The crystal structure reveals hydrogen bonding in one direction, thus forming infinite chains of grids, whereas in the second direction of a layer, only weak attractive interactions are found. Anions and solvent molecules are situated between the layers, thus inhibiting any direct interaction between them. Cocrystallisation of the complementary complexes should enable the recognition-controlled alternating arrangement of grids incorporating different metal ions in a chessboard-like manner.

Introduction

In the last few years, a vast amount of work has been dedicated to the generation of discrete inorganic architectures in order to establish the principles of inorganic self-assembly processes as well as in view of their possible application in nanotechnology.[1] Of particular interest is the combination of metal coordination with hydrogen bonding in order to achieve the controlled arrangement of such inorganic entities by means of molecular recognition-directed formation of well-defined two- and three-dimensional structures of hydrogen-bonded networks.[2] This amounts to a two-level, sequential self-organisation process in which the initial assembly of coordination architectures from given ligands and metal ions is followed by their organisation into specific arrangements. The use of ligands fitted with complementary hydrogen-bonding subunits provides the possibility of positioning inorganic entities which may contain different metal ions in extended arrays, a feature potentially of great interest to nanotechnology and molecular electronics.

Our laboratory has recently described a new class of polypyridine-derived, tetranuclear metal complexes of the [2×2] M^{II}_4 grid-type (M = transition metal)[3,4] formed by self-assembly from ligands containing two tridentate, terpyridine-like, binding subunits and from metal ions of octahedral coordination geometry (Scheme 1). They have been found to present a range of interesting structural[3] and physicochemical (electrochemical,[3a,5] magnetic[6]) properties. In addition, it has been shown that these grid-type compounds self-assemble in monolayers on gold and can be examined and manipulated on a molecular level by means of scanning tunnelling microscopy (STM).[7] Although they assemble in a chessboard-like order, the stability of the monolayer is low and the mobility of the grids on the surface is still high. For possible future applications in the field of information storage devices, a high stability of the monolayer of grids will be required. Furthermore, it would be of great interest to be able to rigorously control the relative positioning of grid structures incorporating different metal ions (and therefore presenting different physicochemical properties) within either two-dimensional layers or three-dimensional lattices. This would for instance lead to "grid-of-grids"-type structures as schematically represented in Figure 1. It would also by-pass the demanding synthetic efforts involved in the generation of grids of higher nuclearity by the replacement of large grids by grids-of-grids, thus making further use of the powerful tool of self-assembly through a two-level sequential process.

In order to increase the stability of layers of grids as well as to allow the introduction of different metal ions into such an assembly, we synthesised the ligands **2** and **3** containing complementary and self-complementary hydrogen-bonding moieties and their corresponding metal complexes **4−7**. The complementary interaction of the ligands is schematically shown in Scheme 2. The suitability of aminopyrazine and aminopyrimidine as designed hydrogen-bonding motifs, as used here, has been shown before in mononuclear complexes with terpyridine-derived ligands.[8]

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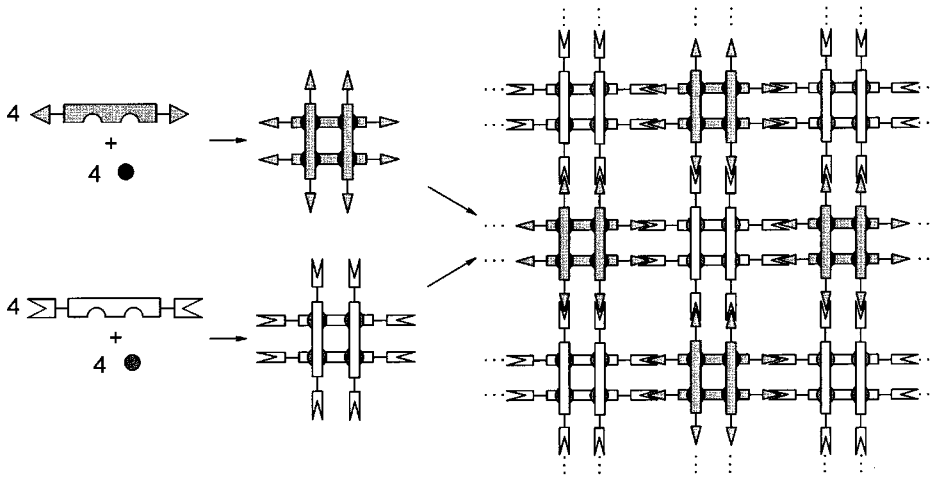
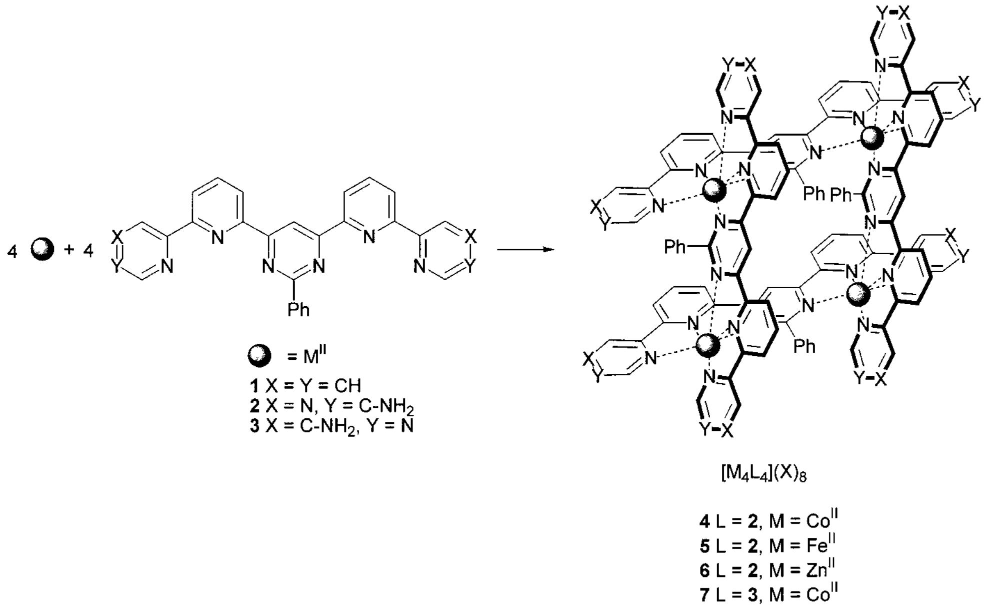
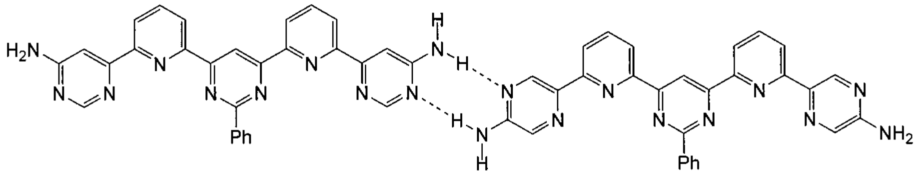


