Grid Expansion: a Rhombiclike [L₄Fe₂(Ag₂)₂] Complex Containing Ag₂ Dumbbells at Two Vertices

Benjamin Schneider, Serhiy Demeshko, Sebastian Dechert, and Franc Meyer*

Institute of Inorganic Chemistry, Georg-August-University Göttingen, Tammannstraße 4, D-37077 Göttingen, Germany

S *Supporting Information*

ABSTRACT: The pyrazolate-based ditopic ligand HL forms a strongly hydrogen-bonded corner complex dimer $[Fe^{II}(HL)_2]_2(BF_4)_4$ (**1**) with a $[2 \times 2]$ gridlike arrangement of four ligand strands. The two empty vertices can then be filled with $\{Ag_2\}^{2+}$ dumbbells, yielding the unprecedented diferric complex $[L_4Fe^{III}_2(Ag^I_2)_2](BF_4)_6$ (**2**) that features a rhombiclike structure with an almost planar hexagon of metal ions.

Multinuclear grid-type metal complexes, in which perpendicular ligand strands containing n binding pockets form 2D $[n \times n]$ metalloarrays composed of $2n$ ligands and n^2 metal ions, have gained immense popularity during the past decade.[1] This is not only because grid complexes are aesthetically attractive molecular architectures but also because switchable grids might become components of future information storage and processing devices.[2] While most of the known grids are homometallic and squarelike, elaborate strategies for the toposelective synthesis of heterometallic systems and molecular rectangles have been developed.[1] These strategies include (i) the use of heteroditopic ligands with distinct coordination sites that recognize and selectively bind different metal ions,[3] (ii) protection/deprotection routes starting from homoditopic ligands,[4] and (iii) sequential two-step syntheses via (kinetically inert) mononuclear corner complexes, the so-called "Coupe du Roi" strategy.[5]

Some pyrazolate (pz)-based compartmental ligands[6] have proven to be well-suited for the assembly of grid complexes.[7,8] Using the rigid bis(tridentate) pyrazole ligand HL (HL = 3,5-bis(bipyridyl)pyrazole; Scheme 1), we recently reported a novel type of $[2 \times 2]$ Fe₄ grid complex that exhibits unprecedented multistability with respect to spin crossover and redox switching.[7] In some experiments aimed at oxidizing the $[LFe^{II}_4]^{4+}$ grid to the mixed-valent $[L_4Fe^{II}_2Fe^{III}_2]^{6+}$ species, we now observed, as a minor side product, the formation of an unusual heterometallic $[L_4Fe^{III}_2(Ag^I_2)_2]^{6+}$ complex. It appears that partial grid degradation and replacement of some Fe^{II} by Ag^I, concomitant with oxidation of the remaining Fe, had occurred in that reaction. In this Communication, we present a targeted high-yield synthesis and full characterization of the unique hexametallic Fe^{III}/Ag^I complex. While Ag^I ions have been used to assemble discrete $[2 \times 2]$ Fe₄ complexes bearing peripheral N-donor groups into 1D and 2D superstructures,[9] this appears to be the first report of a system containing both Ag and Fe *within* a gridlike motif.

Scheme 1. Ligand HL and Schematic Illustration of the One-Pot Synthesis of 2 via the Intermediate Corner Complex 1[a]
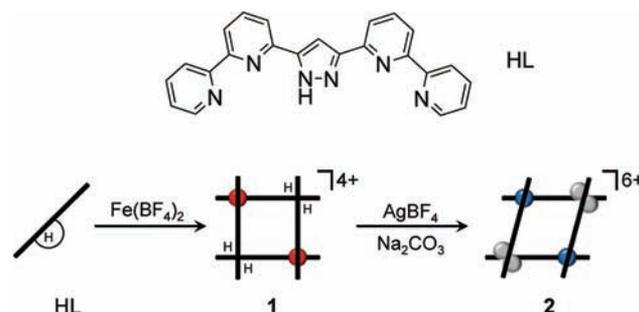
[a]Black bar: ligand molecule. Red balls: Fe^{II}. Blue balls: Fe^{III}. Gray balls: Ag^I.

