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Full Paper

Formation of Ternary Complexes of Iron(III) Cations in Solution and Gas Phase

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Formation of labile 1 : 1 : 1 ternary mononuclear complexes of iron(III) cation with η^3-terdentate meridional binders was studied using electrospray ionisation mass spectrometry (ESI-MS) titration and UV-Vis titration in solution phase. Low selectivities towards formation of ternary heteroleptic complexes in the solution phase vs. symmetric 2 : 1 complexes were obtained with combinations of dianionic 2,6-bis[hydroxy(methyl)amino]-1,3,5-triazine (BHT) ligands with monoanionic terdentate ligands such as 2-[(2-pyridinylmethylene)amino]phenol. Moderate selectivities were observed in formation of ternary iron(III) complexes of iron(III) between BHT ligands and neutral terdentate ligands such as pyridin-2-ylmethylpyridin-2-ylmethyleneamine. Results obtained by MS titrations were in a reasonable agreement with UV titration data indicating that quantitative ESI MS spectrometry can be applied to these labile iron(III) complexes.

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Introduction

Preferential binding of different types of ligands by metal cations is a basic process that is far from being properly understood. Generally, it follows the well known tendency of 'hard' metal cations such as Mg^{2+} or Fe^{3+} to bind anionic oxygen ligands such as carboxylates or hydroxamates while 'soft' metal cations such as Ag^{+} or Hg^{2+} preferentially bind 'soft' nitrogen, sulfur, or phosphine ligands.[1] However, because most metal cations form four or more coordination bonds, the highest stability of metal complexes may require a combination of 'hard' and 'soft' ligands. This situation is commonly observed in metalloproteins. For example, the 'hard' iron(III) cation in transferrin protein is simultaneously bound by 'hard' carboxylate and phenolate ligands but also by a 'soft' imidazole ligand. The preferential formation of complexes with different types of ligands has not been rationalised and no theoretical or empirical rules have been suggested. Despite the progress achieved in understanding factors influencing energies of covalent bonding using computational approaches, application of these methods to coordination bonding in solution phase is hindered by a strong contribution of solvation energy, which cannot be computed with sufficient precision. Understanding factors that influence formation of metal complexes with both 'hard' and 'soft' ligands, and finding ligands that display complementarity of coordination bonding can be important for several applications.

For example, metal-ligand interactions are extensively used for self-assembly owing to high thermodynamic stability of coordination bonds that can be rapidly formed under very mild conditions. The inventory of available metal cations allows a high degree of control over geometry of the bonding, as well as a possibility for directed disassembly of coordination bonds through redox reactions. Coordination bonding has been used for self-assembly of metal oxide framework coordination polymers,[2–4] molecular grids,[5–8] molecular cages and nanocapsules,[9–11] helicates,[12,13] topologically defined macrocycles,[14–17] trigger type molecules,[18] artificial base pairing in DNA,[19] and other applications.[20–22] The majority of these assemblies consist of a single binding motif, i.e. it is homoleptic in nature thus putting a major limitation on their use.[23] In contrast to the intrinsic complementarity of hydrogen bonding, metal ions exposed to a mixture of different ligands in solution phase form a mixture of homoleptic and heteroleptic complexes even for the simplest case of octahedral complexes with two tridentate ligands. To date, there are few reports on metal coordination-driven dynamic heteroleptic aggregates that exist as exclusive species in solution,[23] often referred to as 'mixed complexes',[24] 'mixed ligand complexes',[25,26] and 'ternary complexes'.[27,28] Regardless of the terminology used, selective formation of these species can be achieved through simple mixing of two different ligands A and B and a metal cation M^{n+}:

$$A + B + M^{n+} \rightleftharpoons A\text{-}M\text{-}B + A\text{-}M\text{-}A + B\text{-}M\text{-}B$$

Selective *mononuclear* heteroleptic binding can be obtained either by enhancing stability of the heteroleptic complex A-M-B, or by simultaneous destabilisation of both homoleptic complexes A-M-A and B-M-B. This has been achieved using several strategies including formation of pentacoordinated metal complexes with tridentate ligand A and bidentate ligand B[29–31]; topologically constrained systems with introduction of a macrocycle into one of the ligands effectively precludes formation of its homoleptic complexes.[32] However, the most

