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Control of molecular architecture by use of the appropriate ligand isomer: a mononuclear "corner-type" *versus* a tetranuclear [2 × 2] grid-type cobalt(III) complex†

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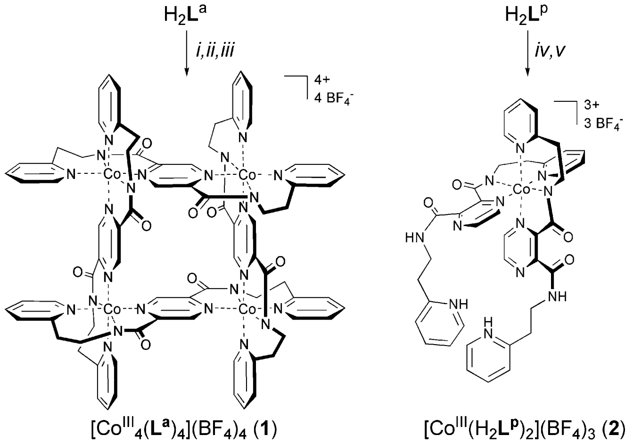
Employing two isomeric pyrazine-based ligands a [2 × 2] grid-type tetranuclear cobalt(III) complex, incorporating doubly deprotonated $(\mathbf{L^a})^{2-}$ ligands, and a "corner-type" mononuclear cobalt(III) complex, incorporating neutral $\mathbf{H_2L^p}$ ligands in a zwitterionic form, have been synthesised and structurally characterised.

In the presence of metal ions, carefully designed polydentate ligands can direct the self-assembly of metal complexes with a variety of supramolecular architectures.[1] Such metal-based supramolecular assemblies are promising candidates for the development of novel materials. For example, grid-type compounds have been reported which incorporate interesting magnetic[2] or electronic[3] features. Grid-type compounds incorporating one type of metal centre are easily synthesised by self-assembly reactions between appropriate polytopic ligands and metal ions.[4] The synthesis of mixed-valent or heterodimetallic [2 × 2] grid-type complexes is possible using a stepwise approach to construction.[5] In the first step a mononuclear "corner-type" complex, which contains a relatively inert metal centre coordinated by two perpendicularly bis-terdentate ligands, is formed. Each ligand still has a free terdentate binding pocket available, so when a second metal ion is introduced a mixed metal grid can self-assemble.[5]

Here we report the syntheses and crystal structures of two very different cobalt(III) complexes, a [2 × 2] grid-type (**1**) and a "corner-type" (**2**) complex, of two isomeric pyrazine-based diamide ligands (Scheme 1). Both ligands contain two identical bis-terdentate binding pockets: the key differences between them are that $H_2\mathbf{L^a}$ features antiparallel coordinate vectors and two well separated amide functional groups, whereas $H_2\mathbf{L^p}$ features parallel coordinate vectors and two adjacent amide functional groups. These ligands, $H_2\mathbf{L^a}$ and $H_2\mathbf{L^p}$, were prepared in good yields by reacting dimethyl pyrazine-2,5-dicarboxylate[6] or dimethyl pyrazine-2,3-dicarboxylate,[7] respectively, with 2-(2-aminoethyl)pyridine, resulting in colourless crystalline solids.



$[Co^{III}_4(\mathbf{L^a})_4](BF_4)_4$ (**1**) $[Co^{III}(H_2\mathbf{L^p})_2](BF_4)_3$ (**2**)

Scheme 1 Synthesis of **1** and **2**. Reagents and conditions: (*i*) 1 eq. $Co(BF_4)_2{\cdot}6\,H_2O$, MeCN, RT; (*ii*) 2 eq. NEt_3; (*iii*) Et_2O, vapour diffusion; (*iv*) $\frac{1}{2}$ eq. $Co(BF_4)_2{\cdot}6\,H_2O$, MeCN; (*v*) EtOH, slow evaporation.

