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Synthesis and characterization of manganese(II) and iron(III) d⁵ tripodal imidazole complexes. Effect of oxidation state, protonation state and ligand conformation on coordination number and spin state

Cynthia Brewer^a, Greg Brewer^{*a}, Ray J. Butcher^b, Everett E. Carpenter^c, Luciann Cuenca^a, Bruce C. Noll^d, W. Robert Scheidt^d, Carol Viragh^e, Peter Y. Zavalij^f, and Daniel Zielaski^a

^aDepartment of Chemistry, The Catholic University of America, Washington, DC 20064 USA. Email: brewer@cua.edu

^bDepartment of Chemistry, Howard University, Washington, DC 20059 USA.

^cDepartment of Chemistry, Virginia Commonwealth University, Richmond, VA USA 23284-2006

^dDepartment of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556

^eVitreous State Laboratory, The Catholic University of America, Washington, DC 20064 USA

^fDepartment of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742-4454

Summary

The 1:3 Schiff base condensates of tris(2-aminoethyl)amine (tren) or tris(3-aminopropyl)amine (trpn) with 4-methyl-5-imidazolecarboxaldehyde, H₃L¹ and H₃L², respectively, were generated in situ and used to prepare complexes with manganese(II) and iron(III). The resultant complexes, [MnH₃L¹](ClO₄)₂, [MnH₃L¹](ClO₄)₂·EtOH·H₂O, [MnH₃L²](ClO₄)₂, [FeH₃L¹](ClO₄)₃·1.5(EtOH) and [FeHL¹](I₃)_{0.525}(I_{0.475}·2.625H₂O), have been characterized by EA, IR, ES MS, variable temperature magnetic susceptibility, x-ray crystallography, and Mössbauer spectroscopy for the iron complexes. The three manganese(II) complexes are high spin with [MnH₃L²](ClO₄)₂ exhibiting coordination number seven while the others are six coordinate. [FeH₃L¹](ClO₄)₃·1.5(EtOH) has two iron sites, a seven coordinate and a pseudo seven coordinate site. The complex is high spin at room temperature but exhibits a magnetic moment that decreases slightly at liquid He temperatures. [FeHL¹](I₃)_{0.525}(I_{0.475}·2.625H₂O) is low spin even at room temperature. In the present complexes the apical nitrogen atom, N_{ap}, of the tripodal ligand is pyramidal and directed toward the metal atom. The data show that the M-N_{ap} distance decreases as the oxidation state of the metal increases, as the number of bound imidazole protons on the ligand increases, and as the number of carbon atoms in the

Graphical Contents Entry. In a series of tripodal d⁵ iron(III) or manganese(II) complexes derived from the condensation of tris(2-aminoethylamine) or tris(3-aminopropylamine) with 4-methyl-5-imidazolecarboxaldehyde it is found that the metal, M, to apical nitrogen atom, N_{ap}, distance responds to changes in the charge of the complex due to oxidation state or protonation state changes. These changes correlate with spin state (high spin vs low spin) and coordination number (6 vs 7) selection and follow the trend that short M-N_{ap} distances favor high spin and long M-N_{ap} distances favor low spin.

backbone of the ligand (tren vs trpn) increases. In a limiting sense, short M-N_{ap} distances result in high spin seven coordinate mono capped octahedral complexes and long M-N_{ap} distances result in low spin six coordinate octahedral complexes.

Introduction

The study of spin crossover (SC) complexes of d⁴ – d⁷ first row transition metal complexes has experienced a great deal of activity¹ in recent years and the area has been reviewed recently.² The resurgence in interest is partly attributed to the potential applications of molecules with two electronic ground states that are interconverted by changes in temperature, pressure, or light as memory devices³ and switches⁴. Most work has focused on iron (II) (d⁶, ¹A ⇌ ⁵T) and iron(III) (d⁵, ²T ⇌ ⁶A) complexes as the requirement for SC that the crystal field splitting parameter (Δ) equals the pairing energy is easily met with these cases and readily available ligands. The SC condition is met for iron(II) and iron(III) with ligands that have N₄O₂ – N₆ donor sets. With tris(2-aminoethyl)amine (tren) it is possible to alter the ligand field from N₄O₂ to N₆ simply by selecting an appropriate aldehyde for a Schiff base condensation with tren.⁵ In this manner the spin state of the resultant iron complexes can be controlled.

An important class of ligands that can exhibit SC behavior with iron(II) and iron(III) are the 1:3 Schiff base condensates of tren and tris(3-aminopropyl)amine (trpn) with imidazole carboxaldehydes (Fig.1). These ligands can bind to metals in different oxidation states and protonation states which allows for a wide variety of resultant complexes. Recent work in this laboratory⁶ and others⁷ has examined the structural and magnetic properties, including SC, of the iron(II) and iron(III) complexes of these and related ligands.

In this work the synthesis, magnetic characterization and structural properties of the d⁵ complexes, [MnH₃L¹](ClO₄)₂ **1**, 1·EtOH·H₂O, [MnH₃L²](ClO₄)₂ **2**, [FeH₃L¹](ClO₄)₃·1.5 (EtOH) **3**, and [FeHL¹](I₃)_{0.525}(I)_{0.475}·2.625H₂O **4** are reported. The effect of charge of the complex, which varies with oxidation state or protonation state, hydrogen bonding, and ligand flexibility on coordination number and spin state can be examined by comparisons within these isoelectronic complexes. An understanding of the factors that contribute to spin state selection can be used in the design of complexes with specific properties.

Results and Discussion

Synthesis

The ligands employed in this study are triprotic and can form complexes as the neutral ligands, H₃L, or their deprotonated anions, H₂L[−], HL^{2−}, and L^{3−} with either the M(II) or M(III) cation as illustrated below with iron.

