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COMMUNICATION

Anion-controlled formation of an aminal-(bis)imine Fe(II)-complex

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2014,

Accepted 00th January 2014

DOI: 10.1039/x0xx00000x

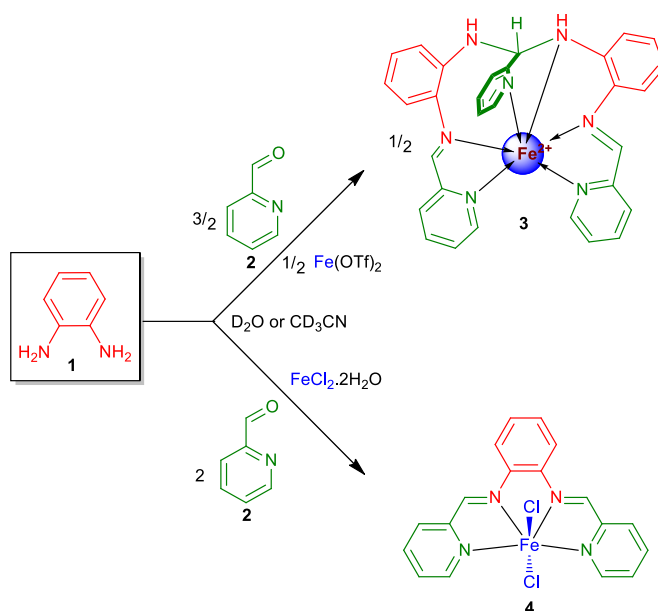
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In presence of triflate as the counter anion, 1,2-diaminobenzene and 2-formylpyridine self-sort with iron(II) to a low-spin [Fe(L1)](OTf)₂ complex in which both aminal and imine moieties coexist simultaneously, while under similar conditions chloride anion leads to a high-spin [Fe(L2)Cl₂] complex.

Nature manifests myriad beautiful creations^{1,2} which involve complex self-assembled architectures made from simple building blocks with the effective use of weak non-covalent interactions.^{3,4} Due to this, supramolecular science⁵ and systems chemistry^{6,7} have been among the most rapidly developing areas of chemical research over the last decade.^{8,9} Systems chemistry aims to provide detailed understanding of the organizational principles of complex molecular systems with functions different from conventional materials.^{10,11} This approach can offer an easy access to new materials simply by changing the inputs of a multicomponent system. Thus the self-sorting systems,¹²⁻¹⁴ including subcomponent self-assembly approach,¹⁵⁻¹⁷ are now a well-adopted methodology in supramolecular chemistry to create the complex systems with topological diversity by exploiting imine bonds as one of the key building blocks. In 1960s Busch¹⁸ first introduced the concept of template synthesis¹⁹ to form and stabilize imine bonds through coordinative bond (L→M) formation using nickel(II) ion.¹⁸ This approach has subsequently been expanded to other transition metals like copper(I),²⁰ copper(II),²¹ zinc(II),²² cobalt(II),²³ nickel(II),²⁴ iron(II)²⁵ etc. Thus formed imines have been extensively used to design and construct different functional supramolecular architectures. Aminals and hemiaminals²⁶ (as a hemiaminal metal complex) have been observed to exist in an equilibrium with corresponding imines in solution resulting from *intramolecular* cyclisation,²⁷⁻²⁸ with the metal complexation switching the equilibrium towards the imine form.^{27,28} However, to the best of our knowledge, there

are no previous reports of an aminal resulting from a metal-templated *intermolecular* reaction.

We thus report here a stable chiral iron(II) complex of an aminal-(bis)imine ligand, synthesized directly from amine-aldehyde condensation via dynamic self-sorting methodology.²⁹ To the best of our knowledge, this is the first report of the coexistence of imine and acyclic aminal generated in the presence of a metal ion by sub-component self-assembly in a single-pot reaction mimicking the more common multistep synthesis.³⁰



Scheme 1 Synthesis of ML-type complexes via sub-component self-assembly approach.

The iron(II)-templated one-pot synthesis of the amina-(bis)-imine complex **3** from its sub-components is shown in Scheme 1, starting from 1,2-diaminobenzene **1** (two equivalents), 2-formylpyridine **2** (three equivalents) and an iron(II) salt (one equivalent). The reaction was also performed in different solvents like methanol/acetonitrile and varying ratios of the sub-components, all of which led to similar results. The amina complex **3** is asymmetric which was proved unambiguously both by the ^1H NMR spectrum (Fig. 1) and single crystal X-ray diffraction study (Fig. 2a). As can be seen from ^1H NMR spectrum both the iminic proton H_u and H_e are found to be non-equivalent and are downfield shifted. Furthermore, a singlet was observed for H_p due to the dihedral angle of $\text{H}_k\text{-C-N-H}_p$ being 90° , which is in good agreement with the crystal structure of **3** ($\text{H}_k\text{-C-N-H}_p$ being 83.43°).

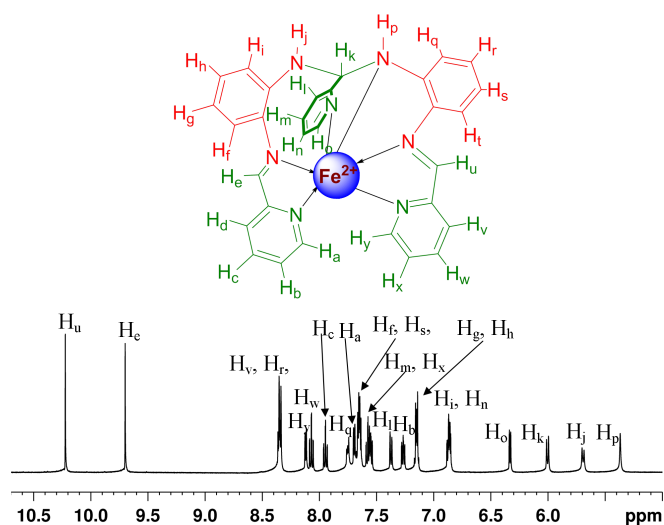


Fig. 1 The 500 MHz ^1H NMR spectrum of the complex **3** in CD_3CN .