The reactions of the two ligands with $Co(BF_4)_2{\cdot}6H_2O$ in a 1 : 1 molar ratio in MeCN solution, followed by air oxidation, resulted in the isolation of two cobalt(III) complexes with very different ligand-to-metal ratios. Vapour diffusion of diethyl ether into the reaction solution containing $H_2\mathbf{L^a}$ gave red-brown crystals of the tetranuclear [2 × 2] cobalt(III) grid $[Co^{III}_4(\mathbf{L^a})_4](BF_4)_4$ (**1**) in about 30% yield, along with some unidentified red-brown solid. Slow evaporation of the reaction solution containing $H_2\mathbf{L^p}$ gave the mononuclear "corner-type" complex $[Co^{III}(H_2\mathbf{L^p})_2](BF_4)_3$ (**2**) as a dark brick red crystalline solid, in about 20% yield.

The synthesis of **1** was repeated under identical reaction conditions except that two equivalents of NEt_3 were added (Scheme 1). This resulted in the clean isolation of $\mathbf{1}{\cdot}10H_2O$ as a red-brown crystalline solid in 85% yield.† The vapour diffusion of diethyl ether into a MeCN solution of $\mathbf{1}{\cdot}10H_2O$ afforded single crystals of $\mathbf{1}{\cdot}12.75$MeCN suitable for an X-ray crystal structure determination (Fig. 1).‡ In this tetranuclear complex of near-222 (D_2) symmetry and approximate 422 (D_4) symmetry the cobalt(III) ions are bridged *via* the ligand pyrazine rings which gives rise to a grid-like arrangement of interwoven ligand strands. Each cobalt(III) ion is

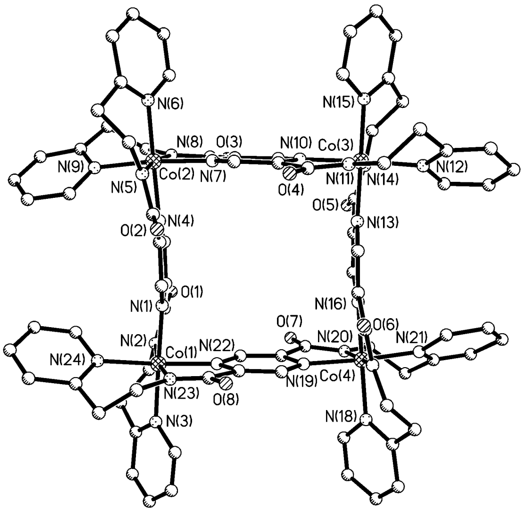


Fig. 1 Molecular structure of $[Co^{III}_4(\mathbf{L^a})_4]^{4+}$, the complex cation of the racemic compound $\mathbf{1}{\cdot}12.75$MeCN (hydrogen atoms omitted for clarity). Only one of the enantiomers is shown. Selected distances (Å) and angles (°): Co(1)–N(1) 1.941(3,6), Co(1)–N(2) 1.931(4,11), Co(1)–N(3) 2.003(3,15), Co(1)–N(22) 1.933(3,11), Co(1)–N(23) 1.929(3,7), Co(1)–N(24) 1.988(4,6), Co(1)···Co(2) 6.605(3), Co(2)···Co(3) 6.636(3), Co(3)···Co(4) 6.592(3), Co(4)···Co(1) 6.641(3), Co(1)···Co(3) 9.283(3), Co(2)···Co(4) 9.400(3); N(1)–Co(1)–N(2) 82.0(2,9), N(1)–Co(1)–N(3) 174.8(2,5), N(1)–Co(1)–N(22) 87.4(2,8), N(1)–Co(1)–N(23) 91.2(2,2), N(1)–Co(1)–N(24) 88.2(2,6), N(2)–Co(1)–N(3) 92.9(2,6), N(2)–Co(1)–N(22) 90.6(2,4), N(2)–Co(1)–N(23) 170.4(2,4), N(2)–Co(1)–N(24) 94.4(2,3), N(3)–Co(1)–N(22) 91.3(2,6), N(3)–Co(1)–N(23) 93.7(2,3), N(3)–Co(1)–N(24) 93.5(2,8), N(22)–Co(1)–N(23) 82.2(2,6), N(22)–Co(1)–N(24) 172.9(2,12), N(23)–Co(1)–N(24) 92.2(2,4). The estimated standard deviations (in parentheses) are, respectively, the least-squares value for the individual parameter and the e.s.d. for the scatter of the chemically equivalent values about their mean, assuming 222 (D_2) symmetry. See Supplementary Data†‡.