The controlled synthesis of $[L_4Fe^{III}_2(Ag^I_2)_2]^{6+}$ is best carried out as a one-pot reaction. In a first step, the ligand HL and 0.5 equiv of Fe(BF₄)₂ are combined to give the "corner complex" $[Fe^{II}(HL)_2](BF_4)_2$ (**1**) as a key intermediate. **1** has been isolated and characterized by X-ray diffraction. Its solid-state structure reveals that this compound forms dimers that are held together by four N^{pz}–H···N^{py} (py = pyridine) hydrogen bonds (Figure 1). Hence, **1** is best described as $[Fe^{II}(HL)_2]_2(BF_4)_4$,
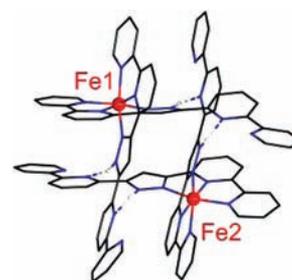

Figure 1. Molecular structure of the hydrogen-bonded dimer $\{[Fe(HL)_2]^{2+}\}_2$ of **1**. Solvent molecules and counterions are omitted for clarity.

which essentially is a $[2 \times 2]$ grid devoid of the metal ions at two opposite corners of the square. The 80 K Mössbauer spectrum confirms the low-spin ferrous nature of **1** ($\delta = 0.32$ mm s^{-1} and $\Delta E_Q = 0.88$ mm s^{-1}; Figure S1 in the Supporting Information, SI). N^{pz}···N^{py} distances of 2.90−2.99 Å (Table S4

in the SI) indicate the presence of hydrogen bonds at the metal-free vertices.[10] Thus, **1** appears to be well-preorganized for inserting additional metal ions at the two empty vertices to complete a regular metallosquare. This again underlines the high tendency of HL to form $[2 \times 2]$ grid structures. Electrospray ionization mass spectrometry spectra of MeCN solutions of **1**, however, do only show signals characteristic for the mononuclear species $[Fe(H_xL)_2]^{y+}$ (x = 0, 1 and y = 1, 2; see Figure S3 in the SI), suggesting that the gridlike arrangement observed in the solid state largely dissociates when dissolved (at least in polar solvents such as MeCN).

Treatment of a solution of **1** in nitromethane with an excess of AgBF$_4$ and the subsequent addition of Na$_2$CO$_3$ lead to oxidation of the Fe^{II} ions and ligand deprotonation and eventually to the incorporation of Ag$^+$ to give the target product $[L_4Fe^{III}_2(Ag^I_2)_2](BF_4)_6$ (**2**). Thin blue crystal plates suitable for X-ray diffraction were grown by the slow diffusion of diethyl ether into a solution of **2** in nitromethane.

The molecular structure of the hexametallic Fe$_2$Ag$_4$ complex **2** has been determined by X-ray crystallography. In **2**, the roughly parallel arrangement of pairs of ligands is retained, but the protons found at two corners of **1** have been replaced by Ag$^+$ and the grid is distorted to a rhomboid. Thus, the {N$_6$} pockets at those opposite corners of the rhomboid each host a Ag$^I_2$ dumbbell with a remarkably short Ag—Ag distance (2.93 Å for Ag1—Ag2 and 2.88 Å for Ag3—Ag4), which is indicative of d^{10}—d^{10} interactions.[11] Ag—N distances range from 2.134 Å (Ag—N^{pz}) to 2.914 Å. When the Ag—Ag interaction is neglected, the coordination environment of the Ag$^+$ ions is best described as {3 + 1}: three N donors are arranged almost in a plane, and one of them (a pyridine N) forms a weak asymmetric bridge to the apical position of a neighboring Ag$^+$. Additionally, on the backsides, the Ag$^+$ ions appear to be stabilized by close contacts (3.12 and 2.99 Å) with the π system of a proximate bipyridine unit that is bound to Fe^{III}. These distances are above the usual Ag—π interactions[12] but below the sum of the van der Waals radii.[13]