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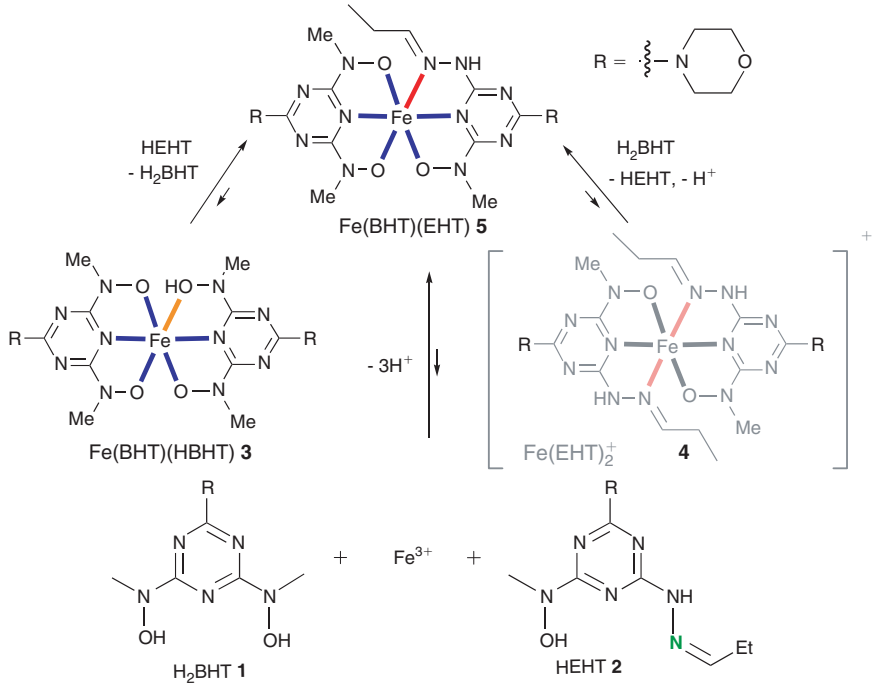

Fig. 1. Dynamic equilibria in formation of ternary complex **5** and symmetric complex **3** from H_2BHT ligand **1** and HEHT ligand **2** with iron(III) cations, which provides a 97 : 3 ratio of **5** : **3** under weakly acidic conditions at which deprotonation of complex **3** is suppressed.

direct approach to selective formation of ternary complexes involves using two ligands possessing different electric charges. This effect has been observed in selective formation of copper(II) complexes involving α-amino acids as ligand A and 2,2′-bipyridine as ligand B, and in formation of ternary nickel(II) complexes involving nitrilotriacetic acid as ligand A and a hexahistidine tag of recombinant proteins as ligand B. Selective formation of ternary ligands around iron(III) cation was achieved with a pair of complementary η^3-terdentate meridional binders (pincer ligands) H_2BHT **1** and HEHT **2** (BHT = 2,6-bis[hydroxy(methyl)amino]-1,3,5-triazine, EHT = 2-(ethylmethylene)-hydrazino-6-hydroxy(methyl)amino-1,3,5-triazine), both belonging to the hydroxyamino-1,3,5-triazine family (Fig. 1).[33] Preferential formation of heteroleptic complex **5** was caused by lower stability of homoleptic complex **3** due to weaker energy of the Fe-OH coordination bond, while homoleptic complex **4** was less stable than heteroleptic complex **5** because of intrinsically lower energy of the coordination bond between a 'hard metal' iron(III) cation and 'soft' sp^2 nitrogen-containing ligands. As a result, under weakly acidic conditions the equilibrium is shifted towards formation of complex **5** while only minor amounts of homoleptic complex **3** are present and no complex **4** is observed. Depending on substituents at the triazine ring, the ratio of heteroleptic : homoleptic complexes ranged from 94 : 6 to 97 : 3. Neutralisation of pH results in complete reversal of the equilibrium towards deprotonated homoleptic complex **3**.

It can be anticipated that preferential formation of 1 : 1 : 1 ternary complexes can be a general property for ligands possessing a different number of anionic groups. In that case preferential formation of either a symmetric homoleptic complex such as **3** or ternary heteroleptic complex such as **5** can also be dynamically controlled by the acidity of the media. Extending these studies here we report the formation of ternary iron(III) complexes between H_2BHT ligand **1** and other tridentate meridional binders, and we determine the reaction equilibrium using ESI mass-spectrometry.

Results and Discussion

We chose ligands **6** and **7** (Fig. 2) as a typical monoanionic counterpart, to be used with the dianionic BHT ligand **1**, to form neutral complexes of type **10** and **11**. As a more distant analogy, we also tested neutral tridentate meridional binders, terpyridines **8** and **9**, that were expected to form cationic ternary complexes of type **12** and **13**. Synthesis of all of these ligands was done in one step using reactions of pyridine-2-aldehyde or imidazole-4-aldehyde with either 2-aminomethylpyridine (compounds **8** and **9**) or 2-aminophenol (compounds **6** and **7**).

The ESI-MS (positive mode) spectrum of BHT iron(III) complex **3** shows a strong peak of $[(HBHT)_2Fe]^+$ at *m/z* 566 (Fig. 3a). Along with it there was a strong peak of a free $[H_3BHT]^+$ cation at *m/z* 257, yet no traces of $[BHTFe]^+$ complex (*m/z* 312) were present. Instead, a 3 : 1 complex $[H_2BHT(HBHT)Fe]^+$ at *m/z* 822 was observed. The formation of a 3 : 1 BHT-iron complex has not been previously observed in solution phase.[34] Its formation can be attributed to disproportionation of kinetically labile complex **3** under conditions of the electrospray ionisation. With excess H_2BHT ligand **1** (13 equiv.) peaks at *m/z* 257 and 822 increased in intensity, and new peaks at *m/z* 513 $[H(HBHT)_2]^+$, 535 $[(HBHT)_2Na]^+$, and 1077 $[H(HBHT)_4Fe]^+$ were observed.