The syntheses of **1**, **1**·EtOH·H₂O, **2**, and **3** were accomplished by the direct reaction of a manganese(II) or iron(III) salt with a solution of H₃L¹ or H₃L² (generated in situ) followed by isolation of the complex cation as its perchlorate salt. The reaction of iron(III) salts with H₃L² resulted in the immediate precipitation of an orange-red solid. But this product does not appear to be the iron(III) analogue of **2**, [FeH₃L²](ClO₄)₃. ESMS of this product showed peaks corresponding to the iron complexes of the 3:1 and 2:1 Schiff base condensates of 4-methyl-5-imidazole carboxaldehyde with trpn. Attempts at purification were unsuccessful due to the poor solubility of this species. Attempts were made to generate [MnH₃L¹](ClO₄)₃ by reaction of a manganese(III) salt or complex with H₃L¹. These reaction mixtures were initially brown or green, but resulted only in the isolation of the offwhite Mn(II) complex as described in the experimental section. The tendency of these ligands to prefer one oxidation state of the metal over another to the point of promoting redox changes is well established with iron. While uncommon, the isolation of an iron(II) N₆ complex from the reaction of an iron(III) salt with nitrogenous ligands has been observed with terpyridyl,⁸ ethylenediamine⁹ and, most recently, with several 1:3 Schiff base condensates of tren with pyridine,¹⁰ imidazole,^{6,7} or pyrazole¹¹ carboxaldehydes. This same tendency is now reported with manganese and H₃L¹. In contrast to the iron chemistry of these ligands, the reaction of **1** with sodium hydroxide or sodium methoxide did not result in deprotonation or deprotonation accompanied by oxidation to manganese(III). The lack of reactivity of **1** to deprotonation is surprising as the acidity of metal bound imidazoles is greatly enhanced relative to free imidazole.¹² Further, the lack of reactivity of **1** to aerial oxidation in the presence of base was unanticipated as the Schiff base condensate of tren with pyrrole-2-carboxaldehyde promoted the oxidation of manganese(II) to manganese(III) accompanied by deprotonation in the presence of base.¹³

The synthesis of [FeHL¹](I₃)_{0.525}(I)_{0.475}·2.625H₂O **4** involved some unusual redox changes. Reaction of iron(III)chloride with a solution of H₃L¹ in methanol produced the characteristic purple color of [FeH₃L¹]³⁺. Addition of an excess of iodide resulted in a color change from purple to orange brown indicating a reduction to iron(II) with the production of iodine and/or triiodide in the presence of excess iodide. On standing, the orange solution darkened and deposited large black crystals which were identified by structural investigation to contain the di-deprotonated iron(III) cation, [FeHL¹]⁺, isolated as a mixed iodide/triiodide salt. The precipitation of a cation with mixed anions as observed here for **4** has been observed in bismuth (III) halides,¹⁴ in dipyrindinium iodide triiodide, [(C₅H₆N)(I)_{0.500}(I₃)_{0.500}],¹⁵ and with the closely related [FeH₃L³]²⁺ and [FeH₃L³]³⁺ salts.¹⁶ The value of x in [FeHL¹](I₃)_(1-x)(I)_x which reflects the anion composition, iodide vs triiodide, is variable. The composition of the bulk material from EA (x= 0.142, see experimental section) differs from that observed in the single crystal structure analysis (x=0.475). However, the anion composition (iodide/triiodide ratio) does not affect the formulation of the iron(III) cation as [FeHL¹]⁺ as both iodide and triiodide are uninegative anions. The following series of reactions summarizes the apparent changes.

The di-deprotonated iron(III) cation, [FeHL¹]⁺, produced in the aerial oxidation precipitates as a mixed iodide and triiodide salt, the former anion being present in excess and the latter produced by the reaction of iodine with iodide. The fully protonated iron(III) cation, [FeH₃L¹]³⁺, produced in the second step can in turn be re-used in the first step until iodide is depleted. A similar aerial oxidation of a metal(II) triprotic tren complex, [CoH₃L⁸]²⁺, to a di-deprotonated metal(III) complex, [CoHL⁸]⁺, has been observed previously.¹⁷ The conversion of [FeH₃L¹]²⁺ to [FeHL¹]⁺ provides another example of a proton-coupled electron transfer

reaction; these reactions are abundant among transition metal complexes.¹⁸ Not surprisingly reaction of **4** with base results in the immediate deprotonation of the dark green $[\text{FeHL}^1]^+$ to the previously characterized royal blue $[\text{FeL}^1]$.⁶

IR and ES MS

The initial characterization of complexes was carried out by EA, IR and ES MS. The most useful regions for examination in the IR were the N-H, C=N, and perchlorate regions. The IR spectra of **1**, **1**·EtOH·H₂O, **2**, and **3** show the characteristic absorption bands attributable to the imidazole $\nu_{\text{N-H}}$ (3100–3400 cm^{-1}), imine $\nu_{\text{C=N}}$ (1633–1620 cm^{-1}), and perchlorate $\nu_{\text{Cl-O}}$ (1147–1154 and 625 cm^{-1}). In addition to the $\nu_{\text{N-H}}$ and $\nu_{\text{NC=N}}$, the IR of **4** exhibits a broad band at ~2100–1800 and a weaker one at 2350 cm^{-1} , which are not observed in the IR spectra of the other complexes. These bands have been observed in hemi-deprotonated tren imidazole complexes and are attributed to intermolecular hydrogen bonding.¹⁹ Direct evidence of an intermolecular hydrogen bonding interaction is seen in the structure of the complex and is discussed in the molecular structure section. **4** exhibits imine absorptions at 1624 and 1588 cm^{-1} , which differ from the analogous bands of $[\text{FeH}_3\text{L}^1](\text{ClO}_4)_3 \cdot 1.5(\text{EtOH})$ **3** observed at 1622 and 1587 cm^{-1} in that in **4** the lower wavenumber band is much more intense than the higher while in **3** the reverse is true. This suggests that **4** is LS and **3** is HS as the position of the imine band has been observed to correlate with spin state.²⁰ This observation is supported by the magnetic, Mössbauer and structural data presented below.

The main feature observed for the ES MS of these complexes (see experimental) is very little fragmentation, which allows easy identification of the molecular ion. The ionization pathways involve loss/gain of an imidazole proton and/or pairing with an anion.