The two Fe^{III} ions located at the other two vertices of the rhomboid are crystallographically distinct, although their coordination environment is very similar. Their {N$_6$} donor sets originate from two ligand strands, and the coordination sphere is strongly distorted from octahedral (some angles deviate up to 11% from the ideal octahedral angles). The average Fe—N bond length is 1.94 Å; bonds involving the terminal pyridine N atoms are, however, slightly longer (average 1.99 Å). Overall, the six metal ions in **2** form an almost perfectly planar hexagon (maximum out-of-plane deviation 0.2 Å; Figure 2) with two short Ag—Ag edges.

The Mössbauer spectrum of a crystalline sample of **2** at 80 K features an unsymmetric doublet (Figure 3, left); this signature is largely independent of the temperature (see Figure S2). Experimental data have been fitted by assuming two subspectra with slightly different isomer shifts (δ_1 = 0.16 mm s^{-1} and δ_2 = 0.05 mm s^{-1}) and quadrupole splittings ($\Delta E_{Q,1}$ = 3.04 mm s^{-1} and $\Delta E_{Q,2}$ = 3.25 mm s^{-1}), both typical for low-spin Fe^{III}. Observing two subspectra for the solid material may be rationalized in view of the presence of two crystallographically distinct Fe^{III} vertices in the crystal structure.[14] Unexpectedly, however, the Mössbauer spectrum of a solution of **2** in MeNO$_2$ (10 mM) looks very much alike and again requires the assumption of two subspectra for proper fitting of the experimental data (δ_1 = 0.12 mm s^{-1} and δ_2 = 0.05 mm s^{-1}; $\Delta E_{Q,1}$ = 3.15 mm s^{-1} and $\Delta E_{Q,2}$ = 3.26 mm s^{-1}; Figure 3,
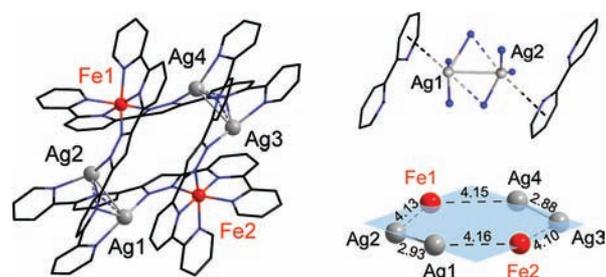

Figure 2. Left: Molecular structure of **2**, determined by X-ray diffraction at 133 K. Solvent molecules and counterions are omitted for clarity. Top right: Coordination environment of the Ag$_2$ units. Dashed blue line: Ag—N distances above 2.7 Å. Bottom right: Hexagon of metal ions in **2**.
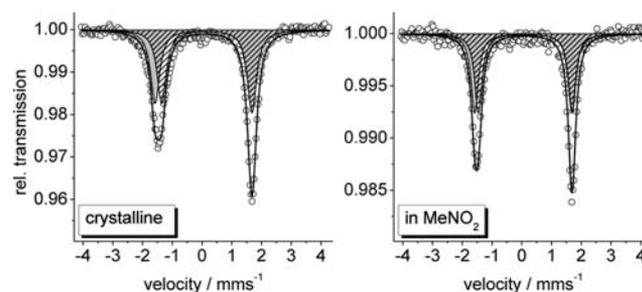

Figure 3. Mössbauer spectra recorded at 80 K for a crystalline sample (left) and a frozen solution sample (MeNO$_2$, 10 mM). Subspectrum 1: gray color. Subspectrum 2: patterned.

right). The reason for the nonequivalence of the two Fe^{III} ions in solution remains unclear.