Addition of tridentate ligand **6** to a solution containing 15 : 1 ratio of H_2BHT ligand **1** and iron(III) acetate resulted in formation of a peak corresponding to ternary heteroleptic metal complex **10** (*m/z* 508) along with a peak of protonated ligand **6** with *m/z* 199 (Fig. 3b). While all peaks of BHT-iron complex **3** and BHT ligand **1**, including $[H_2BHT(HBHT)Fe]^+$ (*m/z* 822) were observed, there were no traces for a 2 : 1 complex of ligand

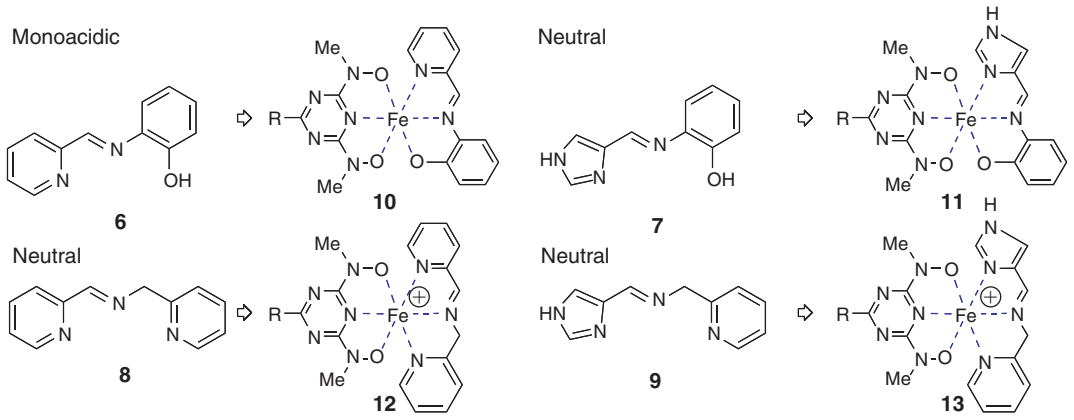

Fig. 2. Structures of ligands **6**–**9** and expected ternary complexes **10**–**13** produced from these ligands with H_2BHT ligand **1**.

