Zuschriften

Three-Level Synthetic Strategy Towards Mixed-Valence and Heterometallic [2 × 2] Gridlike Arrays**

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The metal-directed self-assembly of polydentate ligands provides a convenient route to a variety of supramolecular architectures.[1] Examples to date that illustrate the versatility of the process include helicates,[2] cages,[3] ladders,[4] racks,[5] and grids.[6, 7] Interest in these assemblies has also been fueled by their potential for a wide range of applications. For example, inorganic arrays have been used as hosts for neutral,[8] cationic,[9] and anionic species,[10] with the possibility of electrochemical[10d] or optical sensing.[11] Metal-based assemblies are also prospective candidates for the development of novel materials incorporating magnetic,[12] electronic,[13] or optical features.[11,14] In particular, gridlike arrays possessing two different metals could exhibit interesting physicochemical properties arising from the precise positioning of the metallic centers.[7b] For example, the possibility of addressing the metal ions individually through an external stimulus would allow information to be written and stored at specific sites within the array.[15]

[2 × 2] Grids incorporating one type of metal center are easily constructed by one-step self-assembly reactions between the appropriate ditopic ligand and metal cation.[6a, 7a] In contrast, the synthesis of heterometallic grids with precisely located metal ions is more problematic. One approach towards this type of grid has been described and involves sequential self-assembly coupled with a protection/deprotection step.[7b] We now report a novel methodology for the generation of mixed valence and heterometallic [2 × 2] grid-type architectures **1** based on a stepwise constructed bis(hydrazone) ligand **2** containing both an ionizable NH site and a non-ionizable NMe center (Scheme 1). This synthetic pathway utilises a three-level strategy involving 1) steric control of regioselectivity, 2) modulation of the redox state through protonation, and 3) chiroselective-toposelective self-assembly.

The key intermediate in the synthesis is the monometallic "corner-type" complex **3** (Scheme 1). It contains a substitutionally inert Co^{III} center to prevent scrambling when a second ion is introduced to assemble the grid. A stepwise, controlled route was employed to construct complex **3** (Scheme 2).

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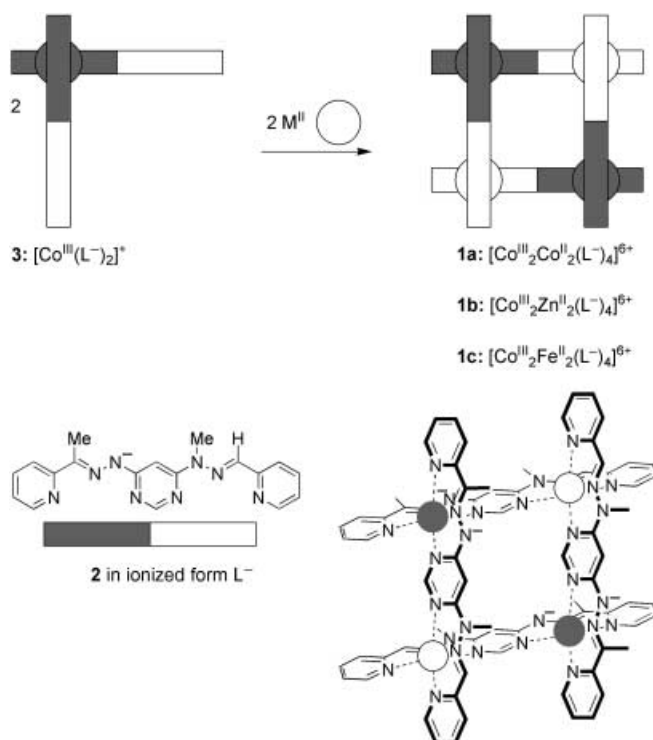
Scheme 1. Self-assembly of the [2×2] grid-type metallosupramolecular architectures **1** from the "corner" precursor **3** incorporating ligand **2**.
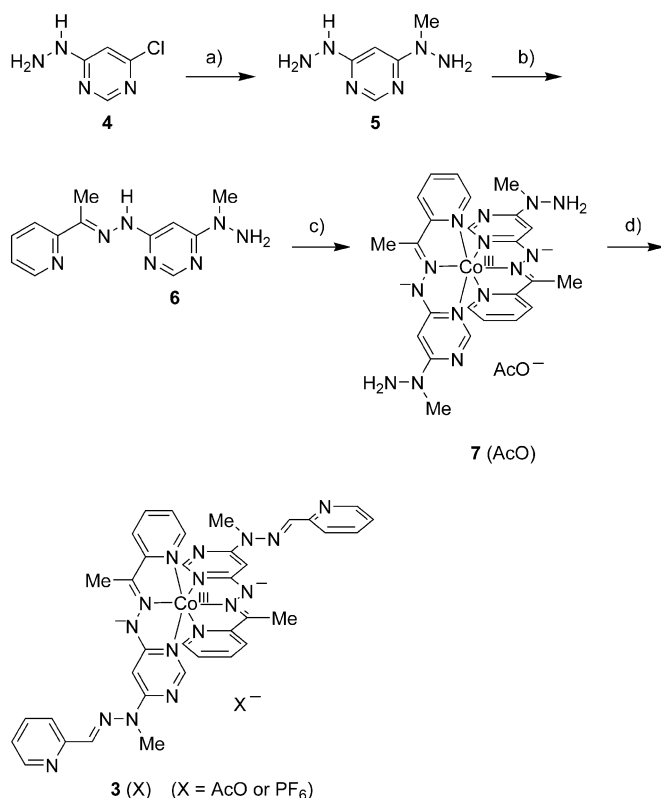
Scheme 2. Synthesis of complex [Co^{III}(L$^-$)$_2$]$^+$ (**3**): a) MeNHNH$_2$, MeOH; b) 2-acetylpyridine, MeOH; c) Co(OAc)$_2$·4H$_2$O, MeOH; d) 2-pyridinecarboxaldehyde, MeOH.