Mössbauer

Mössbauer data were collected on $[\text{FeH}_3\text{L}^1](\text{ClO}_4)_3 \cdot 1.5(\text{EtOH})$ **3** and $(\text{I}_3)_{0.525}(\text{I})_{0.475} \cdot 2.625\text{H}_2\text{O}$ **4** and subjected to Lorentzian analysis. The spectra of **3** at 295 and 77K consist of a single broad peak with the 77K spectrum being broader than the 295K spectrum. The 295K spectrum of **3** was fitted to two doublets (QS = 0.00 and IS = 0.017 mm/s and QS = 0.44 and IS = 0.43 mm/s) with populations of 50.5 and 49.5% respectively. The fitting of the spectrum to two doublets is supported by the x-ray structure (see subsequent section), which shows that **3** contains two iron(III) sites, a CN=7 site $[\text{Fe}(1)]$ and a pseudo seven coordinate site, $[\text{Fe}(2)]$. The assignment of Mössbauer values to the two sites cannot be done with certainty, but the CN=7 site is more likely the one with higher values of IS and QS. In any event both sets of values support a HS ⁶A ground state for **3** at 295K, which is consistent with both the magnetic and structural data given in subsequent sections. At 77K the spectrum of **3** was fitted to three doublets (QS = 2.48, IS = -0.25 mm/s, 17.9%; QS = 0.39, IS = 0.14, 31.3%, and QS = 1.34, IS = 1.31 mm/s, 50.8%). This data suggests that one of the iron sites (most likely Fe(2)) is SC and is partially (17.9%) converted to the LS form while the other iron site is still HS at 77K. This interpretation of the data is consistent with the magnetic data presented in the next section. The Mössbauer values reported here for **3** are consistent with those observed for structurally characterized CN=7 iron(III) complexes.²¹

Investigation of **4** was problematic due to possible solid state reactions and the presence of iodine, which has been shown to absorb a significant amount of gamma radiation and results in a very noisy spectrum.²² To overcome the noise effect, the spectrum (Fig. 2) was recorded at room temperature for a month. The spectrum shows that the majority (67%) of the sample is LS iron(III) but that there is also a very significant (33%) high spin iron(II) component. Possible interpretations of this result are a mixed valence compound or a simple chemical impurity. However, these explanations are not consistent with the variable temperature magnetic susceptibility data or x-ray crystallography results (see following sections) which

support a single LS iron(III) environment. If high spin iron(II) is not present in the sample prior to the Mössbauer experiment, the possibility of sample decomposition due to time, exposure to air, or exposure to gamma radiation must be considered. The IR of a sample stored at room temperature in the air for 9 days was identical to that of the freshly prepared complex. In contrast, the IR of a sample exposed to gamma radiation for the same period of time showed subtle changes throughout the spectral range and drastic changes in the imine region. Specifically the imine region of the gamma ray exposed material showed greater absorption in the 1624 cm^{-1} band and less absorption in the 1587 cm^{-1} band, which suggests the conversion of a LS species to a HS species.²⁰

Exposure of **4** to gamma rays also results in magnetic susceptibility data (see following section) that are different from the complex not exposed to gamma rays and that are consistent with the production of a high spin species. A possible reaction pathway in the presence of gamma rays is shown below.

Support for this reaction is given by the observation that iodide is converted to triiodide in the presence of gamma rays,²³ which would promote the reduction of iron(III) to iron(II). In addition the spin state of $[\text{FeHL}^1]$ at 295 K is almost certainly HS as another iron(II) $[\text{FeHL}]$ species in which 2-imidazole carboxaldehyde has been substituted for 4-methyl-5-imidazolecarboxaldehyde has been structurally characterized and shown to be high spin.¹⁶ The conclusion based on these observations is that **4** is initially a low spin iron(III) species which undergoes partial decomposition on prolonged exposure to gamma rays to a high spin iron(II) species, possibly $[\text{FeHL}^1]$.

Magnetic Data

Plots of the magnetic moments with temperature for **1**, **2**, **3** and **4** are shown in Fig. 3. **1** and **2** exhibit the HS ^6A ground state throughout the temperature range, consistent with their offwhite color and long Mn-N1 and Mn-N2 bond distances discussed in the next section. **3** also exhibits a HS ^6A ground state, which is consistent with the Mössbauer spectrum discussed earlier and the long Fe-N1 and Fe-N2 bond distances given in the next section. In contrast to the manganese(II) complexes, the moment of **3** decreases gradually with decreasing temperature to $\sim 4.5\text{ BM}$ at 6K, which suggests a partial conversion to a LS species which is consistent with the Mössbauer data presented in the previous section. A 50/50 mixture of HS and LS iron (III) would produce a moment of $\sim 4.4\text{ BM}$. There are two distinct iron sites in **3**, a CN=7 and a pseudo CN=7 site as described in the following section, and further discussion of the magnetism of this complex will be continued there.

The magnetic moment of **4** is essentially temperature invariant with a moment of $\sim 1.90\text{ BM}$, which is entirely consistent with a LS ^2T ground state, as was previously reported for the fully deprotonated $[\text{FeL}^1]$.⁶ This data clearly demonstrates an increase in Δ with deprotonation of the ligand. The Δ for the ligands varies as follows, $\text{H}_3\text{L} < \text{H}_2\text{L}^- < \text{HL}^{2-} < \text{L}^{3-}$. A sample of **4** that was exposed to gamma radiation in the Mössbauer data collection (and showed changes in the IR imine region consistent with production of a HS species) was also examined by magnetic susceptibility. The magnetic susceptibility of a sample exposed to gamma rays deviated from a sample not exposed to gamma rays (described above) in that its moment gradually increased over the temperature range to a value of 3.5 BM at 300 K which is consistent with a sample that is 33% HS iron(II) ($\mu_{300\text{K}} = 5.4\text{ BM}$) and 67% LS iron(III) ($\mu_{300\text{K}} = 2.1\text{ BM}$). Analysis of the Mössbauer data for **4** (see previous section) indicated that the composition was 33% HS iron(II) and 67% LS iron(III), which closely agrees with the magnetic data of the same gamma ray exposed material. This experiment provides further evidence that **4** is changed

on prolonged exposure to gamma rays in a manner that is consistent with the production of a HS species.

Molecular Structure

The crystallographic data of **1**, **1**·EtOH·H₂O, **2**, **3** and **4** are given in Table 1. Table 2 gives selected bond distances and angles for the new complexes as well as values for two closely related complexes from the literature.