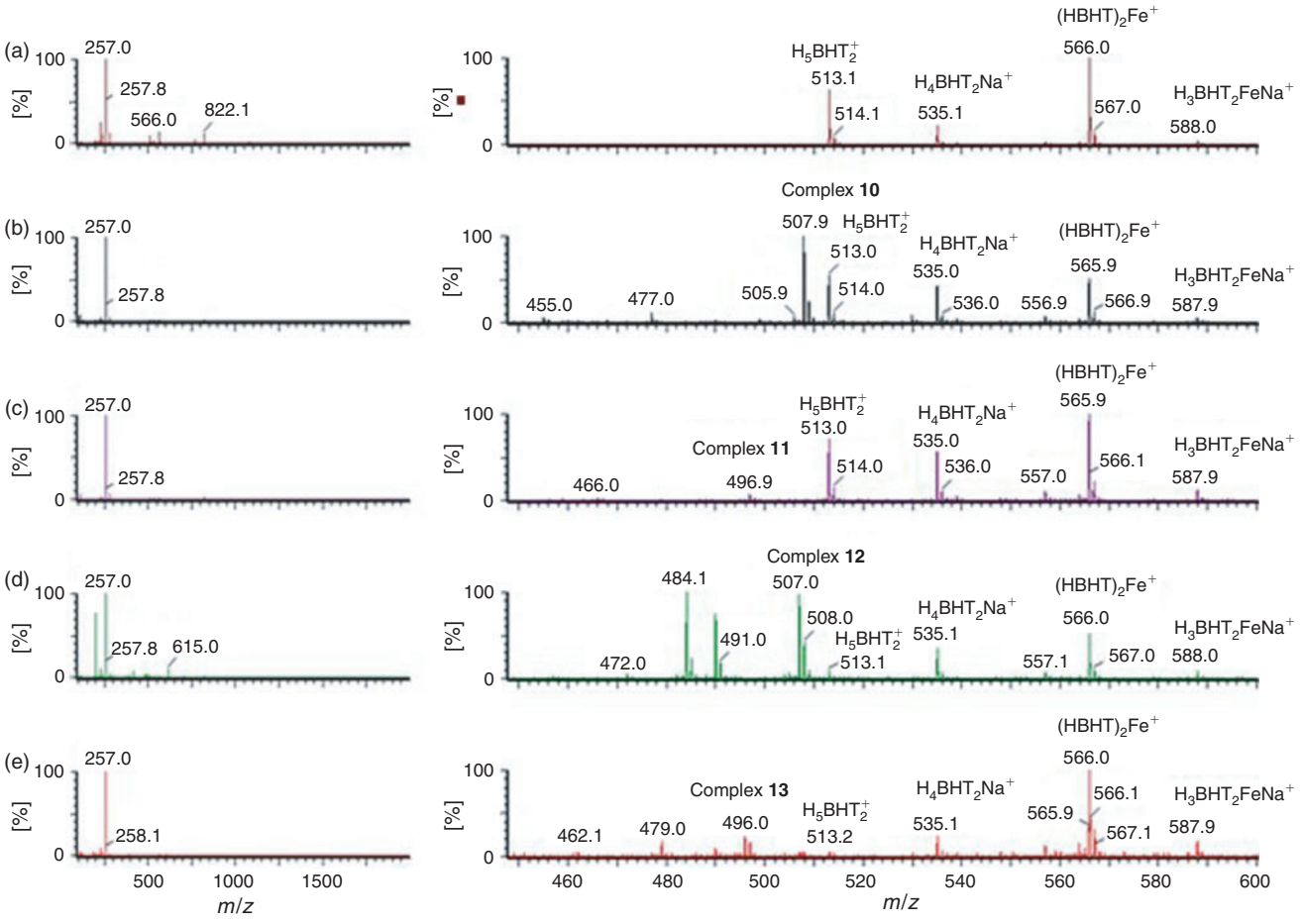

Fig. 3. ESI-MS spectra (left) and expanded spectra for *m/z* 400–600 (right) of (a) complex **3** in the presence of 6.5 equiv. of ligand **1**; (b) solution containing a 15 : 1 : 4 mixture of **1** : iron(III) : **6**; (c) solution containing a 15 : 1 : 4 mixture of **1** : iron(III) : **7**; (d) solution containing a 15 : 1 : 4 mixture of **1** : iron(III) : **8**; (e) solution containing a 15 : 1 : 4 mixture of **1** : iron(III) : **9**.

6 with iron(III) cation (expected *m/z* 450). Analogous changes in MS were observed using ligand **7**, although both the peak corresponding to the ternary complex **11** (*m/z* 497) and the peak of protonated ligand **7** (*m/z* 188) were observed with very low intensity (Fig. 3c). Peaks of ternary complexes **12** (*m/z* 507) and **13** (*m/z* 496) were also observed in solutions containing 4 equiv. of ligand **8** or **9**, 15 equiv. of BHT ligand **1**, and 1 equiv. of iron(III) acetate (Fig. 3d, e). In all of these cases no peaks with *m/z* corresponding to 2 : 1 symmetric complexes of ligands **7**–**9** with either iron(III) or iron(II) cations were detected.

A study of the equilibrium between symmetric complex **3** and ternary complex **10** was done by titration of a solution of ligand **1** (3.75 mM) and iron(III) acetate (0.25 mM) in a 1% solution of acetic acid in ethanol with ligand **6** (Fig. 4). Excess of ligand **1** was used to shift the equilibrium towards formation of the less stable symmetric complex **3** thus increasing the