First, the terdentate ligand **6** containing just one metal binding pocket was prepared by a regioselective synthetic approach. 4-Chloro-6-hydrazinopyrimidine (**4**)[16] was treated with *N*-methylhydrazine to give compound **5**, which was subsequently condensed with one equivalent of 2-acetylpyridine (Scheme 2). It was reasoned that the condensation reaction would occur preferentially at the hydrazino site possessing an ionizable NH hydrazone group. This site selectivity results from the fact that reaction with the *N*-methylhydrazine moiety involves an unfavorable 1,3-steric repulsion between its methyl group and that of the 2-acetylpyridine reagent. Indeed, the ratio of products from the condensation at the NHNH$_2$ and NMeNH$_2$ sites of **5** was 13.5:1.

Second, the pathway towards complex **3** takes advantage of the ionizable NH site of **6** to promote a redox reaction at a bound metal center (Scheme 2). Thus, Co^{II}(OAc)$_2$·4H$_2$O reacts with **6** to generate the Co^{III} complex **7** in a process promoted by the synergistic coupling between the deprotonation of ligand **6** by the acetate anion of Co^{II}(OAc)$_2$·4H$_2$O, which acts as a base, and the aerial oxidation of cobalt(II) to cobalt(III) facilitated by its stabilization by two negatively charged ligands.[17] Thereafter, condensation of **7** with 2-pyridinecarboxaldehyde yields complex **3** containing two free metal-ion binding sites which cannot be deprotonated because they incorporate an *N*-methyl-protected hydrazone. This allows Co^{II} ions to be introduced at these sites without oxidation to Co^{III}.

The final step rests on a coupled chiro- and toposelective process to construct a heterometallic grid (Scheme 1). The [2×2] grid array is assembled from two corner complexes **3** of the *same* chirality; the connection of (*R*)- and (*S*)-**3** is geometrically prohibited.[7b] As a result, each assembly reaction yields one enantiomer of the chiral grid structure **1**.

Solubility problems in the self-assembly step hindered attempts to prepare **1a** from Co(BF$_4$)$_2$·6H$_2$O and **3** in MeCN. The counterion in **3** was therefore changed to the hexafluorophosphate salt **3**·PF$_6$. This complex reacts with Co(BF$_4$)$_2$·6H$_2$O in acetonitrile to afford the mixed valence array **1a** (Scheme 1). Evidence for the tetranuclear core was obtained from electrospray mass spectrometry. The spectrum reveals a series of peaks which can be attributed to sequential loss of PF$_6^-$ and/or BF$_4^-$ counterions (**1a**(PF$_6$)$_2$(BF$_4$)$_4-x$PF$_6-y$BF$_4$)$^{(x+y)+}$ ($x = 0$–2, $y = 0$–4).