Some general features that are applicable to this class of complex are mentioned below prior to discussion of the individual molecules. For consistency in the following discussion N_{ap} is defined as the apical nitrogen atom of tren or trpn, N1 is defined as the imine nitrogen atom and N2 is defined as the metal bound imidazole nitrogen atom for all of the complexes, regardless of the labeling scheme employed in the individual ORTEPs. The metal atom in all five complexes is bound in a facial manner to the three N1 atoms and the three N2 atoms. There is not a significant difference between the average M-N1 and M-N2 bond distances within these complexes. N_{ap} caps the imine face in a symmetric fashion and has exhibited the four conformations illustrated in Fig. 4. These are pyramidal with N_{ap} pointed toward the metal atom and within bonding distance ("N bound"), pyramidal with N_{ap} pointed toward the metal atom but not within bonding distance ("N in"), trigonal planar with N_{ap} not within bonding distance (P) and pyramidal with N_{ap} pointed away from the metal atom and not within bonding distance ("N out"). The bonding distance criterion is the sum of the van der Waals radii of the metal and nitrogen atoms, and for a first row transition metal is ~ 2.8 Å. For a metal atom to nitrogen atom distance less than 2.8 Å, the "N bound" conformation results in CN=7 complexes that are mono-capped octahedral. Examples of structurally characterized CN=7 complexes have been observed for tren with iron,²⁴ trpn with cadmium,²⁵ and most recently for [MnH₃L⁴](ClO₄)₂, [MnL⁶](ClO₄)₂ and [FeL⁶](ClO₄)₂.²⁶ The term pseudo seven coordinate is used for those complexes in which the metal to nitrogen atom distance is ~ 2.8 Å. The dominance of Fe-N_{ap} nonbonded interactions ("Nin" and P) vs "N bound" is illustrated in the histogram shown in Fig. 5. The "N out" conformation (Fe-N_{ap} ~ 3.9 Å, not included in fig. 5) has only recently been observed for Schiff base complexes derived from tris(2-aminoethyl) methylammonium such as [FeH₃L⁷](ClO₄)₃ and favors a LS configuration exclusively.²⁷

The structures of **1** and **1**·EtOH·H₂O are isomorphous to one another and to the closely related [FeH₃L¹](ClO₄)₂,²⁷ [CuH₃L¹](ClO₄)₂ and [NiH₃L¹](ClO₄)₂.²⁸ They are also very similar to [MnL⁵](ClO₄)₂ and a closely related species,²⁹ which are the only other structurally characterized tren imidazole complexes of manganese. The ORTEP of **1** is shown in Fig. 6 while **1**·EtOH·H₂O is not illustrated separately as it differs only slightly from **1**. These complexes exhibit the "N in" conformation with **1**·EtOH·H₂O being pseudo seven coordinate. A HS ground state is strongly suggested by the long Mn-N₁ and Mn-N₂ bond distances (all > 2.20 Å), which is supported by the magnetic data.

The ORTEP of [MnH₃L²](ClO₄)₂ **2** is shown in Fig. 7. The conformation is clearly "N bound" with a short Mn-N_{ap} bond distance of 2.52 Å. The effect of the capping nitrogen is to pull the metal towards the plane of the imine nitrogen atoms as is observed in the "N bound" form of **3** (discussed in the following paragraph), but the effect is even greater in the manganese complex. If the metal atom were pulled entirely into the plane of the three imine atoms the average N1-M-N1 angle would be 120° rather the observed 114.60°. The analogous angles in **1** and **1**·EtOH·H₂O which are "N in" are 101.67 and 104.62°, respectively. In contrast the average N2-Mn-N2 angles of all three manganese(II) complexes only vary by 4° and are close to that for a pure octahedron.

[FeH₃L¹](ClO₄)₃·1.5(EtOH) **3** (shown in Fig. 8) is only the second iron(III) tren N₆ cation that has been isolated to date. This reflects the general instability of the iron(III) tren N₆ complexes

toward reduction to their iron(II) analogues.^{6,7,10} **3** contains two independent iron sites, Fe(1) and Fe(2). Based on the Fe-N_{ap} distance, the Fe(1) and Fe(2) sites of **3** are “N bound” and pseudo seven coordinate “N in”, respectively. Both sites are HS at 100K judging from the Fe-N1 and Fe-N2 bond distances (all > 2.10 Å). **3** exhibits a gradual decrease in magnetic moment with temperature to 4.5 BM at 6K which is consistent with a composition that is 50% LS iron(III) and 50% HS iron(III) as given in the previous section. At 77K the Mössbauer data show that there is partial conversion (18%) to a LS iron(III) species which is consistent with the decreasing magnetic moment. To date there are no structurally characterized examples of LS or SC iron complexes with CN=7 regardless of geometry, with the possible exception of one partially characterized (HS form only) pentagonal bipyramidal biscyano iron(II) macrocycle.³⁰ This complex is HS and seven coordinate at 295 K but on cooling becomes LS. However, it is thought that the complex achieves the LS state by becoming six coordinate. The difficulty of obtaining LS complexes in a seven coordinate environment is in part due to the inherently long bonds in these systems as well as the splitting of the d orbitals in the various CN=7 limiting geometries, which in certain cases rule out LS complexes.³¹ A SC in **3** more likely involves the pseudo seven coordinate site, Fe(2), rather than the “N bound” site, Fe(1), as it would involve less structural reorganization.

The structure of [FeHL¹](I₃)_{0.525}(I)_{0.475}·2.625H₂O **4**, shown in Fig. 9, is unusual in that it features a partially deprotonated ligand and mixed uninegative anions, iodide (I1) and triiodide (I2-I4). The overall conformation of the ligand is “N in”, which is a geometry normally associated with HS iron; but clearly the iron atom is LS as evidenced by its short Fe-N1 and Fe-N2 bonds (< 2.0 Å), its magnetic susceptibility data and its Mössbauer spectrum (see previous sections). The only imidazole bound proton, H91 (site occupancy factor of 0.40), is hydrogen bound to the non iron bound imidazole nitrogen atom, N9', of an adjacent molecule. The N9-H91·····N9' distances, N9-H91 (0.870 Å), H91·····N9' (1.824 Å) and N9·····N9' (2.685 Å), and angle N9-H91·····N9' (169.88°) are normal. This intermolecular imidazole hydrogen bonding was strongly suggested in the IR spectrum of this complex. There is also a weak hydrogen bonding interaction between the water and I4 (disordered) of the triiodide.

A number of observations regarding the effect of charge (due to changes in oxidation or protonation state), hydrogen bonding and flexibility of the aliphatic backbone of H₃L¹ or H₃L² on coordination number and spin state can be made from examination of the data from Table 2. The overall charge of the complex can be varied by changing the oxidation state of the central metal ion ([FeH₃L¹](ClO₄)₃·1.5(EtOH) **3** vs [MnH₃L¹](ClO₄)₂ **1** and [MnH₃L¹](ClO₄)₂·EtOH·H₂O **1**·EtOH·H₂O) while keeping the protonation state constant or by altering the protonation state of the ligand ([FeH₃L¹](ClO₄)₃·1.5(EtOH) **3** vs [FeHL¹](I₃)_{0.525}(I)_{0.475}·2.625H₂O **4** vs [FeL¹]) while holding the metal oxidation state constant. The effect of charge on coordination number and spin state of the complexes can thus be examined.