Figure 1. Schematic representation of the generation of the two-level sequential self-assembly of an ordered alternating “grid-of-grids” pattern of two [2×2] M_4^{II} grid-type species (such as **4−7**) incorporating different metal ions; the long range organisation is provided by secondary interactions, such as complementary hydrogen bonding (as represented), but also electrostatic interaction or metal ion coordination, between the termini of the ligands from grid to grid



Scheme 1. Self-assembly of the [2×2] M_4^{II} grid-type complexes **4−7** from ditopic ligands **2** and **3**



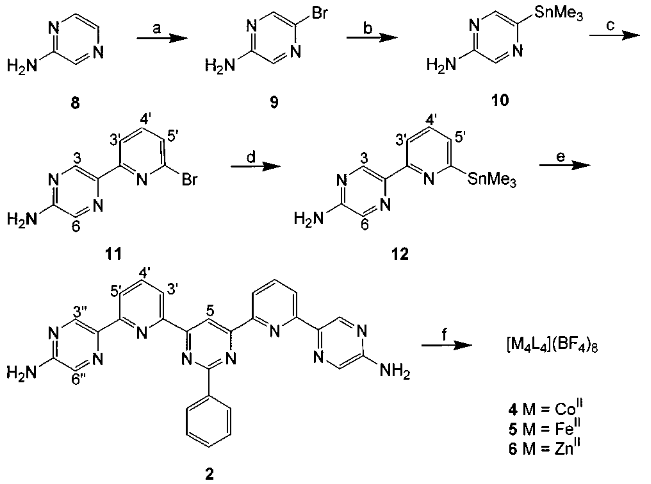
Scheme 2. Representation of the hydrogen-bonding pattern between the complementary subunits of ligand **2** (right) and **3** (left)

Results and Discussion

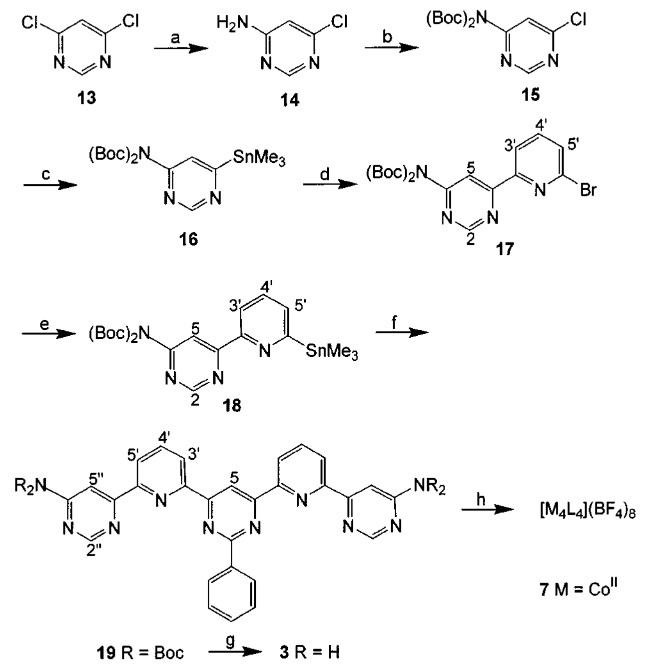
Synthesis of Ligands 2 and 3

The synthesis of ligand **2** and complexes **4−6** is outlined in Scheme 3.

Ligand **2** is produced by palladium-catalysed stannylations followed by coupling reactions of the Stille type. The yields obtained by using a one-pot reaction for the stannylation of **9** and the coupling of **10** with 2,6-dibromopyridine to give **11** were superior to those obtained when purification of the tin compound was performed. This can be explained by the rather low stability of the tin derivative during chromatographic purification. **2** precipitates from the reaction mixture as the analytically pure compound. It is insoluble in most organic solvents and only moderately sol-



Scheme 3. Synthesis of ligand **2**: a) Br_2, $CHCl_3$ (32%); b) Me_6Sn_2, $Pd(PPh_3)_4$, toluene; c) 2,6-dibromopyridine, $Pd(PPh_3)_4$, toluene (68% over 2 steps); d) Me_6Sn_2, $Pd(PPh_3)_4$, toluene; e) 4,6-dichloro-2-phenylpyrimidine, $PdCl_2(PPh_3)_2$, DMF (69% over 2 steps); f) $M(BF_4)_2{\cdot}xH_2O$ (**4**: M = Co^{II}; **5**: M = Fe^{II}; **6**: M = Zn^{II}), CH_3CN/H_2O



Scheme 4. Synthesis of ligand **3**: a) NH_3, MeOH (44%); b) $(Boc)_2O$, DMAP, CH_3CN (79%); c) Me_6Sn_2, $Pd(PPh_3)_4$, toluene; d) 2,6-dibromopyridine, $Pd(PPh_3)_4$, toluene (41% over 2 steps); e) Me_6Sn_2, $Pd(PPh_3)_4$, toluene; f) 4,6-dichloro-2-phenylpyrimidine, $Pd(PPh_3)_4$, toluene (50% over 2 steps); g) HCl, EtOAc (88%); h) $Co(BF_4)_2{\cdot}6H_2O$, CH_3CN/H_2O

uble in DMSO. This already points to the suitability of this compound for the formation of hydrogen-bonded networks as the low solubility can be explained by strong intermolecular hydrogen bonds between the self-complementary moieties on the edges of the ligand.