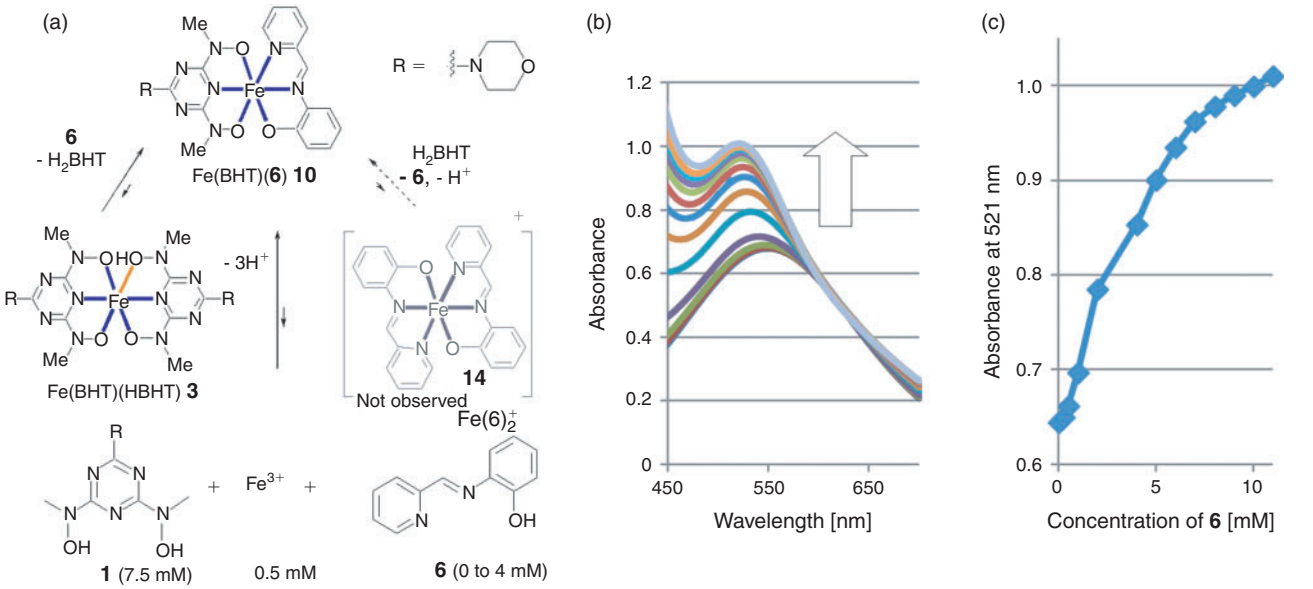

Fig. 4. (a) Equilibria between ternary complex **10** and symmetric complex **3**. No traces of symmetric complex **14** were observed. (b) Visible spectra upon titration of BHT ligand **1** (3.75 mM) and iron(III) acetate (0.25 mM) with 0–22 mM of ligand **6**. (c) Changes in absorbance at 521 nm with addition of ligand **6**.

precision of determining the equilibrium constant. Addition of ligand **6** (11 mM solution) resulted in changes in the absorbance spectra in the visible range; the maximum shifted from 550 nm ($\varepsilon = 2716\ M^{-1}\ cm^{-1}$) for symmetric complex **3** to 521 nm, along with increased absorbance ($\varepsilon = 4042\ M^{-1}\ cm^{-1}$). Additionally, a very strong absorbance band below 450 nm appeared which obscured the second isosbestic point at lower wavelength. These changes proceed progressively with the addition of ligand **6**, slowing down after addition of ~6 mM of ligand **6** but not reaching saturation. These changes are consistent with formation of ternary complex **10** which does not further convert to a symmetric 2 : 1 complex of ligand **6** with iron(III) cation under these conditions.

These data allowed estimation of an equilibrium constant between symmetric complex **3** and ternary complex **10**. It can be assumed that 50 % change in absorbance at 506 nm, upon addition of 4 mM of ligand **6**, indicates a 50 % drop in concentration of complex **3**. Under these conditions 50 % of iron(III) cations are bound in complex **10**, which allows us to estimate the equilibrium constant between complexes **3** and **10**. Substituting BHT ligand with A and ligand **6** with B, equilibrium constants were calculated at 480 nm according to Eqn 1:

$$K = \frac{[FeAB][A]}{[FeA2][B]} \qquad (1)$$

where $[FeAB] = [FeA2] = 0.1125$ mM, $[A] = 7.38$ mM, and $[B] = 3.98$ mM so that the equilibrium constant is less than 1.85. Analogous results were observed in titration of complex **3** under the same conditions with monoacidic ligand **7** (Fig. 5a). The observed lack of selectivity towards formation of ternary complexes is in contrast to the high selectivity in the BHT/EHT ligands with equilibrium constants in the range of 30–35.[34] The drop in selectivity for ligands **6** and **7** is likely caused by lower acidity of OH groups (pK_a in the range of 9–10) in comparison to pK_a 8 of the hydroaminotriazine group.[34]

In contrast to the absence of selectivity in formation of ternary complexes **10** and **11**, substantially higher selectivity was achieved with neutral ligands **8** and **9**. Titration of a solution of ligand **1** (7.5 mM) and iron acetate (0.25 mM) with ligand **8** (Fig. 5b) caused a gradual shift of the maximum from 574 nm ($\varepsilon = 2620\ M^{-1}\ cm^{-1}$) to 615 nm ($\varepsilon = 1700\ M^{-1}\ cm^{-1}$) with saturation practically achieved after addition of 8 mM of ligand **8**. Fifty percent change in absorbance was achieved at concentration of ligand **8** = 1.0 mM, which corresponds to an equilibrium constant of 10. Titration under the same conditions with ligand **9** proceeded analogously (Fig. 5c), with the 50 % change in absorbance achieved only after addition of 3.0 equiv. of ligand **9**, corresponding to an equilibrium constant of only 2.6.

Finding additional pairs of tridentate ligands capable of selective formation of ternary complexes necessitates development of newer methods for determination of equilibrium constants. Detection of the formation of kinetically labile ternary complexes such as **10**–**13**, and determination of the corresponding equilibrium constants between heteroleptic and homoleptic metal complexes, can constitute a substantial challenge. Data on the stoichiometry and the stability constants of kinetically labile metal complexes formed in solution are generally obtained from potentiometric, spectrophotometric, or calorimetric measurements. However, despite their reliability and high precision in the case of complicated systems, these methods are considerably less valuable because of the intrinsically poor ability to identify these species. NMR spectroscopy, the most commonly used method to study dynamic equilibria of complexes, is frequently unsuitable for these purposes as most transition metal cations are paramagnetic. Mass spectral data of metal complexes[35,36] provide a very useful characterisation technique in these cases. It has been successfully used for detection of ternary copper complexes of amino acids with neutral bidentate ligands.[37–41]

ESI-MS spectra were obtained for ternary complexes **10**/**11** and **12**/**13**; these showed substantial differences in response factors between otherwise very similar compounds. To quantify the relative concentration of species in the solution, particularly of symmetric complex **3** and ternary complex **10**, a quantitative ESI MS analysis was performed. Mixtures containing 0.5 mM of iron(III) acetate (total amount 5 nmol), 7.5 mM of BHT ligand **1** (total amount 75 nmol), and 0–4 mM of ligand **6** (total amount 0