Comparison of the structures of **3** with the analogous Mn(II) complexes (**1** and **1**·EtOH·H₂O) shows that the higher charge on the iron(III) complex draws N_{ap} closer to the iron atom than it does in the manganese(II) complexes. Both the Fe(1)-N_{ap} and Fe(2)-N_{ap} distances of **3** are less than the analogous values for the Mn(II) complexes. The effect is great enough that Fe(1) is seven coordinate. Another structural feature that is affected is the N1-M-N1 angle. As the charge on the metal ion increases, the M-N_{ap} distance decreases, which draws the metal further into the plane of the three imine nitrogen atoms, causing the N1-M-N1 angle to widen.

The protonation state of [FeHL¹]⁺ is between the HS [FeH₃L¹]³⁺ and LS [FeL¹]. Similarly, its structure exhibits elements between these two extremes. These elements are the Fe-N_{ap} distance, the bite, trans, N1-Fe-N1, N2-Fe-N2, and C1-N-C1 angles. In each case the values for [FeHL¹]⁺ lie between the analogous values for HS [FeH₃L¹]³⁺ and LS [FeL¹], which

suggests that there are stepwise structural and electronic changes between the HS $[\text{FeH}_3\text{L}^1]^{3+}$ and LS $[\text{FeL}^1]$. As protons are removed from HS $[\text{FeH}_3\text{L}^1]^{3+}$, the Fe-N1 and Fe-N2 bonds shorten due to the increased basicity of imidazolate vs imidazole and increased electrostatic attraction, which causes the capping nitrogen atom, N_{ap} , to move farther away from the iron to accommodate the shorter Fe-N1 and Fe-N2 distances. The motion of the capping N_{ap} atom has the effect of opening up the C1-N-C1 angle to the sp^2 angle of 120° and narrowing the N1-Fe-N1 bond angle as the imine nitrogen atoms are now less repulsed by the capping N_{ap} atom. Even though $[\text{FeHL}^1]^+$ lies structurally between HS $[\text{FeH}_3\text{L}^1]^{3+}$ and LS $[\text{FeL}^1]$, it is electronically clearly LS. In fact, it is the only case of the “N in” conformation reported so far that is LS. Synthesis and structural characterization of $[\text{FeH}_2\text{L}^1]^{2+}$ is being pursued to determine if it is consistent with the above arguments.

The effect of hydrogen bonding on spin state can be seen in the comparison of $[\text{FeH}_3\text{L}^3]^{3+}$ with $[\text{FeH}_3\text{L}^1]^{3+}$. The latter is HS at 100K while in contrast $[\text{FeH}_3\text{L}^3]^{3+}$ (isolated as its tetrafluoroborate salt) is LS at 93K and experiences stepwise SC behavior on warming.³² The difference in magnetic properties between these very similar iron(III) cations may be due to the fact that $[\text{FeH}_3\text{L}^3]^{3+}$ is involved in an extensive hydrogen bonding arrangement with 4-imidazolecarboxaldehyde and water while $[\text{FeH}_3\text{L}^1]^{3+}$ lacks these long range hydrogen bonding interactions. The effect of hydrogen bonding is to increase the CFSE of the ligand by partial ionization of the ligand. The stabilization of a LS state by hydrogen bonding has been observed with SC iron(II) complexes and may be responsible for the stabilization of the LS state in $[\text{FeH}_3\text{L}^3]^{3+}$.³³

The adoption of “N bound” CN=7 in **2** rather than “N in” CN=6 as observed in **1** and **1**-EtOH-H₂O is somewhat surprising as the greater flexibility in the three carbon atom backbone of trpn relative to the two carbon atom backbone of tren would allow the apical nitrogen atom, N_{ap} , to move farther away from the metal and avoid congestion around the small first row transition metal ion. Evidence of distortion to achieve CN=7 is seen in a comparison of the aliphatic backbone of trpn, $\text{N}_{\text{ap}}\text{-C1-C2-C3-N1}$ (imine) with the aliphatic backbone of tren, $\text{N}_{\text{ap}}\text{-C1-C2-N1}$ (imine). The average $\text{N}_{\text{ap}}\text{-C1-C2}$ (117.06°), C1-C2-C3 (115.20°), and C2-C3-N1 (112.61°) angles of **2** deviate considerably from 109.5° , suggesting some conformational strain while the average $\text{N}_{\text{ap}}\text{-C1-C2}$ (110.79°) and C1-C2-N1 (108.89°) angles of **1** are close to 109.5° , which suggests little conformational strain. The stabilization provided by the relatively short seventh Mn- N_{ap} bond in **2** may explain the formation of the “N bound” conformation in **2** rather than the “N in” CN=6 conformation observed in **1**.

In summary, the data for the d^5 complexes of H_3L ligands presented in Table 2 show that the M- N_{ap} distance decreases due to a) an increase in oxidation state of the metal b) an increase in the number of bound imidazole protons c) an increase in the number of aliphatic carbon atoms in the backbone of the ligand and d) a lack of significant hydrogen bonding of the metal H_3L complex. If the M- N_{ap} decreases sufficiently the complex adopts the “N bound” (CN=7) capped octahedral conformation and is HS while longer M- N_{ap} distances push the conformation toward P and stabilize the LS state. An illustration of these effects is seen in Fig. 10.

In iron SC complexes of tren imidazole carboxaldehyde ligands there is a structural equilibrium between the “N in” and “P” conformations that is coincident with the SC, LS(“P”) $\rightleftharpoons$ HS(“N in”). In contrast the “N bound” and “N out” are locked into HS and LS states, respectively. No LS manganese(II) complexes have been observed with the fully protonated ligands despite their N_6 donor sets. However, if deprotonation conditions can be found it may be possible to observe the LS state with this ion as well.

Experimental

Elemental analyses were determined by MHW Laboratory, Phoenix, AZ or Galbraith Laboratories, Knoxville, TN. Mass spectral analyses were obtained from HT Laboratories, San Diego, CA. Tris(2-aminoethyl)amine and 4-methyl-5-imidazole carboxaldehyde were obtained from Aldrich. Tris(3-aminopropyl)amine was obtained from TCI. Manganese(II) perchlorate hexahydrate and manganese(II) chloride were obtained from Alfa. Sodium perchlorate monohydrate and sodium iodide were obtained from Fisher. All solvents were of reagent grade and used without further purification. $[\text{FeH}_3\text{L}^1](\text{ClO}_4)_3$ was prepared as described earlier⁶ and recrystallized from ethanol to obtain suitable crystals of **3**.

