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Protonic modulation of redox properties in ionisable [2 × 2] grid-like metalloarrays†

Lindsay H. Uppadine,[a] Jean-Paul Gisselbrecht[b] and Jean-Marie Lehn*[a]

[a] *ISIS, Université Louis Pasteur, 8 allée Gaspard Monge, F-67083 Strasbourg, France.*
E-mail: lehn@isis.u-strasbg.fr
[b] *Laboratoire d'Electrochimie et de Chimie-Physique du Corps Solide, UMR 7512, CNRS, Université Louis Pasteur, 4 rue Blaise Pascal, 67000 Strasbourg, France*

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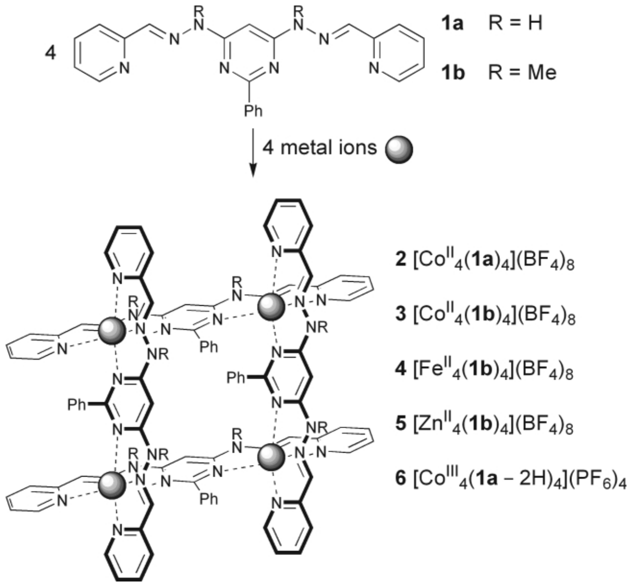
The oxidation state of the cobalt centres can be controlled by modification of the protonation state in [2 × 2] grid-like arrays based on ionisable bis(hydrazone) ligands, allowing conversion of the paramagnetic Co^{II}_4 into the diamagnetic Co^{III}_4 grid.

Multimetallic architectures display intriguing physical properties arising from the well-defined spatial array of metallic and ligand components.[1] These physical characteristics include redox,[2] optical[3] and magnetic[4,5] features, which could be exploited in a variety of fields including molecular sensing[2b,3b] and materials science.[1] In particular, metalloarrays exhibiting multistable behaviour are promising candidates for high-density information storage devices.[2a,5b] External stimuli can be used to control multistability on the molecular level, *via* manipulation of intrinsic molecular properties such as spin crossover[5] or redox state.[2a] To this end, we report here the synthesis and electrochemistry of tetranuclear [2 × 2] grid-like arrays incorporating bis(hydrazone) ligands. The oxidation state of the cobalt centres may be modulated through the protonation state of the hydrazone group.

Ligands **1a**[3a] and **1b**[6] present bis(terdentate) coordination sites based on pyridine and pyrimidine groups linked by hydrazone moieties (Scheme 1). Complexation with transition metals of octahedral coordination generates [2 × 2] grid-type arrays **2–6**. Grid complexes based on ligand **1a** possess ionisable NH groups, whereas ligand **1b** contains non-ionisable NMe sites.

The equimolar reaction of $Co(BF_4)_2{\cdot}6H_2O$ and **1a** in MeCN afforded the paramagnetic Co^{II}_4 grid **2**, as described previously.[3a] The *N*-methylated complexes **3–5** were synthesised analogously from **1b** and $M^{II}(BF_4)_2{\cdot}6H_2O$ (M^{II} = Co^{II}, Fe^{II} and Zn^{II}, respectively). Crystals of complex **2** were obtained from MeCN–Et_2O and characterised by synchrotron X-ray diffraction.[7] The structure is similar to the previously reported manganese analogue $[Mn^{II}_4(\mathbf{1a})_4](ClO_4)_8$[3a] and unequivocally demonstrates the tetranuclear [2 × 2] grid-like array.



Scheme 1 Metal-directed self-assembly of [2 × 2] grid-like arrays.

The ^1H NMR spectra of complexes **2–4** are broadened and paramagnetically shifted due to the presence of Co^{II} or high spin Fe^{II} ions.[8] Fig. 1a shows the ^1H NMR spectrum of grid **2** as an illustrative example. The complex displays a single set of 12 resonances, attributed to 4 pyridine, 1 pyrimidine, 1 imino, 1 NH and 5 phenyl nuclei arranged in a highly symmetric structure. The observation of 5 phenyl signals is diagnostic of grid formation; it indicates that rotation about the pyrimidine–phenyl bond is sterically hindered in the complex.[9]