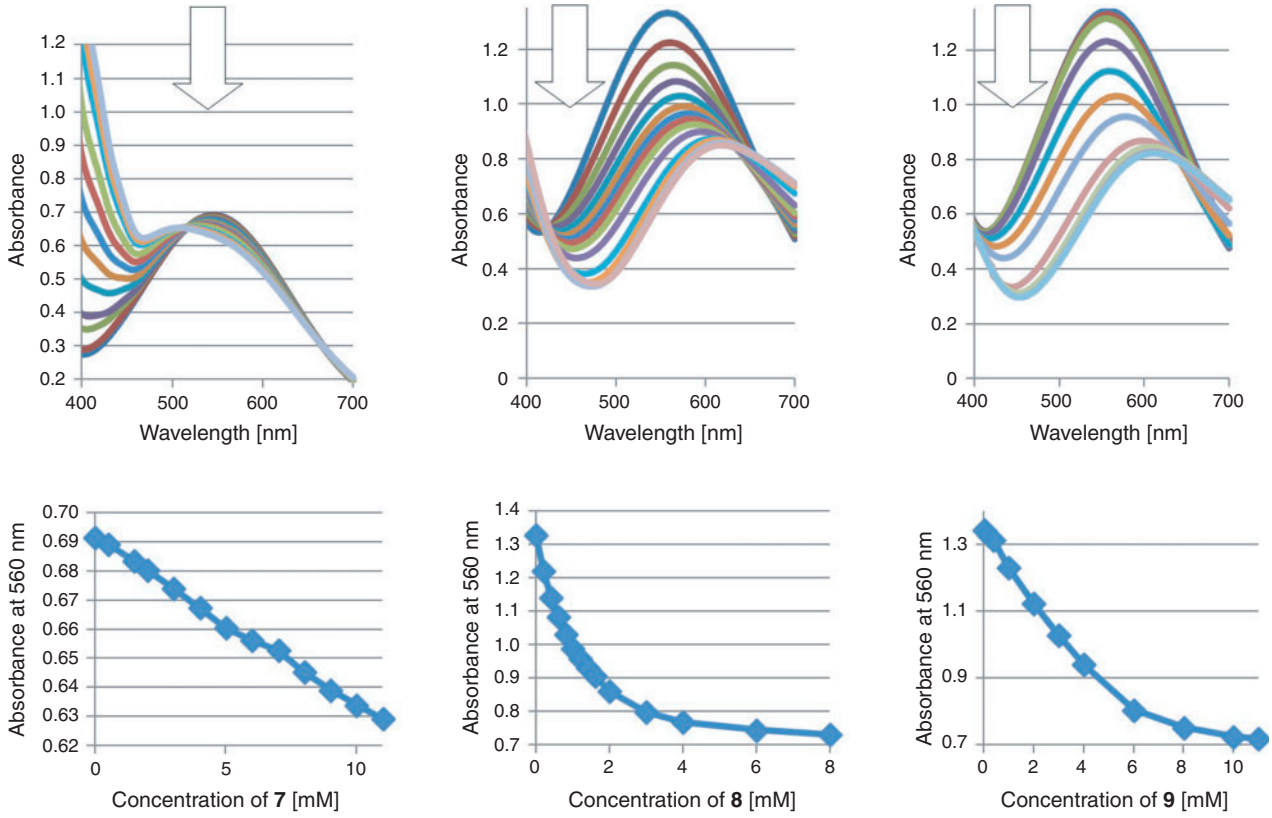

Fig. 5. Changes in visible spectra (above) and absorbance (below) upon titration of (a) BHT ligand **1** (3.75 mM) and iron(III) acetate (0.25 mM) with ligand **7**; (b) BHT ligand **1** (7.5 mM) and iron(III) acetate (0.5 mM) with ligand **8**; (c) BHT ligand **1** (7.5 mM) and iron(III) acetate (0.5 mM) with ligand **9**.

to 4 nmol) were directly injected into an ESI probe through 5 µL loop followed by elution with methanol at 5 µL min^{-1}. Because no traces of 2 : 1 symmetric iron(III) complex **14** were discovered in the solution, it can be assumed that the equilibrium takes place only between iron complexes **10** and **3**. In that case, the concentration of ternary complex **10** can also be detected through the decrease of the intensity of the peak of complex **3** at *m/z* 566. The original peak intensities showed considerable variation in response factors in experiments with different ligands **6**–**9**, and sometimes even with different concentrations of ligands. In order to decrease these variations, instead of using the absolute intensity of counts, we measured relative intensities using the $[H_2BHT]^+$ peak of ligand **1** with *m/z* 257 as an internal standard. In all experiments ligand **1** is present in large excess, so its concentration does not appreciably change in the equilibrium between complex **3** and a ternary complex.