Spectra

The ^{57}Fe Mössbauer spectra were recorded from powdered samples with a constant acceleration MS1200 Ranger Scientific spectrometer and a ca. 1.85 GBq $^{57}\text{Co}/\text{Rh}$ source. The sample thickness was $\sim 50\text{--}80\text{ mg}/\text{cm}^2$. The line width of the calibration spectrum was 0.29 mm/s. The chemical isomer shift data are quoted relative to the centroid of the metallic iron spectrum at room temperature. The data were analyzed by a constrained least squares fit to Lorentzian shaped lines. IR spectra were obtained as KBr pellets on a Perkin Elmer 1600 FT IR spectrometer.

Structure determinations

Crystal data for $[\text{FeH}_3\text{L}^1](\text{ClO}_4)_3 \cdot 1.5(\text{EtOH})$ **3** were collected on a Bruker SMART Apex three circle diffractometer and data for $[\text{MnH}_3\text{L}^1](\text{ClO}_4)_2$ **1**, $[\text{MnH}_3\text{L}^1](\text{ClO}_4)_2 \cdot \text{EtOH} \cdot \text{H}_2\text{O}$ **1-EtOH-H}_2\text{O}, and $[\text{MnH}_3\text{L}^2](\text{ClO}_4)_2$ **2**, and $[\text{FeHL}^1](\text{I}_3)_{0.525}(\text{I})_{0.475} \cdot 2.625\text{H}_2\text{O}$ **4** were collected on a Bruker SMART 1000 CCD system. All structures were solved using the direct methods program SHELXS-97.³⁴ All nonsolvent heavy atoms were located using subsequent difference Fourier syntheses. The structures were refined against F^2 with the program SHELXL,³⁵ in which all data collected were used including negative intensities. All nonsolvent heavy atoms were refined anisotropically. All nonsolvent hydrogen atoms were idealized using the standard SHELXL idealization methods. Complete crystallographic details are given in the Supporting Information and are summarized in Table 1. A note on the refinement of $[\text{FeHL}^1](\text{I}_3)_{0.525}(\text{I})_{0.475} \cdot 2.625\text{H}_2\text{O}$ needs to be mentioned. An unconstrained solution of this structure revealed a single iron complex cation site on a 32e position with a site occupancy of 1 and two anion sites occupied by iodide and triiodide. The former were in a 24c position with a site occupancy of 0.664 and the latter were in a 32e position with a site occupancy of 0.546. The sum of uninegative ions (iodide and triiodide) totaled 33.408 per 32 complex cations in the unit cell, which required a charge on the cation of +1.044. Since this value was close to unity and there was no other experimental evidence to support a nonintegral charge on the cation, a constraint was placed on the formula, $[\text{FeHL}^1](\text{I}_3)_{(1-x)}(\text{I})_x \cdot 2.625\text{H}_2\text{O}$, which requires that the charge on the cation is fixed at +1. Refinement on this constrained solution altered the site occupancy factors of iodide and triiodide from 0.664 to 0.633 and 0.546 to 0.525, respectively, and had no significant impact on R. Thus, the constrained solution was accepted as the correct one.**

Magnetic measurements

Magnetic susceptibility data were collected on a Quantum Design MPMS-5s SQUID magnetometer. Data were corrected for diamagnetism of the ligands using Pascal's constants. A discussion of general magnetic susceptibility measurements and calibration techniques used can be found elsewhere³⁶. Data were collected at a magnetic field between 500 and 1000 Oe from 6 to 300 K.

Syntheses

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care.

Synthesis of $[\text{MnH}_3\text{L}^1](\text{ClO}_4)_2$ **1** from a Mn(II) salt—4-Methyl-5-

imidazolecarboxaldehyde (0.226 g, 2.05 mmol) and tren (0.098 g, 0.67 mmol) were refluxed in methanol (15 mL) for 10–15 minutes to give a yellow solution. $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.147 g, 0.744 mmol) was added as a solid. The mixture was refluxed for 2.5 hours. An excess of sodium perchlorate monohydrate (0.672 g, 4.80 mmol) in methanol (5 mL) was added. The tan colored solution was heated and filtered while hot and the filtrate was set aside to concentrate. After 5 days a fine yellow-white precipitate (0.132 g, 29%) was removed by suction filtration. Elemental analysis calcd for $\text{C}_{21}\text{H}_{30}\text{N}_{10}\text{Cl}_2\text{MnO}_8$ ($[\text{MnH}_3\text{L}^1](\text{ClO}_4)_2$): C 37.29, H 4.47, N 20.71. Found: C 37.23, H 4.34, N 20.60. ES MS analysis: M/e, ion, %base; (+ion mode) 476, $[\text{MnH}_2\text{L}^1]^+$, 100%; 576, $[\text{MnH}_3\text{L}^1 + \text{ClO}_4]^+$, 6%; (-ion mode) 474, $[\text{MnL}^1]^-$, 44%; 588, $[\text{MnHL}^1 + \text{tfa}]^-$, 100%. Crystals of $[\text{MnH}_3\text{L}^1](\text{ClO}_4)_2 \cdot \text{EtOH} \cdot \text{H}_2\text{O}$ **1**·EtOH·H₂O suitable for x-ray analysis were obtained by recrystallization from ethanol. **1** was also synthesized (77% yield) by an analogous procedure using $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ instead of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and excess $\text{NaClO}_4 \cdot \text{H}_2\text{O}$. A crystal suitable for X-ray analysis was obtained directly from the reaction mixture.

Synthesis of $[\text{MnH}_3\text{L}^1](\text{ClO}_4)_2$ **1** from a Mn(III) salt—4-Methyl-5-

imidazolecarboxaldehyde (0.226 g, 2.05 mmol) and tren (0.098 g, 0.67 mmol) were refluxed in methanol (15 mL) for 10–15 minutes to give a yellow solution. Manganese (III) acetoacetate (0.259 g, 0.735 mmol) was added as a solid, which did not completely dissolve. The mixture was refluxed about 12 hours and filtered while hot to remove 0.110 g of unreacted manganese (III) acetoacetate. The dark brown filtrate was set aside to concentrate. A brown oil resulted. The oil was redissolved in methanol (20 mL) and excess sodium perchlorate monohydrate (0.386 g, 2.76 mmol) in methanol (10 mL) was added. After several days a pale yellow solid (0.204 g, 71% based on manganese(III) acetoacetate reacted) was removed by filtration. Elemental analysis calcd for $\text{C}_{21}\text{H}_{30}\text{N}_{10}\text{Cl}_2\text{MnO}_8$ ($[\text{MnH}_3\text{L}^1](\text{ClO}_4)_2$): C 37.29, H 4.47, N 20.71. Found: C 37.14, H 4.35, N 20.65.

