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Complementary Dynamic Assembly around an Iron(III) Cation

Galina Melman, Pavan Vimal, and Artem Melman*

Department of Chemistry & Biomolecular Science, Clarkson University, Potsdam, New York 13699

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A new system for the complementary coordination of two different terdentate ligands based on a 2-(hydroxyamino)-1,3,5-triazine motif around a ferric cation is reported. Prototropic switching between hetero- and homoligand complexes proceeds with more than 95% selectivity.

Metal−ligand interactions are an important tool in self-assembly owing to the high stability and versatility of coordination bonds coupled with the possibility for dynamic change of the formed complex.[1] This approach has yielded state-of-art coordination supramolecular architectures that are of interest as promising electronic,[2] catalytic,[3] and photophysical materials.[4] However, in contrast to the intrinsic complementarity of hydrogen bonding,[5] metal ions exposed to a mixture of different ligands in the solution phase in most cases produce statistical mixtures of homo- and heteroligand complexes[6] unless either of the components crystallizes out of solution.[7]

The critical problem of selective heteroligand binding has been approached by several methods. Most commonly, heteroligand bridging exploits the different kinetic stabilities of ligands, and a variety of polymetallic cages and rings have been prepared using this approach.[8] Selective assembly of heteroligand complexes around a single kinetically labile metal ion has been achieved using chelate ligand immobilized interfaces where the second ligand can be taken in large excess.[9] In homogeneous solutions, selective formation of heteroligand pentacoordinated complexes Zn^{2+} has been achieved by suppressing the formation of hexacoordinated homoligand complexes by steric shielding.[10] However, these methods did not possess the ability for controllable switching between hetero- and homoligand binding that is essential for building dynamic assemblies based on the coordination junction. Hexacoordinated Zn^{2+} was reported to form labile heteroligand complexes in bis η^3-ligand−metal systems with selectivity up to 1:4:1.[11] Commonly used in molecular biology, the NTA−His−tag heteroligand binding system based on the coordination of a single Ni^{2+} cation provides a very low binding constant of $96 \pm 15\ \mu$M.[12]

Herein we describe a reversible system capable of highly selective coordination bonding through controllable formation of either hetero- or homoligand iron(III) complexes that can serve as a complementary junction based on metal−ligand interactions. We demonstrate [H^+]-controlled dynamicity of ligand assemblage around a kinetically labile metal ion with complete interconversion between homo- and heteroligand complexes.

We relied on iron as biologically essential and the most abundant endogenous transition-metal ion with a well-defined octahedral coordination sphere that can adapt two complementary η^3-terdentate meridional binders (pincer ligands). Achieving critical selectivity in heteroligation was based on previous studies of a new type of pincer ligand for iron(III).[13]

*To whom correspondence should be addressed. E-mail: amelman@clarkson.edu. Tel: 1-(315)-268-4405. Fax: 1-(315)-268-6610.

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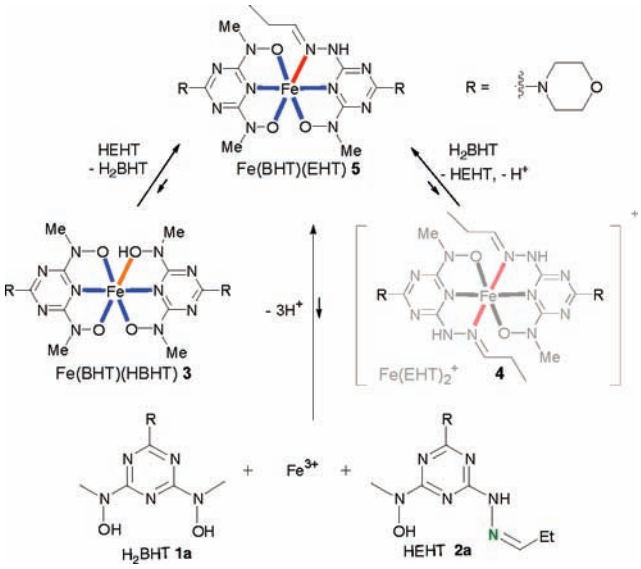
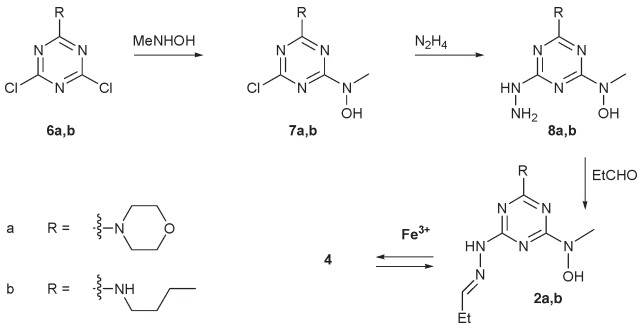
Scheme 1. Structures of H_2BHT **1a** and HEHT **2a** Ligands and a Schematic Representation of Preferential Complementary Complex **5** Formation