A SQUID measurement of solid **2** confirms the presence of two magnetically uncoupled low-spin Fe^{III} ions: χT is largely independent of the temperature and matches the spin-only value expected for two uncoupled $S = \frac{1}{2}$ sites (with g = 2.10; see Figure S2 in the SI). The electronic spectrum of a solution of **2** in a nitromethane solution (380−1500 nm, Figure 4)
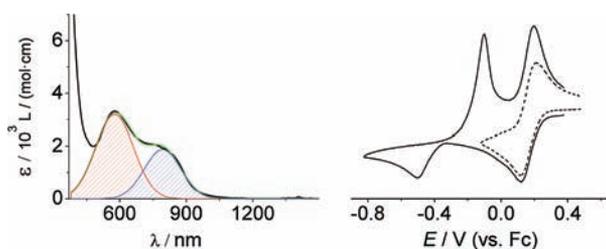

Figure 4. Left: Electronic absorption spectrum of a solution of **2** in MeNO$_2$ (0.1 mmol L^{-1}). Right: Cyclic voltammogram of a solution of **2** in MeCN/0.1 M nBu$_4$NPF$_6$ at a scan rate of 100 mV s^{-1}.

reveals very strong bands in the UV region (<400 nm) due to ligand-based $\pi \rightarrow \pi^*$ transitions. Additional low-energy absorptions at 800 nm (ε = 1900 L mol^{-1} cm^{-1}) and 580 nm (ε = 3200 L mol^{-1} cm^{-1}) are tentatively assigned to ligand-to-metal charge-transfer transitions involving the Fe^{III} ions. The spectrum of **2** closely resembles the spectrum of the related mixed-valent grid complex $[L_4Fe^{III}_2Fe^{II}_2]^{6+}$ (λ_{max} = 587 and 749 nm),[7] which supports the idea that these two absorptions originate from the Fe^{III} chromophore. Cyclic voltammetry of **2** in a MeCN solution reveals a reversible reduction process at relatively high potential ($E_{1/2}$ = +0.165 V; Figure 4), which

likely represents the Fe^{III}/Fe^{II} pair. This implies that the two ferric ions at two opposite vertices are electronically largely uncoupled, as expected. A further reduction process at more negative potential is irreversible ($E_p^{red} = -0.50$ V) and most likely corresponds to the reduction of Ag^I. An anodic wave in the backscan (at $E_p^{ox} = -0.10$ V) might be caused by Ag stripping from the electrode.

While a few $[2 \times 2]$ Ag_4 square complexes have been reported,[15] the presence of dumbbell-like Ag_2^I vertices in **2** appears to be unprecedented for grid-type systems. Also, the combination of Ag^I and Fe in discrete oligonuclear complexes is quite rare because such compounds usually contain Fe^{II},[16] in contrast to the heterometallic Ag^I/Fe^{III} complex **2**. In conclusion, the $[2 \times 2]$ grid $[LFe^{II}_4]^{4+}$, although quite robust, upon oxidation with Ag^I may loose some of its Fe and transform to an unusual and expanded rhombiclike structure with Ag_2^I dumbbells at two opposite vertices. This hexametallic $[L_4Fe^{III}_2(Ag_2^I)_2]^{6+}$ complex has now been prepared selectively and fully characterized. The complete exchange of all four Fe vertices in $[LFe^{II}_4]^{4+}$ by Ag_2^I dumbbells to give an $[L(Ag_2)_4]^{4+}$ gridlike system appears to be an attractive perspective.

■ ASSOCIATED CONTENT

ⓈSupporting Information

X-ray crystallographic data in CIF format, experimental details, Mössbauer data for **1** and **2**, χT versus T data for **2**, crystallographic data with bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: franc.meyer@chemie.uni-goettingen.de.

Author Contributions
All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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