The ^{1}H NMR spectrum of grid **1a** displays several remarkable features consistent with the proposed mixed-valence structure (Figure 1 a, b). The very strongly shifted peaks at lowest field (138.5–213.7 ppm) possess the shortest relaxation times ($T_1 = 0.9$–2.1 ms) and are attributed to the three protons closest to the paramagnetic Co^{II} center (pyr6′, pym2, and H$_{im}$).[18] The remaining ten signals ($\delta = 6.9$–75.7 ppm) were assigned using a combination of COSY and ROESY experiments and are divided into two sets. Protons adjacent to the Co^{II} center exhibit shifted signals at $\delta = 18.2$–75.7 ppm (pyr3′, pyr4′, pyr5′, pym5) and at $\delta = 6.9$ ppm (NMe). In contrast, the cluster of five peaks in the high-field region (7.9–14.3 ppm) is assigned to pyridyl and CMe protons at the Co^{III} site. These protons belong to the coordination sphere of the low-spin, diamagnetic Co^{III} ion,
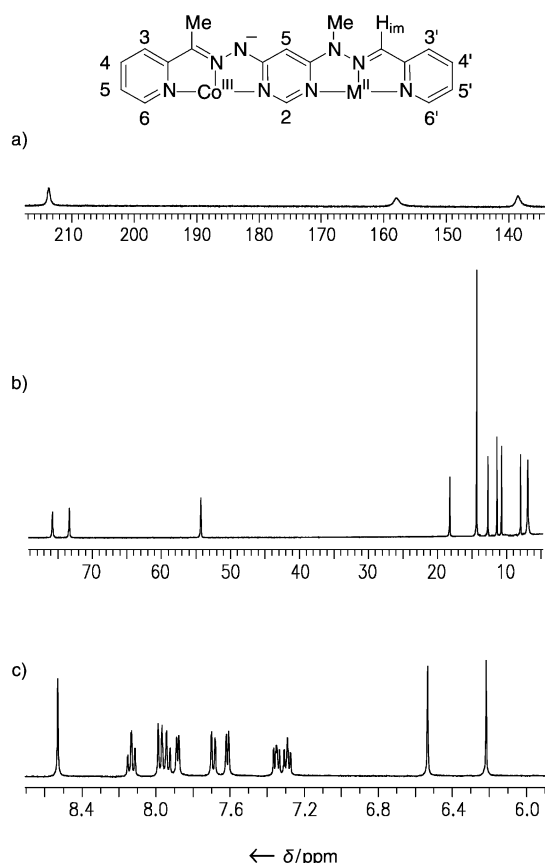
a)

b)

c)

← δ/ppm

Figure 1. ^{1}H NMR spectra (400 MHz, CD$_3$CN) of grid **1a** in the low-field (a) and high-field (b) regions; low-field region of grid **1b** (c).

although the neighboring paramagnetic Co^{II} center clearly affects their chemical shifts and relaxation rates.

The generality of the synthetic strategy was demonstrated by preparing grids **1b** and **1c** from **3**·PF$_6$ and M^{II}(BF$_4$)$_2$ (M^{II} = Zn^{II}, Fe^{II}, respectively; Scheme 1). In contrast to grid **1a** the ^{1}H NMR spectra of these grids are restricted to the diamagnetic region (Figure 1c), which indicates that both iron(II) centers are low spin in complex **1c**.

In conclusion, a three-tiered synthetic strategy was used to construct a mixed valence [2 × 2] Co$_2^{II}$Co$_2^{III}$ grid as well as heterometallic analogues. This strategy, which encompasses regioselective, redox, and chiroselective features, implements the approach and procedures developed for the synthesis of complex organic molecules in the stepwise elaboration of inorganic architectures. The arrays are based on a hetero-ditopic ligand, which contains ionizable and non-ionizable compartments, thus allowing the oxidation state of the cobalt ions to be modified according to the charge on the hydrazone moiety. Such [2 × 2] grid motifs, in which the oxidation states can be locally manipulated and addressed by external effectors (for example, protons),[19] are of interest for future multistable molecular devices incorporating multilevel redox activity.[13] It is noteworthy that molecular spin ladders display grid-type arrays[20] and that cells presenting a four-dot [2 × 2]-type architecture have been considered as components of quantum-dot cellular automated devices.[21]

Experimental Section

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