Scheme 2. Synthesis of Ligands **2a** and **2b**



The structure of 2,6-bis[hydroxy(methyl)amino]-1,3,5-triazine (BHT)−iron(III) complex **3** featuring a highly distorted octahedral geometry has been shown to involve two strong coordinative bonds between the iron cation and endocyclic nitrogen atoms (ca. 2.0 Å) as well as three out of four oxygen atoms (ca. 2.0 Å each). In contrast, the sixth coordination bond, Fe−OH, has been found to be considerably longer (2.45 Å) and therefore weaker than the other Fe−O bonds.

This difference indicates highly unequal binding of two BHT ligands to the iron(III) cation. The binding inequality was exploited for selective formation of a heteroligand complex by the design of another isostructural pincer ligand, 2-(ethylmethylene)hydrazino-6-hydroxy(methyl)amino-1,3,5-triazine (HEHT, **2a**; Scheme 1), capable of binding the iron(III) cation stronger than a half-deprotonated $HBHT^-$ ligand of type **1a** but still weaker than a deprotonated BHT^{2-} ligand of type **1a**. Synthesis of HEHT ligands **2a** and **2b** (Scheme 2) was done from known dichlorides **6a** and **6b** through sequential nucleophilic substitution with *N*-methylhydroxylamine and hydrazine followed by reaction with an excess of propionic aldehyde.

Reaction of the HEHT ligand **2a** with Fe^{3+} results in the formation of a 2:1 complex of type **4** with $M^+ = 616.2386$ possessing broad metal-to-ligand charge-transfer (MLCT) absorption with maximum at 610 nm. Titration of complex **4** in ethanol containing 1% acetic acid with an excess of **2a**

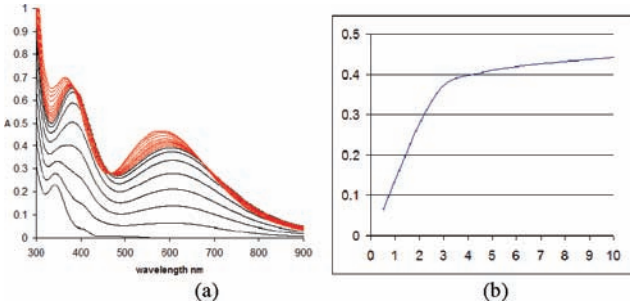


Figure 1. (a) Titration of a solution of $Fe(OAc)_3$ in 1% acetic acid/ethanol with HEHT ligand **2a**. (b) Job's plot of absorption at 610 nm as a function of the number of equivalents of ligand **2a**, indicating a transition from 2:1 to 3:1 stoichiometry.

(Figure 1) revealed a continuous increase of the MLCT band featuring three isosbestic points, most probably due to the formation of new species involving 3:1 stoichiometry, thus indicating that the binding of iron(III) cations with HEHT ligand **2a** is weak.

The addition of a mixture of HEHT **2a** and H_2BHT **1a** ligands to a solution of $Fe(OAc)_3$ produced a 1:1:1 complex **5** with MLCT absorption at 577 nm, which was different from the MLCT absorptions of the homoligand complexes **3** and **4** (558 and 610 nm, respectively). Solution equilibrium between complexes **3** and **5** was studied by titration of complex **3** with HEHT ligand **2a** in a 1% solution of acetic acid in ethanol. The titration revealed two isosbestic points, indicating that no third iron(III) complex such as **4** was present under these conditions in solution. The titrations demonstrated a continuous decrease of the MLCT band of **3** at 558 nm and an increase in MLCT adsorption of heteroligand complex **5** at 577 nm (Figure 2a), which were proportional to the amount of ligand **2a** until saturation at 1 equiv of the ligand.