The synthesis of ligand **3** and complex **7** is outlined in Scheme 4. Whereas the amino group did not cause any problems in the palladium-catalysed stannylation of **9**, the stannylation of **14** required derivatisation of the amino group due to the low solubility of the starting material under the reaction conditions. We introduced two *tert*-butoxycarbonyl groups to solubilise the compound. The rest of the synthesis follows the same reaction pathway as for **2** and the protection groups were split off by HCl in the last step to give **3** as an extremely insoluble compound. As supported by the results of elemental analysis, **3** is probably formed as HCl salt during the reaction.The deprotonation was not possible even by washing with dilute NaOH, due to the low solubility of the compound which presumably includes the HCl in the solid.

Synthesis and Characterisation of the Complexes 4−7

So far complexes of the grid-type were usually obtained by reaction of the ligand with the metal acetate in methanol or with the metal tetrafluoroborate in acetonitrile or nitromethane;[3] however, these reactions failed for **2** and **3** because of their low solubility. For these ligands, the use of mixtures of acetonitrile and water in variable ratios, specific for each of the ligands, as well as elevated temperatures are required to break the intermolecular hydrogen bonds of the ligand and to solubilise the reaction mixtures. Substitution of the solvents by DMSO solubilised the reaction mixture, but did not result in the assembly of the grids. Even the highly charged complexes themselves are only moderately soluble at room temperature in the solvent mixture. Exchange of the tetrafluoroborate counterions for hexafluorophosphate, triflate or perchlorate did not result in an increased solubility.

The complexes were characterised by ^1H NMR spectroscopy, FAB mass spectrometry, elemental analysis, and in the case of **7** by single-crystal X-ray diffraction. The proton NMR spectrum of the diamagnetic complex **6** shows the signals of a symmetrically coordinated ligand as expected for the grid structure. The protons of the phenyl group on the pyrimidine ring give rise to five distinct signals due to inhibited rotation of the phenyl ring in the complex.[3b] The proton NMR spectra of **4**, **5**, and **7** show strongly shifted signals (Co complexes: δ from −100 to +180 ppm; Fe complex: δ from −30 to +80 ppm) as typical for paramagnetic compounds.[9] Although in all cases sharp signals are obtained, which are typically broader for the Fe complex than for the Co complexes, no coupling patterns can be resolved due to low resolution. However, the number of signals provides information about the symmetry of the complexes indicating that the symmetry of the ligand is maintained during the complexation. Combination of this information with the composition of the complexes obtained from mass spectrometry allows the deduction of the grid-type structure for all complexes described here.

The Fe^{II} cation can exist in the diamagnetic low-spin or in the paramagnetic high-spin state, depending on the ligand field strength. From the NMR spectroscopic data, it may be deduced that the Fe complex **5** is essentially high spin as no signals are found in the region expected for diamagnetic aromatic protons. Preliminary measurements of the magnetic susceptibility, however, suggest that there remains a low-spin fraction of the complex at room temperature and that it shows thermal spin-crossover behaviour[10] similar to a Fe^{II} grid-type compound of ligand **1** already described.[6b]

Crystal Structure of Complex 7

Crystals of complex **7** were obtained by diffusion of THF into a solution of the complex in acetonitrile/water and its structure was determined by X-ray crystallography (Figure 2). The grid moiety of the complex is comparable to that of the structures of similar compounds.[3b] The four ligands of one entity are aligned in an almost perfect parallel and perpendicular fashion. The shortest distance between the plane of a phenyl ring on one ligand and a perpendicular ligand (3.30 Å) corresponds to a van der Waals contact and indicates that the grid is stabilised by π-stacking of the ligands with the phenyl substituent on the pyrimidine ring. The Co^{II} ions present pseudo-octahedral coordination. The Co−N bond lengths and N−Co−N bond angles are analogous to those found in the parent Co^{II} grid-type complex of ligand **1**.[3b] This may appear surprising as the electron-poor pyrimidine is usually a weaker binding site than pyridine, but in the present ligand this is compensated for by the electron-donating properties of the amino group in *para* position of the binding N atom. The presence of the hydrogen bonds in only one direction (see below) has no influence on the geometry of the grid unit itself.

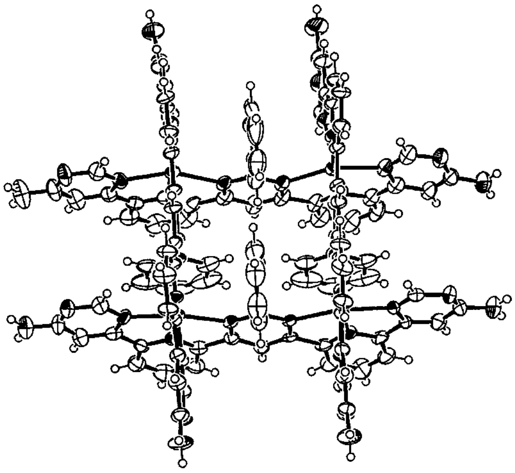


Figure 2. Single-crystal X-ray structure of the grid unit of complex **7** (anions are omitted for clarity); ORTEP representation