As can be seen in Fig. 6a, addition of ligand **6** predictably increased the amount of complex **10** (*m/z* 508, blue) while decreasing symmetric complex **3** (*m/z* 566, red). Increasing the concentration of ligand **6** to 3 mM caused only a 35 % reduction in the intensity of the peak for complex **3** which corresponds to an equilibrium constant of 1.3.

Analogous experiments were conducted with ligands **7**-**9**. Addition of ligand **7** was found to continuously increase the peak of corresponding ternary complex **11** with *m/z* 497 (Fig. 6b). However, the increase was very small and the decrease of peak of symmetric complex **3** at *m/z* 566 was not significant, indicating that the equilibrium constant is less than 1. In contrast, addition of ligands **8** or **9** caused a substantial drop in intensity of signal for complex **3**. For example, addition of 1.2 mM of ligand **8** caused a 73 % drop in intensity of peak of complex 3 which corresponds to equilibrium constant 6.8 (Fig. 6c). For ligand **9**, addition of 1 mM of the ligand caused a decrease of 54 % relative intensity of peak for complex **3** (Fig. 6d) which corresponds to an equilibrium constant of 3.0.

Use of these results for determination of equilibrium constants of metal complexes is challenging. Despite the similarity in structure of ligands **6** and **7**, and almost equal equilibrium constants in formation of ternary complexes **10** and **11**, results of their mass-spectrometric studies were completely different. These results can be attributed to high kinetic lability of these complexes and disruption of equilibrium during the ionisation process which involves protonation of these complexes. More encouraging results were obtained with quantitative mass spectrometry of cationic complexes **12** and **13**, where there was semiquantitative agreement with the results obtained by UV titration. Better agreement in this case can be explained both by lower lability of the complexes **12** and **13**.

Conclusions

We studied the formation of ternary iron(III) complexes with BHT and other tridentate meridional ligands by UV-Vis titration and quantitative mass-spectrometry. A substantial preference was found in formation of ternary complexes with neutral but not monoacidic tridentate ligands. Equilibrium constants obtained by quantitative mass-spectrometry were in semiquantitative agreement with ones obtained by UV-Vis titration. These results indicate potential applicability of ESI MS for the quantitative study of equilibria in formation of labile metal complexes and the need for additional studies in the field.