In line with the expected increased stability of complex **5**, the addition of HEHT **2a** beyond the equivalency point did not result in any sizable alteration of the spectrum. Very similar results were achieved in the reverse titration of complex **4** with H_2BHT ligand **1a** (Figure 2b). Again, the formation of complex **5** with saturation at 1 equiv of **1a** was observed.

X-ray diffraction analysis of crystals obtained by the slow evaporation of an aqueous methanol solution confirmed the formation of heteroligand complex **5** (Figure 3).[14] It revealed a distorted octahedral geometry around the ferric ion with strong three Fe−O (1.97−2.10 Å) and two Fe−N (1.97−2.01 Å) coordination bonds. The Fe−N13 coordination bond is much longer than other Fe−N coordination bonds (2.32 Å). This difference, however, is substantially smaller than that in the isostructural homoligand complex **3** described above. This difference is compatible with the titration data of Figure 2, indicating the preferential stability of the heteroligand complex **5**.

To compensate for the relatively low sensitivity of UV−vis titration in the detection of minor amounts of homoligand

(14) Crystal structure data for **5**: $C_{21}H_{38}FeN_{13}O_7$, $M = 640.49$, $0.24 \times 0.19 \times 0.13$ mm^3, triclinic, space group $P\bar{1}$, $a = 9.6483(8)$ Å, $b = 11.8919(10)$ Å, $c = 13.3296(11)$ Å, $\alpha = 95.8510(10)°$, $\beta = 96.0000(10)°$, $\gamma = 106.7240(10)°$, $V = 1442.6(2)$ Å^3, $Z = 2$, $D_c = 1.474$ g/cm^3, $2\theta_{max} = 27.00°$, Mo Kα radiation ($\lambda = 0.710\,73$ Å), $T = 173(1)$ K, 16 483 collected reflections, 6237 unique reflections ($R_{int} = 0.0365$). R1 = 0.0621, wR2 = 0.1620 for data with $I > 2\sigma(I)$; R1 = 0.0716, wR2 = 0.1685 for all unique data. The crystal contains molecules of partially disordered methanol solvent.

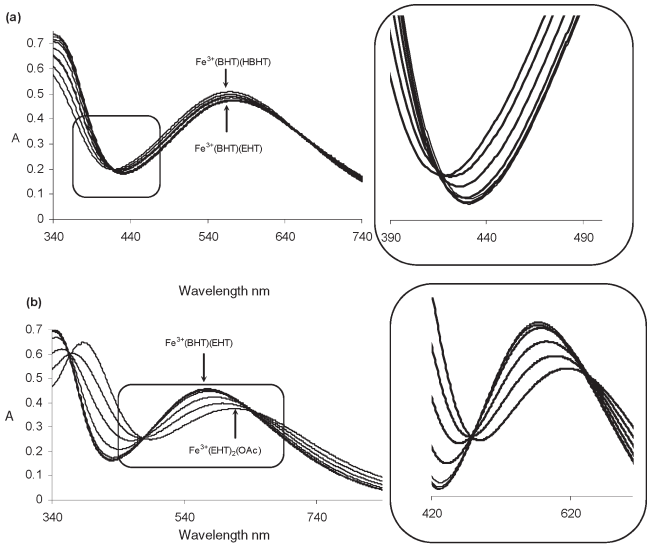


Figure 2. (a) Displacement of one of the $HBHT^-$ groups in homoligand complex **3** with the addition of the HEHT **2a** ligand and the formation of heteroligand complex **5**. (b) Displacement of one of the HEHT groups in homoligand complex **4** with the addition of H_2BHT ligand **1a** and the formation of **5**.