The self-complementarity of **2** and **3** enables their metal complexes to form hydrogen-bonded networks of grids. The availability of hydrogen-bonding sites on each edge of the grid might lead to saturation of the hydrogen bonds in two dimensions. The crystal structure of **7**, though, shows that the hydrogen-bonding motif is present in only one dimension, thus forming infinite one-dimensional chains of grids (Figure 3). The hydrogen bond lengths *d*(N−H−N) lie between 3.01(1) and 3.07(1) Å and are thus in the range of strong hydrogen bonds. The hydrogen bonds are almost linear with N−H−N bond angles between 173 and 180°. In the second dimension of the layer, no strong interactions are found between the grids. Neighbouring complexes without hydrogen-bonding contact show only weak π-stacking between their ligands. Although the rows of ligands are parallel with the shortest distance between their planes around 3.25 Å, they are slanted so that there is only a small overlap of the π-systems. A good overlap in the same range of distances can be found between the amino groups and the pyrimidine moieties of neighbouring complexes. It appears that the crystallisation of the complex in this packing is preferred to the saturation of all hydrogen bonds as it helps to avoid unfilled space in the crystal. Comparison with the similar structure of the parent Co$_4^{II}$ [2×2] grid without hydrogen-bonding sites derived from ligand **1** shows that this complex forms layers with a larger overlap of some of the aromatic rings of neighbouring complexes. Although in that case only two out of eight of the edge pyridine rings show π-stacking, the better overlap results in a more efficient stacking.[3b] Thus, the hydrogen bonds in **7** partially break up this packing motif, but they are not strong enough to generate a completely hydrogen-bonded network which would imply the unfavourable formation of large cavities between the grids. The anions and solvent molecules of crystallisation are found between these layers, thus inhibiting any direct interaction between them.

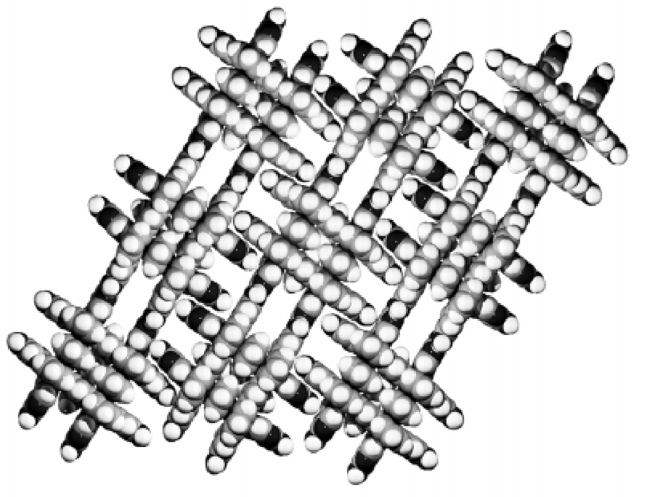


Figure 3. Crystal packing of complex **7** showing the hydrogen bonding in one direction and the formation of infinite chains of grids (anions and solvent molecules from crystallisation are omitted for clarity)

The crystals described here were obtained during an attempt at cocrystallising complexes **5** and **7**. Even though $Co(BF_4)_2 \cdot 6H_2O$ and $Fe(BF_4)_2 \cdot 6H_2O$ were used as metal salts for the complexation, no BF_4^- could be found in the crystal structure. Instead, two chloride anions originating from the last step of the synthesis of **3** and three SiF_6^{2-} units crystallised out. The last one stems probably from the reaction of some free fluoride with the glass vial in which the crystallisation was performed. These rather unexpected results could be further supported by energy-dispersive X-ray scattering (EDX) of crystals of **5** and **7** which indeed showed significant amounts of Si.

Conclusion

As a further step in the recognition-directed self-organisation of metal complexes, the formation of arrays of four tetranuclear complexes, **4−7**, from the oligopyridine-derived ligands **2** and **3** has been achieved by sequential two-step self-assembly. These ligands were designed to form double self-complementary hydrogen bonds by introduction of aminopyrazine and aminopyrimidine moieties on the edges. Generating arrays of such metal complexes is of special interest in view of the remarkable physicochemical properties (e.g. magnetic,[6b] electrochemical[5]) displayed by [2×2] metallogrids. The single-crystal X-ray structure of Co complex **7** shows saturation of the hydrogen bonds in one direction, thus forming an infinite chain of hydrogen-bonded grids. In the other direction of each layer, weak π-stacking is present whereas no direct interactions are found between the layers of grids. Besides the self-complementarity of the ligands, the aminopyrazine and aminopyrimidine hydrogen-bonding units should also be capable of forming heterocomplementary hydrogen-bonding motifs by two-point interaction, thus allowing the arrangement of grids with different metals in a layered chessboard-like manner (Figure 1). Further experiments for the cocrystallisation of complementary hydrogen bonds between **4−7** with different anions are ongoing to explore these possibilities. In addition, the possibility of deposition of heterometallic arrays of these grids as monolayers on surfaces and their observation by STM (scanning tunnelling microscopy) is currently being investigated. The data described here may also be regarded as a step in the exploration of the ways and means to induce the spontaneous, but controlled generation of even larger organised arrays in view of assembling supramolecular architectures and devices of interest for nanotechnology.

Experimental Section

General: 5-Amino-2-bromopyrazine (**9**),[11] 4-amino-6-chloropyrimidine (**14**),[12] and 4,6-dichloro-2-phenylpyrimidine[13] were prepared according to the literature. Toluene was dried by heating under reflux with sodium under argon, acetonitrile by heating under reflux with CaH_2 for several hours. The other reagents and solvents were used without further purification. − The NMR spectroscopic data were obtained with Bruker AC 200 at 200.1 MHz (^1H) and 50.2 MHz (^{13}C), calibrated against the residue solvent signal ($CDCl_3$: $\delta = 7.24$; $[D_6]DMSO$: $\delta = 2.50$; CD_3CN: $\delta = 1.94$) and are given in ppm. − IR data were collected with a Perkin−Elmer 1600 series FTIR spectrometer and are reported in cm^{-1}. − Microanalyses of metal complexes sometimes give unsatisfactory results due to incomplete combustion of the complex. It was not possible to obtain a good microanalysis for complex **7** because of this and perhaps also due to an undefined mixture of anions.