Interestingly, the formation of **3** depends on the nature of the counter anion of the iron(II) salt. The amina complex **3** was the only product with non-coordinating anion from $\text{Fe}(\text{OTf})_2$ or $\text{Fe}(\text{BF}_4)_2$, however FeCl_2 under similar conditions yielded the expected (1,2-bis(2'-pyridylmethyleneamino)benzene)-iron(II) dichloride **4** (Scheme 1).³¹ The complex **4** is reported to be a high spin Fe(II) complex and has previously only been characterized by elemental analysis.³¹ However, we have now confirmed the structure of **4** from single crystal X-ray analysis (Fig. 2b). Strong bond energy of Fe–Cl bond plays the key role here to form the imine metal complex **4**, thus preventing the formation of an amina structure.

The X-ray structure (Fig. 2a) of the amina-(bis)-imine complex **3** reveals that the coordination sphere around the Fe(II) is relatively undistorted octahedron with Fe–N bond distances varying from 1.88 – 1.99 Å, with the N(aminal)-Fe being the longest bond. The complex **3** is chiral but it crystallizes in a centrosymmetric space group ($P\bar{1}$) as a

racemate. The high-spin complex **4** (Fig. 2b) has a clearly distorted octahedral N_4Cl_2 coordination sphere with much longer Fe–N distances (2.17 – 2.22 Å) and Cl–Fe–Cl angle of 149.4° .

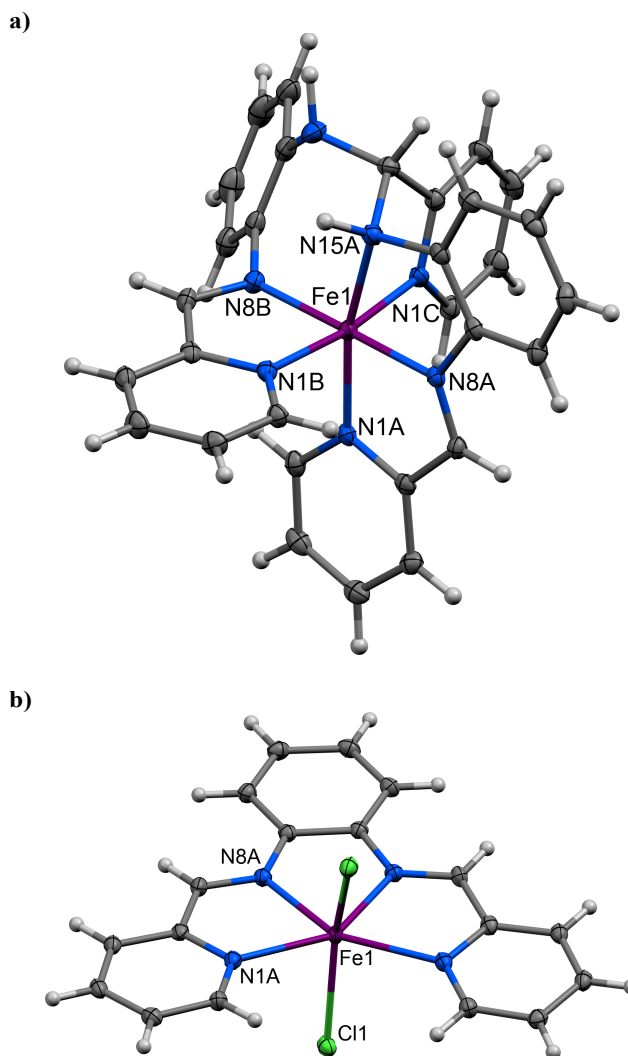


Fig. 2 The crystal structures of complexes **3** (a) and **4** (b). Anions (in a) omitted for clarity. Hydrogen atoms shown with arbitrary radii.

In summary, we have shown for the first time a synthesis of a chiral amina-(bis)imine transition metal complex **3** via anion-controlled self-assembly^{23,32-34} methodology. The formation of **3** is supported by the non-coordinating anion (triflate, tetrafluoroborate) of the Fe(II) salt. With coordinating anion the sub-component self-assembly leads to the formation of the expected transition metal complex **4**. Unprecedentedly, isolated complex **3** manifests acyclic amina, imine and coordination bonds simultaneous in a single complex. The presented

methodology of anion-controlled sub-component self-assembly could open a new route for the supramolecular chemists to design and synthesize new complexes and molecules unavailable via other routes.

The Academy of Finland (KR, grant no. 263256 and 265328) and Department of Science and Technology, New Delhi, India (PM, grant no. INT/FINLAND/P-06 and SR/S1/IC-59/2010), NGS-NANO, Finland for a PhD fellowship (FT) and the University of Jyväskylä, Finland are gratefully acknowledged for the financial support.

Notes and references

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†Electronic Supplementary Information (ESI) available: [Experimental details, NMR and MS spectra and X-ray single crystal structure analysis (CCDC 1006930 and 1006931)]. See DOI: 10.1039/b000000x/.

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Graphic for TOC