Changing the Co^{II} counteranion and solvent used in the self-assembly reaction with **1a** afforded a grid with strikingly different electronic properties compared to **2**. Thus, the equimolar reaction of $Co(OAc)_2{\cdot}4H_2O$ and **1a** in H_2O–MeOH (7 : 3) generated a tetranuclear low spin Co^{III}_4 grid by simultaneous oxidation and deprotonation; it was isolated by precipitation as the hexafluorophosphate salt **6**.‡ The ^1H NMR spectrum of complex **6** is shown in Fig. 1b and clearly illustrates the diamagnetic nature of the grid. The complex displays eleven signals over a range of 2.3 ppm compared to 265 ppm for the Co^{II}_4 version **2**. The phenyl protons again appear as five separate peaks, consistent with a grid-type architecture, but no NH signals were observed. The UV–vis spectrum supports the assertion that ligand **1a** is deprotonated in **6**; the intense violet colour (λ_{max}/nm (MeCN) 546 (ε/10^4 dm^3 mol^{-1} cm^{-1} 19.9) is attributed to $(\mathbf{1a} - 2H)^{2-}$ in the assembly.

The mass spectra of complexes **2–6** confirm the tetrametallic composition of the grids. For example, the ES-MS of **2** displays a series of peaks assigned to $[Co^{II}_4(\mathbf{1a})_4 - xH]^{(8-x)+}$, due to varying degrees of deprotonation and loss of all eight counterions (Fig. 2a). In contrast, an intense peak at *m*/*z* 451.2 dominates the ES-MS of

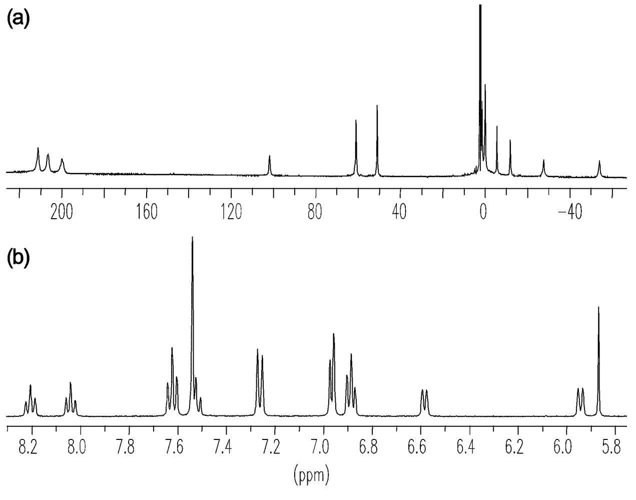


Fig. 1 ^1H NMR spectra of (a) Co^{II}_4 complex **2** (200 MHz, CD_3CN) and (b) Co^{III}_4 complex **6** (400 MHz, CD_3CN).

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† Electronic supplementary information (ESI) available: Cyclic voltammogram of $[Fe^{II}_4(\mathbf{1b})_4](BF_4)_8$ in MeCN vs Fc^+/Fc. See http://www.rsc.org/suppdata/cc/b3/b315352e/

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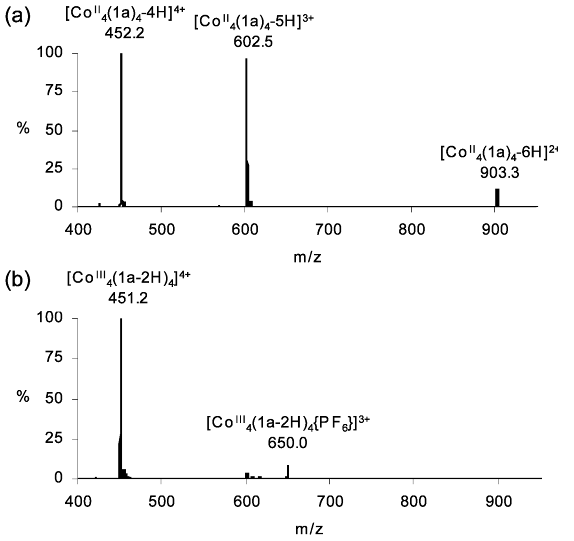

Fig. 2 Electrospray mass spectra of (a) Co^{II}_4 complex **2** and (b) Co^{III}_4 complex **6**.

complex **6** (Fig. 2b). This was attributed to the fully deprotonated complex $[Co^{III}_4(\mathbf{1a} - 2H)_4]^{4+}$.