5-Amino-2-[6′-bromopyrid-2′-yl]pyrazine (11): 5-Amino-2-bromopyrazine (**9**) (500 mg, 2.87 mmol), hexamethyldistannane (1.04 g, 3.16 mmol), and $Pd(PPh_3)_4$ (183 mg, 0.16 mmol) were combined in toluene (15 mL), flushed with Ar, and heated under reflux for 1 h. After cooling to room temp., 2,6-dibromopyridine (952 mg, 4.02 mmol) and $Pd(PPh_3)_4$ (231 mg, 0.20 mmol) were added and the mixture was heated under reflux for 19 h. The solvent was evaporated and the residue purified by column chromatography on silica with hexane/EtOAc (1:1, v/v) to give **11** as a white powder. Yield 492 mg (68%). − ^1H NMR ($CDCl_3$): $\delta = 4.84$ (s, br, 2 H, NH_2), 7.38 (dd, $J = 0.9$ Hz and 7.9 Hz, 1 H, $H_{3' \text{ or } 5'}$), 7.58 (t, $J = 7.9$ Hz, 1 H, $H_{4'}$), 7.97 (d, $J = 1.2$ Hz, 1 H, $H_{3 \text{ or } 6}$), 8.08 (dd, $J = 0.9$ Hz and 7.6 Hz, 1 H, $H_{3' \text{ or } 5'}$), 9.01 (d, $J = 1.5$ Hz, 1 H, $H_{3 \text{ or } 5}$). − ^{13}C NMR ($CDCl_3$): $\delta = 118.3$, 126.8, 130.9, 139.1, 139.9, 141.2, 141.6, 154.5, 156.2. − MS (FAB): $m/z = 251.0$ [M + H^+]. − IR (KBr): $\tilde{\nu} = 3436$, 3316, 3163, 1641, 1586, 1541, 1432, 1380, 1286, 1154, 1124, 1012, 802, 776, 668, 604, 494, 416. − $C_9H_7BrN_4$ (251.1): calcd. C 43.05, H 2.79, N 22.32; found C 43.14, H 2.40, N 22.04.

5-Amino-2-[6′-(trimethylstannyl)pyrid-2′-yl]pyrazine (12): 5-Amino-2-(6′-bromopyrid-2′-yl)pyrazine (**11**) (550 mg, 2.19 mmol), hexamethyldistannane (789 mg, 2.41 mmol), and $Pd(PPh_3)_4$ (76 mg, 0.066 mmol) were combined in toluene (15 mL), flushed with Ar, and heated under reflux for 20 min. The solvent was evaporated and the residue was taken up in $CHCl_3$. The precipitated Pd was centrifuged off and the residue was used for the next coupling step after evaporation of the solvent without further purification. − ^1H NMR ($CDCl_3$): $\delta = 0.34$ [s, 9 H, $Sn(CH_3)_3$], 4.94 (s, br, 2 H, NH_2), 7.35 (dd, $J = 8$ Hz and 1.2 Hz, 1 H, $H_{3' \text{ or } 5'}$), 7.60 (t, $J = 8$ Hz, 1 H, $H_{4'}$), 7.95−7.99 (m, 2 H, $H_{3' \text{ or } 5'}$ and $H_{3 \text{ or } 6}$), 9.19 (d, $J = 1.4$ Hz, 1 H, $H_{3 \text{ or } 6}$).

4,6-Bis[6′-(5′′-aminopyrazin-2′′-yl)pyrid-2′-yl]-2-phenylpyrimidine (2): 5-Amino-2-[6′-(trimethylstannyl)pyrid-2′-yl]pyrazine (**12**) (660 mg, 1.97 mmol), 4,6-dichloro-2-phenylpyrimidine (222 mg, 0.99 mmol), and $PdCl_2(PPh_3)_2$ (55 mg, 0.079 mmol) were combined in anhydrous DMF (15 mL), degassed, and heated to 100 °C for 21 h. The mixture was cooled to room temp. and the precipitation was centrifuged off, washed 2 × with MeOH/acetone and 1 × with Et_2O to give **2** as a white powder. Yield 373 mg (69% over 2 steps). − ^1H NMR ($[D_6]DMSO$): $\delta = 6.96$ (s, br, 4 H, NH_2), 7.60−7.65 (m, 3 H, $H_{meta \text{ and } para}$), 8.03 (d, $J = 1.2$ Hz, 1 H, $H_{3'' \text{ or } 6''}$), 8.15 (t, $J = 7.3$, 2 H, $H_{4'}$), 8.31 (d, $J = 7.9$ Hz, 2 H, $H_{3' \text{ or } 5'}$), 8.67 (d, $J = 7.3$ Hz, 2 H, $H_{3' \text{ or } 5'}$), 8.70−8.76 (m, 2 H, H_{ortho}), 9.12 (d, $J = 1.2$ Hz, 2 H, $H_{3'' \text{ or } 6''}$), 9.36 (s, 1 H, H_5). − ^{13}C NMR ($[D_6]DMSO$): $\delta = 111.4$, 121.2, 121.6, 129.0, 129.7, 132.0, 132.3, 138.0, 138.7, 139.5, 141.1, 153.7, 155.9, 157.1, 164.2, 164.8. − MS (FAB): $m/z = 497.2$ [M + H^+]. − IR (KBr): $\tilde{\nu} = 3313$, 3159, 1654, 1564, 1534, 1488, 1378, 1298, 1019, 818, 752, 691, 637, 606, 415. − $C_{28}H_{20}N_{10}$ (496.5): calcd. C 67.37, H 4.06, N 28.21; found C 67.75, H 4.26, N 28.03.