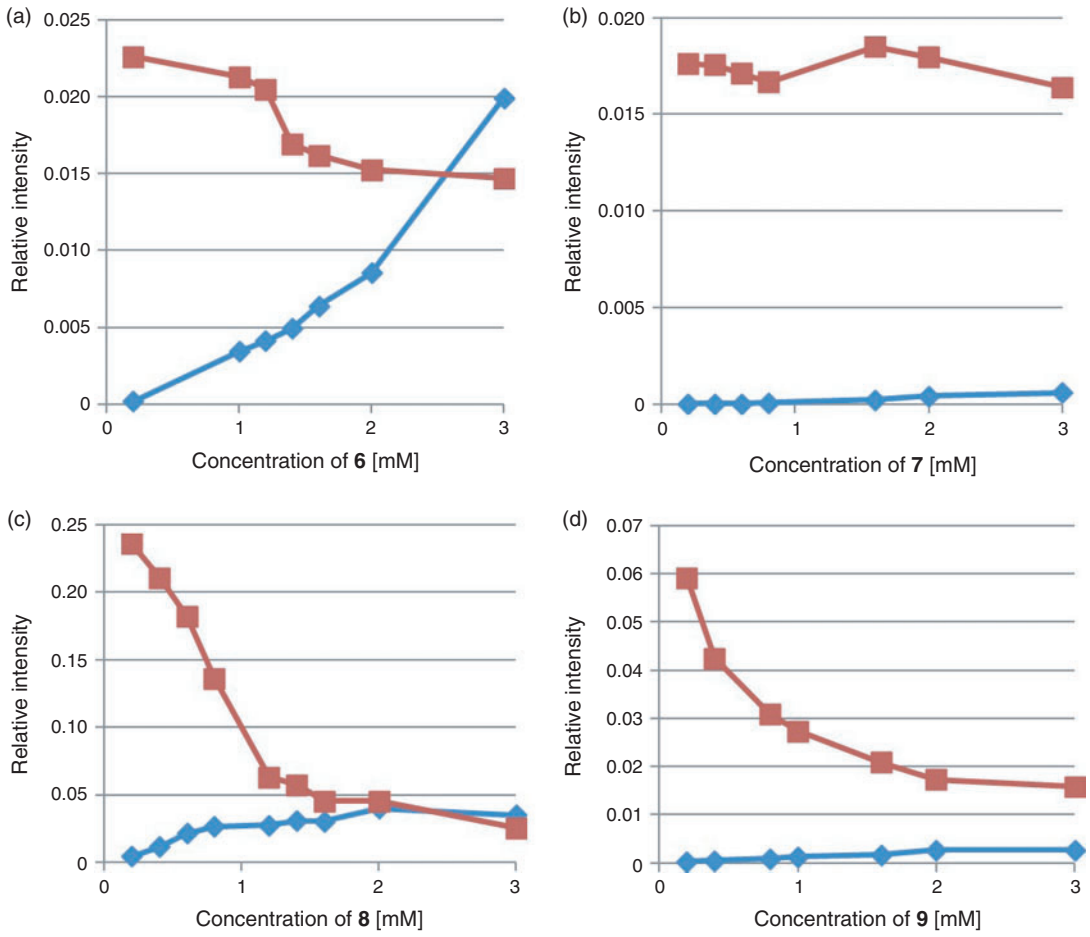

Fig. 6. Changes in peak height relative to $[H_3BHT]^+$ (*m/z* 257) of complex **3** (*m/z* 566, red squares) and ternary complexes (a) **10**, (b) **11**, (c) **12**, and (d) **13** (*m/z* 508, blue diamonds) upon addition of 0–3 mM of ligands **7**–**9**, respectively, to solutions containing 7.5 mM of BHT ligand **1** and 0.5 mM of iron(III) acetate.

Experimental

General Information

Thin layer chromatography was performed on aluminium sheets precoated with silica gel (Merck, Kieselgel 60 F-254). Flash chromatographic separations were performed on silica gel (Merck, Kieselgel 60, 230–400 Mesh ASTM). Unless mentioned specifically, ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-400 spectrometer at room temperature in deuterated chloroform ($CDCl_3$) using the residual solvent peaks for calibration. Unless otherwise stated, all reagents used are commercially available. Glassware was oven-dried before use and solvents were purified by conventional methods. Titration experiments were done on Varian Cary 100 and Lambda 35 Perkin-Elmer UV/Vis spectrometers. Ligands **1**,[34] **8**,[42] and **6**[43] were synthesised according to published procedures.

*(E)-1-(1H-Imidazol-4-yl)-N-(pyridin-2-ylmethyl) methanimine (**9**)*

To a solution of 4-formylimidazole (19.2 mg, 0.2 mmol) in 1 mL of dry CH_2Cl_2 was added dropwise a solution of 2-picolylamine (21.6 mg, 0.2 mmol) in 1 mL of dry CH_2Cl_2 with stirring at room temperature. Anhydrous Na_2SO_4 (200 mg) was then added, and the mixture was stirred for a further 2 h. After filtration and evaporation to dryness, the product was obtained as a solid (32.2 mg, 86 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.89 (s, 2H), 7.20 (t, $J = 7.2$ Hz, 1H), 7.32 (d, $J = 7.6$ Hz, 1H), 7.43 (s, 1H), 7.63–7.69 (m, 2H), 8.38 (s, 1H), 8.58 (d, $J = 4.4$ Hz, 1H).

*2-[(E)-(1H-Imidazol-4-ylmethylidene)amino]phenol (**7**)*

To a solution of 4-formylimidazole (19.2 mg, 0.2 mmol) in 1 mL of dry CH_2Cl_2 was added dropwise a solution of 2-aminophenol (21.8 mg, 0.2 mmol) in 1 mL of dry CH_2Cl_2 with stirring at room temperature. Anhydrous Na_2SO_4 (200 mg) was then added, and the mixture was stirred at room temperature for 2 h. After filtration and evaporation to dryness, the product was obtained as a solid (30.7 mg, 82 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.89 (t, $J = 7.6$ Hz, 1H), 6.98 (d, $J = 7.6$ Hz, 1H), 7.16 (t, $J = 7.6$ Hz, 1H), 7.23–7.26 (m, 1H), 7.59 (s, 1H), 7.79 (s, 1H), 8.60 (s, 1H).

General Procedure for UV Titration

To a 1 % solution of acetic acid in absolute ethanol (3 mL) containing BHT ligand **1** (7.5 mM) and iron acetate (0.5 mM) in a quartz UV cell were added portions of ligands **6**–**9** (50 mM in ethanol containing 1 % acetic acid) by aliquots of 6 µL, initially, and then 12 and 30 µL until a total of 90 µL were added. After every addition the reaction mixture was stirred and UV-Vis spectra (350–700 nm) were recorded.

General Procedure for Quantitative ESI-MS Spectrometry

ESI-MS spectra were measured by a Waters Micromass Micro QTOF spectrometer using direct injection. To a solution of acetic acid in absolute methanol (1% v/v, 3 mL) containing BHT ligand **1** (7.5 mM) and iron acetate (0.5 mM) was added a ligand **6**–**9** (50 mM in methanol containing 1% acetic acid) by 6 μL portions, initially, and then 12 and 30 μL portions until a total of 120 μL were added. 5 μL samples of the resultant solution were injected into the ESI mass spectrometer using a 5 μL min^{-1} stream of methanol under ES+ mode. The ESI was operating under the following conditions: capillary voltage 1600 V; sample cone 40 V; extraction cone 4.0 V; desolvation temperature 20.0°C; source temperature 20.0°C, with instrument parameters: ion energy 1.0 V; collision energy 6.0 V; aperture 7.0 V; MCP detector 2100.0 V; acceleration 200.0 V.

Acknowledgement

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