Synthesis of $[\text{MnH}_3\text{L}^2](\text{ClO}_4)_2$ **2**—4-Methyl-5-imidazolecarboxaldehyde (0.167 g, 1.52 mmol) was added to a solution of tris(3-aminopropyl)amine (0.10 mL, 0.50 mmol) in methanol (10 – 15 mL). The solution was refluxed for thirty minutes. To this solution was added manganese(II) perchlorate hexahydrate (0.183 g, 0.50 mmol) and the solution was refluxed a further 30 minutes. The light yellow solution deposited an offwhite powder over three days. Filtration yielded (0.261 g, 0.350 mmol, 70 %). Suitable crystals for x-ray analysis were obtained by recrystallization from methanol. Elemental analysis calcd. for $\text{C}_{24}\text{H}_{36}\text{Cl}_2\text{MnN}_{10}\text{O}_8 \cdot 1.5\text{H}_2\text{O}$ C 38.67, H 5.27, N 18.79%. Found: C 38.56, H 4.69, N 18.90%. ES MS analysis: M/e, ion, %base; (+ion mode) 518, $[\text{MnH}_2\text{L}^2]^+$, 100%; (-ion mode) 516, $[\text{MnL}^2]^-$, 100%; 552, $[\text{MnHL}^2 + \text{Cl}]^-$, 62%; 616, $[\text{MnHL}^2 + \text{ClO}_4]^-$, 58%; 716, $[\text{MnH}_2\text{L}^2 + 2\text{ClO}_4]^-$, 43%.

Synthesis of $[\text{FeHL}^1](\text{I}_3)_{(1-x)}(\text{I})_x \cdot y\text{H}_2\text{O}$ **4**—4-Methyl-5-imidazolecarboxaldehyde (0.106 g, 0.96 mmol) and tren (0.046 g, 0.31 mmol) were refluxed in methanol (10 mL) for 10–15 minutes to give a yellow solution. Anhydrous ferric chloride (0.054 g, 0.33 mmol) in methanol (5 mL) was added. The solution immediately turned purple. The purple solution was refluxed 10–15 minutes. Excess sodium iodide (0.300 g, 2.00 mmol) in methanol (10–15 mL) was added. The solution immediately turned orange/brown. The reaction mixture was allowed to stand overnight during which time the color darkened. Dark green-black cubic crystals (0.174 g, 64%) were removed from the reaction mixture by filtration. Elemental analysis of

the bulk sample calcd for $\text{C}_{21}\text{H}_{34}\text{Fe I}_{2.716}\text{N}_{10}\text{O}_3$ ($[\text{FeHL}^1](\text{I}_3)_{.858}(\text{I})_{.142}\cdot 3\text{H}_2\text{O}$): C 28.83, H 3.93, N 16.02, I 39.40%. Found: C 28.65, H 3.91, N 16.15, I 39.78%. ES MS analysis: M/e, ion, %base; (+ion mode) 477, $[\text{FeH}_2\text{L}^1]^+$, 59%; 239, $[\text{FeH}_3\text{L}^1]^{2+}$, 100%; (-ion mode) 603, $[\text{FeHL}^1 + \text{I}]^-$, 4%; 510, $[\text{FeL}^1 + \text{Cl}]^-$, 12%; 475, $[\text{FeL}^1]^-$, 100%; 381, $[\text{I}_3]^-$, 13%; 127, $[\text{I}]^-$, 8%. The same reaction was repeated using a Fe:I⁻ ratio of 1:1.5 rather than 1:6 and the same color changes were observed. The resultant dark green-black crystals **4** were analyzed by single crystal x-ray analysis ($x = 0.475$ and $y = 2.625$) and the results are given in Tables 1 and 2. A crystal prepared from the 1:6 Fe:I⁻ ratio was also examined by x-ray and found to be F43c cubic with the same cell constants as **4**.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1.
Line drawings of ligands

Fig. 2.

Mössbauer spectrum of $\text{FeHL}^1](\text{I}_3)_{0.525}(\text{I})_{0.475} \cdot 2.625\text{H}_2\text{O}$ **4** at 295K after one month of data collection. Values for isomer shift and quadrupole splitting are -0.042 , 1.96 mm/s (67%) and 0.910 , 1.79 mm/s (33%) respectively.

Fig. 3. Plot of magnetic moment vs temperature for $[\text{MnH}_3\text{L}^1](\text{ClO}_4)_2$ (o) **1**, $[\text{MnH}_3\text{L}^2](\text{ClO}_4)_2$ (+) **2**, $[\text{FeH}_3\text{L}^1](\text{ClO}_4)_3 \cdot 1.5(\text{EtOH})$ (•) **3** and $[\text{FeHL}^1](\text{I}_3)_{0.525}(\text{I})_{0.475} \cdot 2.625\text{H}_2\text{O}$ (Δ) **4**.

Fig. 4.
Conformations of N_{ap} in iron tren imidazole complexes

Fig. 5.

Histogram of structurally characterized N_6 and N_7 iron complexes of tren. The Fe- N_{ap} distance is on the x axis and the number of complexes from the CCDC database on the y axis. The light blue color corresponds to the CN=7 and pseudo seven coordinate complexes.

Fig. 6. ORTEP diagram of $[\text{MnH}_3\text{L}^1](\text{ClO}_4)_2$ **1**. Atoms are contoured at the 50% probability level. Perchlorate anions have been omitted for clarity.

Fig. 7. ORTEP diagram of [MnH₃L²](ClO₄)₂ **2**. Atoms are contoured at the 50% probability level. Perchlorate anions have been omitted for clarity.

Fig. 8. ORTEP diagram of $[\text{FeH}_3\text{L}^1](\text{ClO}_4)_3 \cdot 1.5(\text{EtOH})$ **3**. Fe(1) CN=7 is pictured on left and Fe(2) pseudo seven coordinate on right. Atoms are contoured at the 50% probability level. The perchlorate anions and hydrogen atoms have been omitted for clarity.