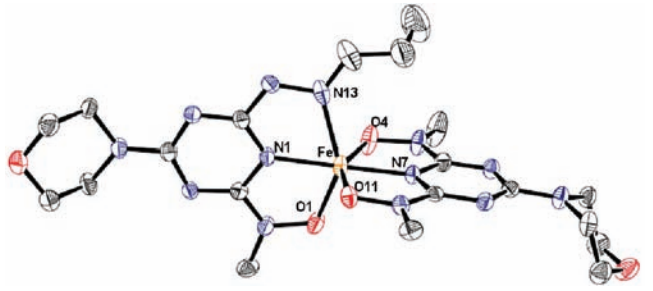


Figure 3. Single-crystal ORTEP view (thermal ellipsoids drawn at 50% probability) of the crystal structure of **5**. Selected bond lengths (Å): Fe1−N1 2.007(2), Fe1−N7 1.971(2), Fe1−N13 2.322(3), Fe1−O1 2.000(2), Fe1−O4 1.974(2), Fe1−O5 2.096(2).

complex **3** in the presence of the preferential heteroligand complex **5**, the equilibrium constant for the exchange reaction between complexes **3** and **5** in the solution phase was obtained by repeating the titration in the presence of a large excess (13 equiv) of competing ligand **1a**. The average equilibrium $[H^+]$-independent constant in the ethanolic solution containing 1% acetic acid for the range 0.25−1.5 equiv of HEHT ligand was found to be 36.4 ± 3.6. Extrapolation of this data to a solution containing equal concentrations of ligands **1a** and **2a** predicts a 97.3 ± 0.3% equilibrium content of heteroligand complex **5**. Superior stability of heteroligand complexes of type **5** was found to be a general feature for analogous complexes involving other HETH and H_2BHT ligands (**1a**−Fe−**2b**, 32.1 ± 2.0 or 97.0 ± 0.2%; **1b**−Fe−**2a**, 8.8 ± 0.7 or 89.5 ± 0.7%; **1b**−Fe−**2b**, 11.7 ± 0.6 or 92.1 ± 0.4%).

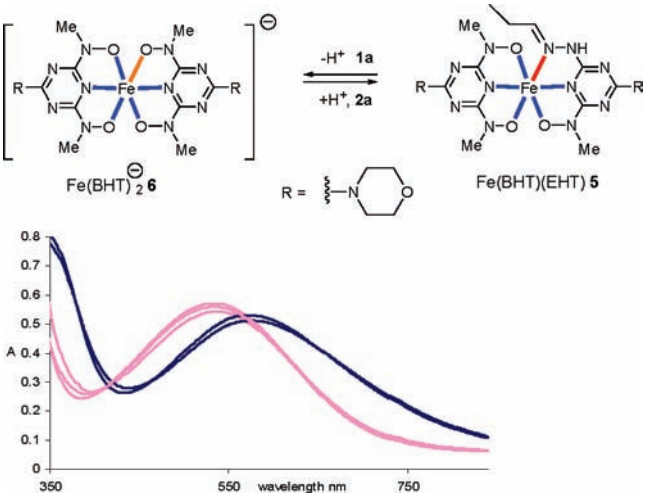


Figure 4. $[H^+]$-controlled transformations between heteroligand complex **5** and anionic homoligand complex **6**. The transformation from **5** to **6** is caused by the addition of 1 equiv of EtOK and the reverse transformation by the addition of 1 equiv of CF_3CO_2H.

Because of the high acidity of the hydroxyamino group in H_2BHT, the preferential formation of heteroligand complexes of type **5** is highly proton-dependent. A transition from a weakly acidic to weakly basic solution dramatically reverses the stability order of the complex, resulting in the exclusive formation of deprotonated homoligand complex **6** and the total disappearance of complex **5** with free ligand **2a** regeneration. The transformation (Figure 4) is fully reversible, and acidification results in the restoration of heteroligand complex **5**. To the best of our knowledge, this is the first reported example of essentially complete prototropic switching between homo- and heteroleptic octahedral complexes involving two tridentate ligands.

In conclusion, we designed and synthesized a system capable of dynamic complementary self-assemblage through coordination bonding around kinetically labile iron(III) cations. The complementarity is achieved by exploiting the inequality in binding of the iron(III) cation by two pincer-type 2,6-bis[hydroxy(methyl)amino]-1,3,5-triazine ligands resulting in the preferential binding of isostructural pincer ligands carrying a sp^2 nitrogen donor group instead of a hydroxyamino group. The system demonstrates essentially complete (>95%) and reversible prototropic switching between hetero- and homoligand states. The applicability of the system for supramolecular dynamic assemblies is currently under investigation.

Supporting Information Available: Experimental procedures and spectral characterization of chelate ligands and complexes **4** and **5**, UV−vis titration experiments, and calculation of equilibrium constants. This material is available free of charge via the Internet at http://pubs.acs.org.