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† Electronic supplementary information (ESI) available: experimental section. See http://www.rsc.org/suppdata/cc/b4/b403905j/

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encapsulated, in a distorted N_6 octahedral coordination sphere, by two N_3-terdentate binding pockets of a pair of perpendicularly arranged, doubly deprotonated $(\mathbf{L}^a)^{2-}$ ligands. As the coordinate vectors of the bis-terdentate ligands are antiparallel, the metal ions are coordinated once from "above" and once from "below" the Co^{III}_4 mean plane. The complex crystallises as a racemate. Only two chiral pyrazine-based [2 × 2] grid-type complexes, both of zinc(II), have been reported previously.[8] The ligand strands in **1**·12.75MeCN are not flat and the angles formed between the pyridine rings and the pyrazine ring of the same ligand range from 31.5 to 42.5°. The $Co^{III}–N_{py}$ distances in **1**·12.75MeCN (1.969–2.003 Å) are longer than in a related mononuclear cobalt(III) complex of *N*-(2-picolyl)picolinamide (1.941–1.947 Å).[9] The $Co^{III}–N_{pz}$ distances in **1**·12.75MeCN range from 1.933 to 1.959 Å and are comparable to other reported $Co^{III}–N_{pz}$ distances.[10] In **1**·12.75MeCN, two shorter [Co(1)···Co(2): 6.605(3) Å, Co(3)···Co(4): 6.592(3) Å] and two slightly longer [Co(2)···Co(3): 6.636(3) Å, Co(4)···Co(1): 6.641(3) Å] $Co^{III}\cdots Co^{III}$ distances are observed. Similar copper(II)[11] and nickel(II)[12] [2 × 2] grid-type complexes of the lower ligand homologue of $H_2\mathbf{L}^p$, namely *N*,*N*′-bis(2-pyridylmethyl)pyrazine-2,3-dicarboxamide ($H_2\mathbf{L}^{pm}$), have been described recently.

As the reaction of $H_2\mathbf{L}^p$ and $Co(BF_4)_2{\cdot}6H_2O$ in a 1 : 1 molar ratio afforded the "corner-type" complex $[Co^{III}(H_2\mathbf{L}^p)_2](BF_4)_3$ (**2**), exhibiting a 2 : 1 ligand-to-metal ratio, the synthesis was repeated using the correct ligand-to-metal ratio (Scheme 1). The slow evaporation of the MeCN : EtOH 1 : 4 reaction solution resulted in the isolation of **2**·EtOH in 63% yield in the form of a dark brick red crystalline solid.† Single crystals of **2**·2EtOH suitable for X-ray crystal structure determination were obtained by slow evaporation of a MeCN/EtOH (1 : 3) solution of **2**·EtOH (Fig. 2).‡ Both $H_2\mathbf{L}^p$ ligands of **2**·2EtOH act as mono-terdentate ligands and exist in a neutral, zwitterionic form. The single cobalt(III) ion adopts a distorted N_6 octahedral coordination environment, built up of two terdentate binding pockets of two ligand strands. The mean planes of the two meridionally coordinating terdentate binding pockets N(1)–N(2)–N(3) and N(7)–N(8)–N(9), are arranged perpendicularly (89.9°). The resulting structure can therefore be described as "corner-type" precursor, as it defines one corner of a square, contains a substitutionally inert cobalt(III) centre and has further binding pockets available. A similar mononuclear cobalt(III) complex of the lower ligand homologue $H_2\mathbf{L}^{pm}$ has recently been described by Stoeckli-Evans and co-workers.[13] The zwitterionic ligands of **2**·2EtOH are formed through relocation of a former N–H amide proton from the coordinating terdentate half of the ligand to the pyridine nitrogen atom of the non-coordinating half of the ligand. This effectively results in the blockage of the latter as a chelating site. Each former N–H amide proton is involved in a strong N–H···O hydrogen bond to the amide oxygen atom of the coordinating deprotonated amide group of the same ligand [N(6)···O(1) 2.678(2) Å, N(12)···O(3) 2.729(2) Å]. As in **1**·12.75MeCN, the planes of the pyrazine rings in **2**·2EtOH are not coplanar with the planes of the respective pyridine rings, instead forming an average angle of 51.7°. The $Co^{III}–N_{amide}$ and $Co^{III}–N_{py}$ distances in **2**·2EtOH are around 0.02–0.05 Å longer than in the related compound of $H_2\mathbf{L}^{pm}$,[13] and are more similar to those found in **1**·12.75MeCN. The uncoordinated amide groups of **2**·2EtOH are still N-protonated and are almost perpendicular to the respective pyrazine ring mean planes (average angle of 82.8°). These N–H amide protons are involved in N–H···F hydrogen bonds to tetrafluoroborate counter ions [N(5)···F(21): 2.996(2) Å, N(11)···F(21A): 3.167(2) Å, N(11)···F(24A): 3.023(2) Å].