Co Complex 4: 4,6-Bis[6′-(5′′-aminopyrazin-2′′-yl)pyrid-2′-yl]-2-phenylpyrimidine (**2**) (1.7 mg, 3.4 μmol) and $Co(BF_4)_2{\cdot}6H_2O$ (1.2 mg, 3.4 μmol) were heated under reflux in CD_3CN (0.4 mL) and D_2O (1 drop) for 3.5 h. The complex was isolated in quantitative yield as a brown powder by evaporation of the solvent. − ^1H NMR (CD_3CN/D_2O): $\delta = -137.98$, −117.95, 12.37, 7.94, 12.70, 24.59, 36.79, 49.11, 80.22, 143.72, 166.16. − MS (FAB): $m/z =$ 2742.5 $[Co_4L_4](BF_4)_6^+$, 2654.5 $[Co_4L_4](BF_4)_5^+$, 2568.4 $[Co_4L_4](BF_4)_4^+$, 2480.6 $[Co_4L_4](BF_4)_3^+$. − $C_{112}H_{80}B_8Co_4F_{32}N_{40}{\cdot}13H_2O$ (3150.5): calcd. C 42.70, H 3.39, N 17.78; found C 42.73, H 3.32, N 17.44.

Fe Complex 5: 4,6-Bis[6′-(5′′-aminopyrazin-2′′-yl)pyrid-2′-yl]-2-phenylpyrimidine (**2**) (10.0 mg, 20.1 μmol) and $Fe(BF_4)_2{\cdot}6H_2O$ (6.8 mg, 20.1 μmol) were heated under reflux in CH_3CN (4 mL) and H_2O (0.5 mL) for 24 h. The complex was isolated as a dark brown powder by evaporation of the solvent in quantitative yield. − ^1H NMR (CD_3CN/D_2O): δ = −13.01, −9.14, −6.06, 40.79, 50.88, 64.64, 75.34. − MS (FAB): *m/z* = 2730.5 $[Fe_4L_4](BF_4)_6^+$, 2643.7 $[Fe_4L_4](BF_4)_5^+$, 2556.3 $[Fe_4L_4](BF_4)_4^+$, 2469.7 $[Fe_4L_4](BF_4)_3^+$. − $C_{112}H_{80}B_8F_{32}Fe_4N_{40}\cdot 7H_2O$ (3030.0): calcd. C 44.40, H 3.13, N 18.49; found C 44.70, H 2.87, N 18.05.

Zn Complex 6: 4,6-Bis[6′-(5′′-aminopyrazin-2′′-yl)pyrid-2′-yl]-2-phenylpyrimidine (**2**) (2.5 mg, 5.0 μmol) and $Zn(BF_4)_2\cdot 8H_2O$ (1.9 mg, 5.0 μmol) were heated under reflux in CD_3CN (0.5 mL) and D_2O (0.05 mL) for 3.5 h. The complex was isolated as an orange powder by evaporation of the solvent in quantitative yield. − ^1H NMR (CD_3CN/D_2O): δ = 5.68 (d, *J* = 6.9 Hz, 1 H, H_{ortho}), 5.95 (d, *J* = 7.3 Hz, 1 H, H_{ortho}), 6.08 (d, *J* = 1.5 Hz, 2 H, $H_{3'' \text{ or } 6''}$), 6.38 (t, *J* = 7.7 Hz, 1 H, $H_{meta \text{ or } para}$), 6.81 (t, *J* = 7.3 Hz, 1 H, $H_{meta \text{ or } para}$), 6.91 (t, *J* = 7.3 Hz, 1 H, $H_{meta \text{ or } para}$), 8.38 (t, *J* = 8.2 Hz, 2 H, $H_{4'}$), 8.47 (d, *J* = 8.0 Hz, 2 H, $H_{3' \text{ or } 5'}$), 8.79 (d, *J* = 1.1 Hz, 2 H, $H_{3'' \text{ or } 6''}$), 8.80 (d, *J* = 8.0 Hz, 2 H, $H_{3' \text{ or } 5'}$), 9.41 (s, 1 H, H_5). − MS (FAB): *m/z* = 2680.9 $[Zn_4L_4](BF_4)_5^+$, 2593.6 $[Zn_4L_4](BF_4)_4^+$, 2505.6 $[Zn_4L_4](BF_4)_3^+$, $[Zn_4L_4](BF_4)_2^+$. − $C_{112}H_{80}B_8F_{32}N_{40}Zn_4\cdot 13H_2O$ (3176.3): calcd. C 42.35, H 3.36, N 17.64; found C 42.20, H 3.42, N 17.80.

6-[Bis(*tert*-butoxycarbonyl)amino]-4-chloropyrimidine (15): 6-Amino-4-chloropyrimidine (**14**) (2.05 g, 15.8 mmol) was suspended in anhydrous acetonitrile (8 mL). Dimethylaminopyridine (483 mg, 1.45 mmol) and di-*tert*-butyl carbonate (7.37 g, 39.6 mmol) were added and stirred at room temp. for 23 h. The solvent was evaporated and the residue purified by column chromatography on silica with hexane/EtOAc (1:1, v/v) to give **15** as a white powder. Yield 4.12 g (79%). − ^1H NMR ($CDCl_3$): δ = 1.56 [s, 18 H, $C(CH_3)_3$], 7.85 (d, *J* = 0.9 Hz, 1 H, $H_{2 \text{ or } 5}$), 8.66 (d, *J* = 0.9 Hz, 1 H, $H_{2 \text{ or } 5}$). − ^{13}C NMR ($CDCl_3$): δ = 27.5, 84.8, 110.9, 149.4, 157.5, 158.7, 161.4. − MS (FAB): *m/z* = 330.0 [M^+]. − IR (KBr): ṽ = 3149, 2980, 1778, 1737, 1567, 1538, 1456, 1365, 1299, 1259, 1234, 1157, 1138, 983, 843, 786. − $C_{14}H_{20}ClN_3O_4$ (329.8): calcd. C 50.99, H 6.11, N 12.74; found C 50.70, H 5.72, N 12.54.

