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Synthesis of ionisable [2 × 2] grid-type metallo-arrays and reversible protonic modulation of the optical properties of the $[\mathrm{Co}^{\mathrm{II}}_4\mathrm{L}_4]^{8+}$ species

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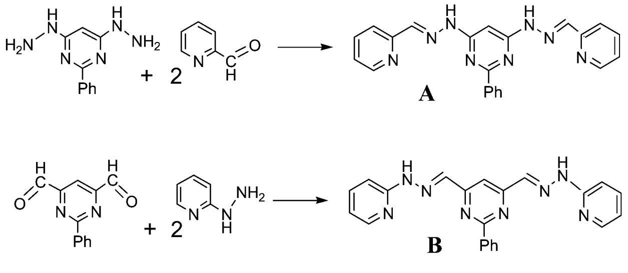
The new bis-hydrazone based ligands A and B form ionisable [2 × 2] grid-type transition metal complexes whose properties may be modulated by multiple protonation/deprotonation as shown by the reversible change in optical properties of the $[\mathrm{Co}^{\mathrm{II}}_4\mathrm{L}_4]^{8+}$ complexes depending on their protonation state.

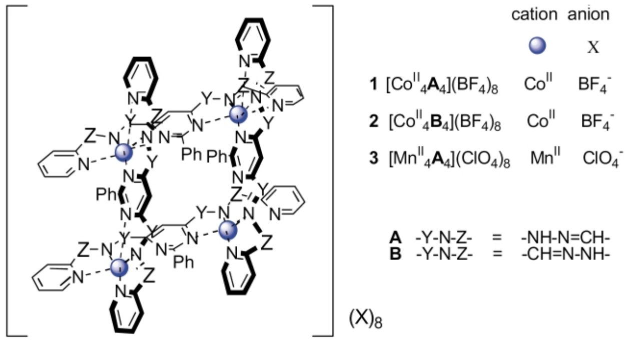
Two-dimensional grid-like coordination complexes have attracted increasing interest for the last decade since a well-defined 2-D arrangement of an exact number of metal ions suggests possible uses in information storage and processing technology.[1] A number of square[2–4] [$n \times n$] and rectangular[5] [$n \times m$] grids with $n, m \leq 4$ have been obtained for metal ions with tetrahedral[2] as well as octahedral coordination geometry. Of special interest are complexes undergoing reversible switching processes of optical, magnetic[6] and redox[7] properties triggered by external parameters like temperature, pressure, light, magnetic or electric potential.

We present herein the synthesis of a new type of bis-hydrazone based ligands **A** and **B** and their conversion into the [2 × 2] grid-like complexes $[\mathrm{Co}^{\mathrm{II}}_4\mathbf{A}_4](\mathrm{BF}_4)_8$ **1** and $[\mathrm{Co}^{\mathrm{II}}_4\mathbf{B}_4](\mathrm{BF}_4)_8$ **2** (Schemes 1 and 2) which show optical switching with intense reversible colour changes depending on the pH of the solution.†

The introduction of a hydrazone group into a terpyridine (terpy) unit gives easy synthetic access to long helical chains[8] as well as to multiple terpy-type ligands and their complexes presenting ionisable N–H sites.[9] This protocol was applied to the synthesis of ligands **A** and **B**, analogs of the bis-terpy type ligands described earlier.[3] The isomeric ligands **A** and **B** were synthesised by condensation of one equivalent of the respective pyrimidine brick with two equivalents of the respectively substituted pyridine compound in a 1 : 1 solution of EtOH–$\mathrm{CH_3Cl}$ and in the presence of molecular sieves (95 and 90% yield respectively, Scheme 1). In analogy to the previously reported formation of grid-type complexes,[3] ligands **A** and **B** react with transition metal ions of octahedral coordination (such as $\mathrm{Zn^{II}}$, $\mathrm{Co^{II}}$, $\mathrm{Fe^{II}}$ and $\mathrm{Mn^{II}}$) to generate tetranuclear [2 × 2] grid-type complexes.[9] Thus, the compounds $[\mathrm{Co}^{\mathrm{II}}_4\mathbf{A}_4](\mathrm{BF}_4)_8$ **1** and $[\mathrm{Co}^{\mathrm{II}}_4\mathbf{B}_4](\mathrm{BF}_4)_8$ **2** were obtained in quantitative yields by the equimolar reaction of $\mathrm{Co(BF_4)_2}$ with **A** or **B** in dry acetonitrile under reflux for 6 hours. Because of their design, both ligands **A** and **B** steer the metal ions into square-like arrangements and simultaneously introduce pH-sensitive NH functionalities into the complexes (Scheme 2).



Scheme 1 Synthesis of ligands **A** and **B**.