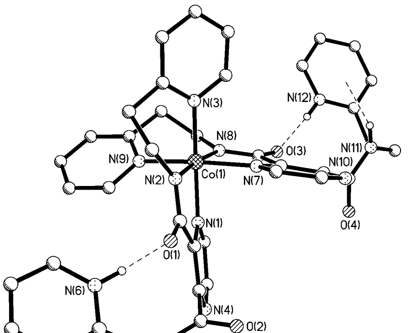

Fig. 2 Molecular structure of $[Co^{III}(H_2\mathbf{L}^p)_2]^{3+}$, the complex cation of compound **2**·2EtOH (hydrogen atoms except H(5N), H(6N), H(11N) and H(12N) omitted for clarity). Selected distances (Å) and angles (°):Co(1)–N(1) 1.956(2), Co(1)–N(2) 1.924(2), Co(1)–N(3) 1.983(2), Co(1)–N(7) 1.972(2), Co(1)–N(8) 1.931(2), Co(1)–N(9) 1.980(2), O(1)···N(6) 2.678(2), O(3)···N(12) 2.729(2); N(1)–Co(1)–N(2) 82.0(1), N(1)–Co(1)–N(3) 171.0(1), N(1)–Co(1)–N(7) 86.0(1), N(1)–Co(1)–N(8) 93.7(1), N(1)–Co(1)–N(9) 89.6(1), N(2)–Co(1)–N(3) 89.7(1), N(2)–Co(1)–N(7) 93.6(1), N(2)–Co(1)–N(8) 173.7(1), N(2)–Co(1)–N(9) 93.5(1), N(3)–Co(1)–N(7) 91.9(1), N(3)–Co(1)–N(8) 94.2(1), N(3)–Co(1)–N(9) 94.5(1), N(7)–Co(1)–N(8) 81.5(1), N(7)–Co(1)–N(9) 171.1(1), N(8)–Co(1)–N(9) 91.1(1). H(5N), H(6N), H(11N) and H(12N) were observed in difference Fourier maps.

In summary, two very different cobalt(III) complexes of two isomeric pyrazine-based ligands have been prepared due to the contrasting behaviour of adjacent *vs.* well-separated amide functional groups. The racemic compound $[Co^{III}_4(\mathbf{L}^a)_4](BF_4)_4$ (**1**) exhibits a [2 × 2] grid-type structure and involves doubly deprotonated ligands $(\mathbf{L}^a)^{2-}$ whereas the mononuclear complex $[Co^{III}(H_2\mathbf{L}^p)_2](BF_4)_3$ (**2**) exhibits a "corner-type" structure and involves neutral $H_2\mathbf{L}^p$ ligands in a zwitterionic form. The latter complex may provide access to mixed-metal and mixed-valent complexes and this is the subject of ongoing studies.

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‡ CCDC 233195–233196. See http://www.rsc.org/suppdata/cc/b4/b403905j/ for crystallographic data in .cif format.

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