6-[Bis(*tert*-butoxycarbonyl)amino]-4-(trimethylstannyl)pyrimidine (16): 6-[Bis(*tert*-butoxycarbonyl)amino]-4-chloropyrimidine (**15**) (611 mg, 1.85 mmol), hexamethyldistannane (670 mg, 2.04 mmol), and $Pd(PPh_3)_4$ (86 mg, 0.074 mmol) were combined in toluene (10 mL), flushed with Ar, and heated under reflux for 45 min. The solvent was evaporated and the residue used for the following coupling reaction without further purification. − ^1H NMR ($CDCl_3$): δ = 0.35 [s, 9 H, $Sn(CH_3)_3$], 1.51 [s, 18 H, $C(CH_3)_3$], 7.77 (d, *J* = 1.5 Hz, 1 H, $H_{2 \text{ or } 5}$), 8.95 (d, *J* = 1.2 Hz, 1 H, $H_{2 \text{ or } 5}$).

4-[6′-Bromopyrid-2′-yl]-6-[bis(*tert*-butoxycarbonyl)amino]-pyrimidine (17): 6-[Bis(*tert*-butoxycarbonyl)amino]-4-(trimethylstannyl)pyrimidine (**16**) (763 mg, 1.76 mmol), 2,6-dibromopyridine (671 mg, 2.83 mmol), and $Pd(PPh_3)_4$ (98 mg, 0.084 mmol) were combined in toluene (10 mL), flushed with Ar, and heated under reflux for 21 h. The solvent was evaporated and the residue purified by column chromatography on silica with hexane/EtOAc (9:1 changing to 4:1, v/v) to give **17** as a white powder. Yield 345 mg (41%). − ^1H NMR ($CDCl_3$): δ = 1.53 [s, 9 H, $C(CH_3)_3$], 7.58 (dd, *J* = 0.9 and 7.9 Hz, 1 H, $H_{3' \text{ or } 5'}$), 7.71 (t, *J* = 7.6 Hz, 1 H, $H_{4'}$), 8.41 (dd, *J* = 1.2 and 7.3 Hz, 1 H, $H_{3' \text{ or } 5'}$), 8.53 (d, *J* = 1.2 Hz, 1 H, $H_{2 \text{ or } 5}$), 9.00 (d, *J* = 1.2 Hz, 1 H, $H_{2 \text{ or } 5}$). − ^{13}C NMR ($CDCl_3$): δ = 27.7, 84.3, 110.3, 120.5, 129.8, 139.3, 141.9, 154.8, 157.8, 159.9, 162.4. − MS (FAB): *m/z* = 452.9 [M + H^+]. − IR (KBr): ṽ = 2980, 2934, 1777, 1743, 1573, 1534, 1435, 1388, 1370, 1341, 1303, 1279, 1230, 1143, 985, 850, 807, 775, 697, 632. − $C_{19}H_{23}BrN_4O_4$ (451.3): calcd. C 50.57, H 5.41, N 12.41; found C 50.84, H 5.29, N 12.20.

6-[Bis(*tert*-butoxycarbonyl)amino]-4-[6′-(trimethylstannyl)pyrid-2′-yl]pyrimidine (18): 4-[6′-Bromopyrid-2′-yl]-6-[bis(*tert*-butoxycarbonyl)amino]pyrimidine (**17**) (140 mg, 0.32 mmol), hexamethyldistannane (120 mg, 0.36 mmol), and $Pd(PPh_3)_4$ (19 mg, 0.017 mmol) were combined in toluene (2 mL), flushed with Ar, and heated under reflux for 30 min. The solvent was evaporated and the residue used for the next coupling reaction without further purification. − ^1H NMR ($CDCl_3$): δ = 0.38 [s, 9 H, $Sn(CH_3)_3$], 1.53 [s, 18 H, $C(CH_3)_3$], 7.53 (dd, *J* = 1.5 and 7.3 Hz, 1 H, $H_{3' \text{ or } 5'}$), 7.68 (t, *J* = 7.3, 1 H, $H_{4'}$), 8.30 (dd, *J* = 1.5 and 7.9 Hz, 1 H, $H_{3' \text{ or } 5'}$), 8.60 (d, *J* = 1.2 Hz, 1 H, $H_{2 \text{ or } 5}$), 9.04 (d, *J* = 1.2 Hz, 1 H, $H_{2 \text{ or } 5}$).