Scheme 2

Crystals of $[\mathrm{Co}^{\mathrm{II}}_4\mathbf{A}_4](\mathrm{BF}_4)_8$ **1** were obtained from a buffer/acetonitrile solution at pH 5.29 and a single crystal X-ray diffraction study was carried out. Unfortunately, detailed structural analysis was prevented by the low quality of the refined data. Nevertheless, the data set obtained allowed us to conclude that the complex presented the expected [2 × 2] grid-like structure. Additionally, no anions were found, which argues for the loss of all eight protons in accordance with the spectroscopic investigations at the applied pH.

More precise structural insight was gained from the single X-ray structure of the structurally analogous $[\mathrm{Mn}^{\mathrm{II}}_4\mathbf{A}_4](\mathrm{ClO}_4)_8$ **3** complex (Fig. 1),‡ which revealed a tetranuclear complex with four metals in an octahedral $\mathrm{N_6}$ environment. The ligands are found in an almost ideal alignment in perpendicular and parallel directions. The distance between the pyrimidine rings of two parallel ligands averages 7.0 Å. The phenyl substituents are perpendicularly twisted with respect to the pyrimidine rings and are sandwiched between the two opposite ligands at a distance of d = 3.5 Å as found for other [2 × 2] $[\mathrm{M}^{\mathrm{II}}_4\mathrm{L}_4]^{8+}$ complexes.[3] Because these crystals were grown from an anhydrous nitromethane solution, all eight anions (and so presumably all eight N–H protons) were still present.

In addition to the synthetic aspects, ligands **A** and **B** present the interest that in their grid complexes $[\mathrm{M}^{\mathrm{II}}_4\mathbf{L}_4]^{8+}$ the high positive charge should render the eight hydrazone N–H protons (two per ligand) acidic, thus allowing protonic modulation of

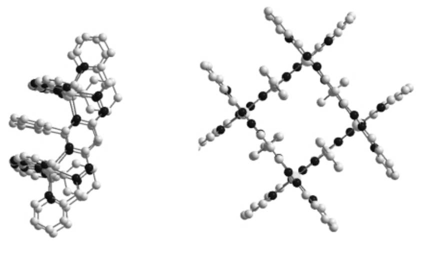


Fig. 1 Side (left) and top (right) views of the X-ray structure of $[\mathrm{Mn}^{\mathrm{II}}_4\mathbf{A}_4](\mathrm{ClO}_4)_8$ **3** (protons, anions and solvent are omitted for clarity).

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the properties (optical, redox, magnetic, *etc.*) of these complexes, up to a fully deprotonated, overall neutral species.[10]

The pH-dependency of $[\mathrm{Co}^{\mathrm{II}}_4\mathbf{A}_4](\mathrm{BF}_4)_8$ **1** was studied by UV-vis spectroscopy in a 50/50 vol% mixture of acetonitrile and Britton–Robinson buffer.[11] Fig. 2 shows the spectroscopic changes observed when the pH of a solution of **1** was increased in a stepwise manner. Starting from low pH (0.51–3.79), a new peak at λ = 527 nm emerges progressively at the expense of the main peak at λ = 378 nm. Intermediately, a third peak at λ = 450 nm evolves and disappears at pH values between 3 and 5.5. From moderately acidic to neutral pH values (4.64–7.22) the band at λ = 527 nm ($\varepsilon = 42 \times 10^3$ cm^2 mol^{-1}) surmounts all remaining peaks in intensity and exhibits saturation behaviour at pH values above 7. Subsequent decrease of the pH reestablishes the low pH spectra and repeated cycling indicates that the process is completely reversible. The colour of the solution changes from pale-yellow at low pH to orange and finally deep-violet above neutral pH (Fig. 3).

A very similar spectroscopic behaviour is observed on titration of a 4.5×10^{-7} M solution of **1** in anhydrous acetonitrile with water exhibiting saturation above 3 vol% of water.

Likewise, the UV-vis spectra of $[\mathrm{Co}^{\mathrm{II}}_4\mathbf{B}_4](\mathrm{BF}_4)_8$ **2** displays reversible pH modulation of the optical properties. However, **2** exhibits already in the fully protonated state at low pH an absorption band in the visible range (λ = 421 nm) which decreases as a more intense band at λ = 620 nm emerges and saturates at neutral pH by progressive titration. The colour of complex **2** changes from blue to deep-green and the process is completely reversible. The analogous $[\mathrm{Zn}^{\mathrm{II}}_4\mathbf{L}_4]^{8+}$ complexes exhibit a similar pH dependency of the spectrocopic properties (between colourless at acidic pH and dark-blue above neutral pH) indicating the primary involvement of ligand orbitals in such pH modulation processes. In addition, the $[\mathrm{Zn}^{\mathrm{II}}_4\mathbf{L}_4]^{8+}$ complexes exhibit also an emission at $\lambda_{\max}$ = 452 nm, which might be tuned by pH modulation.