The electrochemical properties of grids **2–6** were investigated by cyclic voltammetry in MeCN (Table 1). Complex **2** exhibits a pair of two-electron ligand-based reductions as well as a quasi-reversible four-electron wave assigned to the oxidation of Co^{II} to Co^{III}. The cyclic voltammograms of **3–5** consist of two sets of three or four reversible reduction steps, whose potentials depend on the type of metal ion. The first group of four one-electron waves is attributed to reduction of the four ligands in the complex, as confirmed by spectroelectrochemical studies.[2a] The second set is found at significantly lower potential (−1.65 to −2.12 V) and is due to further reduction of the ligand radical anions.[2a] The four one-electron oxidation waves in **4** can be ascribed to the redox couple Fe^{III}/Fe^{II}, but no oxidation was observed for the Co^{II} ions in **3**, in contrast to the results for **2**. This indicates that the Co^{III} oxidation state is stabilised by deprotonation of the NH sites in grid **2**. Co^{III}_4 complex **6** displays four reversible one-electron oxidation waves and two sets of four reversible one-electron reductions. The oxidation process may be attributed to electron loss from the electron rich dianionic ligands $(\mathbf{1a} - 2H)^{2-}$,[10] while the first set of four reductions may involve the metal due to the relatively small values of the redox potentials. The second cluster of four very negative reduction waves may occur on the ionised ligands.

Table 1 Redox potential *E*/V of **2–6** in MeCN (0.1 M Bu_4NPF_6, Pt electrode, *versus* Fc^+/Fc)

Complex	2	3	4	5	6
E_{ox}/V^a	$+1.09^b$		+1.14		+0.75
			+1.18		+0.83
			+1.45		+0.93
			+1.52		+1.01
E_{red}/V^a	-0.84^c	−0.81	−1.04	−1.30	−0.39
		−0.83	−1.07	−1.34	−0.44
	-1.05^c	−0.99	−1.19	−1.40	−0.77
		−1.02	−1.29	−1.52	−0.92
	-1.95^d	−1.89	−1.65	−1.71	−1.89
		−1.93	−1.77	−1.82	−1.99
		−2.09	−1.93	-1.93^d	−2.18
		−2.12	−2.01		−2.34

[a] 1 e^- processes unless otherwise stated. [b] 4 e^- oxidation. [c] 2 e^- reduction. [d] No. of e^- cannot be determined due to electrode inhibition.

A comparison of grids **2** and **6** indicates that a synergism exists between ligand protonation state and metal oxidation state. Thus, self-assembly affords the protonated Co^{II}_4 grid **2** when nonbasic BF_4^- counteranions are used in MeCN. However, metal oxidation occurs concomitantly with ligand ionisation to yield deprotonated Co^{III}_4 grid **6** when basic AcO^- anions are employed in 7 : 3 H_2O–MeOH.[11] The Co^{III} state is electrostatically stabilised by the negatively charged ligands in **6**, whereas Co^{II} is favoured when **1a** is present as its protonated, neutral form in **2**.

In summary, protonic modulation of oxidation state has been demonstrated for tetranuclear cobalt grids containing ionisable NH hydrazone sites. Furthermore, electrochemical investigations show that [2 × 2] grid-like arrays based on hydrazone ligands act as electron reservoirs, capable of exhibiting up to eight well-resolved reduction steps. This type of multimetallic array therefore holds great promise for the development of future multilevel electronic devices displaying connection to and addressability by external triggers.

Notes and references

‡ *Synthesis of* **6**: $Co(OAc)_2·4H_2O$ (56.8 mg, 0.228 mmol) and ligand **1a** (90.0 mg, 0.228 mmol) were stirred in H_2O–MeOH (10 mL, 7 : 3 v/v) at rt for 15 h. The solvent was evaporated and the residue redissolved in water (5 mL). Addition of KPF_6(aq) afforded a precipitate, which was recrystallised from MeOH–H_2O to yield a purple solid (129 mg, 92%). ^1H NMR (400 MHz, CD_3CN) δ: 8.20 (1H, t, J = 7.7 Hz, *p*-Ph), 8.04 (1H, t, J = 7.5 Hz, *m*-Ph_{outer}), 7.62 (2H, t, J = 7.5 Hz, pyr4), 7.52 (3H, m, H^{im}, *m*-Ph_{inner}), 7.26 (2H, d, J = 8.1 Hz, pyr3), 6.96 (2H, d, J = 5.8 Hz, pyr6), 6.88 (2H, t, J = 6.8 Hz, pyr5), 6.58 (1H, d, J = 7.3 Hz, *o*-Ph_{outer}), 5.94 (1H, d, J = 7.3 Hz, *o*-Ph_{inner}), 5.87 (1H, s, pym5). ^{13}C NMR (100 MHz, CD_3CN) δ: 170.59, 168.50, 159.84, 150.27, 141.12, 140.74, 132.39, 128.90, 128.61, 127.94, 125.77, 125.60, 123.62, 89.75. Found: C, 43.1; H, 3.1; N, 17.8. Calc. for $Co_4C_{88}H_{64}N_{32}P_4F_{24}·4H_2O$: C, 43.0; H, 3.0; N, 18.2%. ES-MS *m/z* 650.0 $(M - 3PF_6)^{3+}$, 601.7 $(M - 4PF_6 + H)^{3+}$, 451.2 $(M - 4PF_6)^{4+}$. λ_{max}/nm (MeCN) 296 ($\varepsilon/10^4$ dm^3 mol^{-1} cm^{-1} 8.0), 429 (2.2), 546 (19.9).

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