4,6-Bis[6-{6-[bis(*tert*-butoxycarbonyl)amino]pyrimidin-4-yl}pyrid-2-yl]-2-phenylpyrimidine (19): 6-[Bis(*tert*-butoxycarbonyl)amino]-4-[6-(trimethylstannyl)pyrid-2-yl]pyrimidine (**18**) (151 mg, 0.28 mmol), 4,6-dichloro-2-phenylpyrimidine (34 mg, 0.15 mmol), and $Pd(PPh_3)_4$ (17 mg, 0.015 mmol) were combined in toluene (2 mL), flushed with Ar, and heated under reflux for 22 h. The solvent was evaporated and the residue purified by column chromatography on silica with hexane/EtOAc (4:1, changing to 1:1, v/v) to give **19** as a pale yellow powder. Yield 72 mg (50%). − ^1H NMR ($CDCl_3$): δ = 1.44 [s, 36 H, $C(CH_3)_3$], 7.52−7.6 (m, 3 H, $H_{meta \text{ and } para}$), 8.09 (t, *J* = 7.9 Hz, 2 H, $H_{4'}$), 8.60 (d, *J* = 7.6 Hz, 2 H, $H_{3' \text{ or } 5'}$), 8.69 (dd, *J* = 0.9 and 7.9 Hz, 2 H, $H_{3' \text{ or } 5'}$), 8.72−8.78 (m, 2 H, H_{ortho}), 8.85 (s, 2 H, $H_{2'' \text{ or } 5''}$), 9.03 (d, *J* = 0.9 Hz, 2 H, $H_{2'' \text{ or } 5''}$), 9.13 (s, 1 H, H_5). − ^{13}C NMR ($CDCl_3$): δ = 27.6, 84.1, 109.5, 112.9, 123.0, 123.9, 128.4, 128.5, 130.8, 137.7, 138.1, 150.2, 153.8, 155.2, 157.7, 159.7, 163.6, 164.3, 164.5. − MS (high-resolution FAB): calcd. for $C_{38}H_{34}N_{10}O_4$: *m/z* = 897.404784, found *m/z* = 897.405728 [M + H^+]. − IR (KBr): ṽ = 3059, 2979, 2933, 1777, 1744, 1576, 1537, 1459, 1394, 1370, 1342, 1304, 1282, 1260, 1142, 1109, 988, 847, 824, 759, 692. − $C_{48}H_{52}N_{10}O_8\cdot 3/4EtOAc$: calcd. C 63.65, H 6.00, N 14.56; found C 63.29, H 5.78, N 14.88.

4,6-Bis[6-(6-aminopyrimidin-4-yl)pyrid-2-yl]-2-phenylpyrimidine (3): EtOAc (5 mL) was saturated with HCl gas. This solution was added to 4,6-bis[6-{6′-[bis(*tert*-butoxycarbonyl)amino]pyrimidin-4-yl}pyrid-2-yl]-2-phenylpyrimidine (**19**) (72 mg, 0.080 mmol) and stirred at room temp. for 16 h. The precipitation was centrifuged off and washed with EtOAc, H_2O, NaOH, DMSO and acetone to give **3** as an off-white powder. Yield 35 mg (88%). Because of the low solubility of this compound, no NMR spectrum could be obtained. − MS (high-resolution FAB): calcd. for $C_{28}H_{21}N_{10}$: *m/z* = 497.195066, found *m/z* = 497.195923 [M + H^+]. − IR (KBr): ṽ = 3311, 3058, 1658, 1560, 1538, 1369, 1318, 1252, 1169, 1086, 992, 822, 760, 652.

Co Complex 7: 4,6-Bis[6-(6-aminopyrimidin-4-yl)pyrid-2-yl]-2-phenylpyrimidine (**3**) (2 mg, 4.03 μmol) and $Co(BF_4)_2\cdot 6H_2O$ (1.37 mg, 4.03 μmol) were heated under reflux in CD_3CN (0.25 mL) and D_2O (0.25 mL) for 23 h. The complex was isolated as a pale brown powder by evaporation of the solvent in quantitative yield. − ^1H NMR (CD_3CN/D_2O): δ = −89.59, −79.40, −42.99, −7.43, −7.18,16.73, 28.99, 49.42, 109.56, 146.53, 177.69. − MS (FAB): *m/z* = 2742.8 $[Co_4L_4](BF_4)_6^+$, 2655.7 $[Co_4L_4](BF_4)_5^+$, 2569.2 $[Co_4L_4](BF_4)_4^+$, 2481.2 $[Co_4L_4](BF_4)_3^+$.

X-ray Structural Analysis for Complex 7: A suitable orange crystal (0.4 × 0.1 × 0.05 mm) of $[C_{112}H_{80}N_{40}Co_4]^{8+} \times 2\ Cl^- \times 3\ SiF_6^{2-} \times 2\ CH_3CN \times 50\ H_2O$ was obtained from acetonitrile/water/THF during the attempt of cocrystallisation with Fe complex **5**; *M* = 3702.0 g mol^{-1}, triclinic $P\bar{1}$, *a* = 15.4976(4), *b* = 18.2114(6), *c* =

31.9538(10) Å, $\alpha = 86.9809(13)$, $\beta = 83.4137(18)$, $\gamma = 67.2828(16)°$, $V = 8263.6(4)$ Å^3, μ(Mo-K_α) = 0.559 mm^{-1}, $Z = 2$, $D_c = 1.447$ g cm^{-3}, $F(000) = 3644$, $T = 173.0(1)$ K. Data were recorded with a Nonius Kappa CCD diffractometer using graphite-monochromatised Mo-K_α ($\lambda = 0.71073$ Å) radiation. $\theta = 2.96-24.97°$ for data collection. 67652 collected reflections, 27325 unique reflections [16258 with $I > 2\sigma(I)$] were used for refinement. The data were processed with DENZO.[14] The absorption correction was made with SORTAV[15] ($T_{\min} = 80.74$ and $T_{\max} = 97.26°$) and L_p correction was applied. Structure solution was done by direct methods[16] and refinement on F^2.[17] The hydrogen atoms were calculated to their idealised positions with isotropic temp. factors (1.2 or 1.5 times the C temp. factor) and were refined as riding atoms. Four temperature factors were equalised. One Cl^- anion is disordered over two positions (occupancy 0.5). Fluorine atoms of one SiF_6^{2-} anion are disordered between two positions with site occupation values of 0.64 and 0.36. The hydrogen-bonded, complicated water system altogether includes 50 molecules of water (hydrogen atoms could not be located), of which 26 are treated with an occupancy of 1.0, while the others are disordered and refined with a population parameter of 0.5. Final R values were $R = 0.1185$, $wR^2 = 0.2778$ [$I > 2\sigma(I)$], $R = 0.1900$, $wR^2 = 0.3190$ (all data) for 2201 parameters, Goodness-of-fit on $F^2 = 1.057$. A final difference map displayed the highest electron density of 1.07 eÅ^{-3}, which is located near to water molecules. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-150832. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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