In conclusion, due to the high accumulated charge of the $[\mathrm{Co}^{\mathrm{II}}_4\mathbf{L}_4]^{8+}$ complex cations, the eight N–H protons can be abstracted progressively and reversibly in solution at relatively low pH (below about 7). Further investigations concerning the protonic modulation of the redox[12a] and magnetic[12b] properties of this new class of grid-like compounds are in progress. In view of the remarkable properties (magnetic,[6] electronic,[7] and optical) of [2 × 2] grid-type complexes of transition metal ions, the hydrazone-type ligands **A** and **B** give access to medium dependent modulation of the physical properties of their complexes through reversible protonation/deprotonation processes. Such a feature is of great interest from the perspective of addressing functional metallo-supramolecular devices through external triggers.

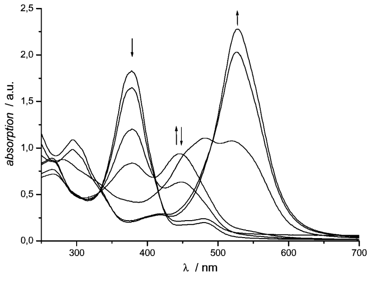

Fig. 2 UV-vis spectra of a 4.5×10^{-7} M solution of $[\mathrm{Co}^{\mathrm{II}}_4\mathbf{A}_4](\mathrm{BF}_4)_8$ **1** in buffer/acetonitrile 50/50 vol% at pH 0.51; 0.75; 3.12; 3.79; 4.64; 5.53 and 7.22.

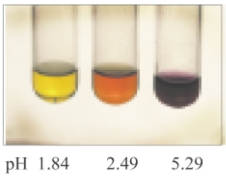

Fig. 3 Colour change of $[\mathrm{Co}^{\mathrm{II}}_4\mathbf{A}_4](\mathrm{BF}_4)_8$ **1** at different pH.

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Notes and references

† Ligands **A** and **B** were fully characterised by ^{1}H and ^{13}C NMR; FAB-MS and elemental analysis.

Synthesis of complexes: A suspension of the ligand (19.8 µmol) and of the respective Co$^{\mathrm{II}}$- (or of the respective Mn$^{\mathrm{II}}$-) salt (19.8 µmol) in ACN (1.5 mL) was heated until the ligand was completely dissolved. The solution was stirred under reflux for 6 h. The complex was isolated by addition of diisopropyl ether to the solution until a precipitate formed. The precipitate was collected, washed with diisopropyl ether and dried *in vacuo* resulting in quantitative yields.

$[\mathrm{Co}^{\mathrm{II}}_4\mathbf{A}_4](\mathrm{BF}_4)_8$, **1**: ^{1}H-NMR (d$_3$-ACN): δ = 215.9, 197.9, 187.3, 63.1, 59.2, 57.2, 11.2, 9.4, 8.1, 6.7, 6.3, −17.3; FAB-MS: *m/z* = 2158.3 [M − 4BF$_4$]$^+$, 2071.1 [M − 5BF$_4$]$^+$, 1982.2 [M − 6BF$_4$]$^+$, 1893.2 [M − 7BF$_4$]$^+$, 1806.2 [M − 8BF$_4$]$^+$, 903.1 [M − 8BF$_4$]$^{2+}$]; elemental analysis calc. (%) for $\mathrm{C_{88}H_{68}B_8N_{32}F_{32}Co_4}$: C 42.21, H 2.74, N 17.90; found C 42.03, H 2.67, N 17.79.

$[\mathrm{Co}^{\mathrm{II}}_4\mathbf{B}_4](\mathrm{BF}_4)_8$, **2**: ^{1}H-NMR (d$_3$-ACN): δ = 238.5, 142.3, 119.8, 116.1, 66.8, 64.5, 51.4, 12.1, 11.4, 8.4, 8.1, 6.2; FAB-MS: *m/z* = 1805.4 [M − 8BF$_4$]$^+$, 903.2 [M − 8BF$_4$]$^{2+}$]; elemental analysis calc. (%) for $\mathrm{C_{88}H_{68}B_8N_{32}F_{32}Co_4}$: C 42.21, H 2.74, N 17.90; found C 41.45, H 2.53, N 17.64.

‡ *Crystal data*: $[\mathrm{Mn}^{\mathrm{II}}_4\mathbf{A}_4](\mathrm{ClO}_4)_8$, 120 K, triclinic, $P\bar{1}$, a = 17.7576(12), b = 17.9133(12), c = 24.6470(15) Å, α = 80.381(1), β = 84.562(3), γ = 70.980(3)°, V = 7301.1(8) Å^3, Z = 2, D_c = 1.564 g cm^{-3}, $\theta_{\max}$ = 14.06°, μ(0.42753 Å) = 0.312 mm^{-1}. 38752 collected reflections, 14971 unique reflections [5838 $I > 2\sigma(I)$] were used for refinement. The final R values were R = 0.1155, wR^2 = 0.2765 [$I > 2\sigma(I)$], R = 0.1393, wR^2 = 0.2902 (all data) for 2010 parameters and 361 restraints. The highest electron density on the final difference map was 1.266 e Å^{-3}. CCDC reference number 207377. See http://www.rsc.org/suppdata/cc/b3/b303922f/ for crystallographic data in CIF or other electronic format.

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