Fig. 9. ORTEP diagram of $[\text{FeHL}^1](\text{I}_3)_{0.525}(\text{I})_{0.475} \cdot 2.625\text{H}_2\text{O}$ 4. The iodide, triiodide and water have been omitted for clarity. Atoms are contoured at the 50% probability level. H91 has a sof of 0.4.

Fig. 10.

Confirmation of the aliphatic backbone of complexes in order of increasing M-N_{ap} bond distance from top left to bottom right. [MnH₃L²](ClO₄)₂ **2** [FeH₃L¹](ClO₄)₃·1.5(EtOH) **3** Fe(1) site, [FeH₃L¹](ClO₄)₃·1.5(EtOH) **3** Fe(2) site, [MnH₃L¹](ClO₄)₂ **1**, [FeHL¹](I₃)_{0.525}(I)_{0.475}·2.625H₂O **4** and [FeL¹].

Table 1

Crystallographic Data for $[\text{MnH}_3\text{L}^1](\text{ClO}_4)_2$ **1**, $[\text{MnH}_3\text{L}^1](\text{ClO}_4)_2 \cdot \text{EtOH} \cdot \text{H}_2\text{O}$ **1**·EtOH ·H₂O, $[\text{MnH}_3\text{L}^2](\text{ClO}_4)_2$ **2**, $[\text{FeH}_3\text{L}^1](\text{ClO}_4)_3 \cdot 1.5(\text{EtOH})$ **3**, $[\text{FeHL}^1](\text{I}_3)_{0.525} \cdot 2.625\text{H}_2\text{O}$ **4**

Empirical formula	1 $\text{C}_{21}\text{H}_{30}\text{Cl}_2\text{MnN}_{10}\text{O}_8$	1·EtOH·H₂O $\text{C}_{23}\text{H}_{38}\text{Cl}_2\text{MnN}_{10}\text{O}_{10}$	2 $\text{C}_{24}\text{H}_{36}\text{Cl}_2\text{MnN}_{10}\text{O}_8$	3 $\text{C}_{16}\text{H}_{26}\text{Cl}_2\text{Fe}_{0.67}\text{N}_{6.67}\text{O}_9$	4 $\text{C}_{21}\text{H}_{33.25}\text{FeI}_{2.05}\text{FeN}_{10}$
M/ g mol ⁻¹	676.39	740.47	718.47	563.90	783.82
Temperature/K	173	173	233(2)	100	233(2)
$\lambda/\text{\AA}$	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal System	Monoclinic	Monoclinic	Triclinic	Rhombohedral	Cubic
Space group	P2(1)/c	P2(1)/c	P-1	R3	F43c
Unit cell dimensions	a=11.3654(3) Å, b=20.6178(6) Å, c=12.9278(4) Å, $\alpha=90^\circ$ $\beta=102.9010(10)^\circ$ $\gamma=90^\circ$	a=16.6695(4) Å b=15.4756(4) Å c=12.9951(3) Å $\alpha=90^\circ$ $\beta=104.1190(10)^\circ$ $\gamma=90^\circ$	a=11.8154(5) Å b=12.2056(6) Å c=12.3982(6) Å $\alpha=78.8630(10)^\circ$ $\beta=70.7890(10)^\circ$ $\gamma=67.4000(10)^\circ$	a=16.5805(8) Å b=16.5805(8) Å c=22.0774(15) Å $\alpha=90^\circ$ $\beta=90^\circ$ $\gamma=120^\circ$	a=29.6863(3) Å $\alpha=90^\circ$
Volume/ Å ³	2952.90(15)	3251.08(14)	1554.20(13)	5256.2(5)	26161.8(5)
Z	4	4	2	9	32
Abs. Coeff./mm ⁻¹	0.690	0.638	0.660	0.737	2.432
F(000)	1396	1540	746	2628	12317
Crystal size/ mm ³	0.49 x 0.46 x 0.11	0.42 x 0.35 x 0.35	0.35 x 0.28 x 0.25	0.5 x 0.4 x 0.4	0.370 x 0.290 x 0.260
Theta range/ °	1.98 to 27.50	2.08 to 27.50	2.61 to 27.50	2.33 to 28.29	2.74 to 27.50
Index ranges	-14 ≤ h ≤ 14 -26 ≤ k ≤ 26 -16 ≤ l ≤ 16	-21 ≤ h ≤ 21 -20 ≤ k ≤ 20 -16 ≤ l ≤ 16	-15 ≤ h ≤ 15 -15 ≤ k ≤ 15 -15 ≤ l ≤ 16	-22 ≤ h ≤ 22 -22 ≤ k ≤ 29 -29 ≤ l ≤ 29	-37 ≤ h ≤ 38 -38 ≤ k ≤ 38 -38 ≤ l ≤ 38
Reflections Collected	47247	61025	14610	18624	54720
Independent Reflections	6775 [R(int)=0.0261]	7462 [R(int)=0.0194]	7042	5525 [R(int)=0.0244]	2519
R1	0.0378	0.0403	.0369	0.0390	.0494
wR2	0.1034	0.1151	.0836	0.1023	.1512
GOF	1.096	1.107	1.020	1.044	1.004

Table 2

Selected bond distances (Å) and angles (°) for a) LS [FeH₃L³](BF₄)₃·(4-fim)^aH₂O^b b) HS[FeH₃L³](BF₄)₃·(4-fim)^a·H₂O^b, c) HS [FeH₃L¹](ClO₄)₃·1.5(EtOH)^{c,d} **3**, d) [FeHL¹](I₃)_{0.525}(I)_{0.475}·2.625H₂O^{c,e} **4**, e) LS [FeL¹]·2H₂O·CH₂Cl₂^f f) HS [MnH₃L¹](ClO₄)₂^c **1**, g) HS [MnH₃L¹](ClO₄)₂·EtOH·H₂O^c **1**·EtOH·H₂O, and h) HS [MnH₃L²](ClO₄)₂^c **2**. The labeling scheme employed for the arms of the tren and trpn complexes is N_{ap}(C1-C2-N1=C3(H)(Im))₃ and N_{ap}(C1-C2-C3-N1=C4(H)(Im))₃. N2 is the metal bound imidazole nitrogen atom.

	a	b	c	D	e	f	g	h
T(K)	93	296	100	233	130	173	173	233
M-N _{ap}	3.170	2.762	2.585, 2.719	3.134	3.346	2.9869	2.8401	2.5176 (15)
M-N1 (imine)	1.974 (2) 1.990 (2) 1.982 (3) average 1.982 M- 1.941 N2 (imidazole) (2) 1.955 (3) 1.961 (2) average 1.952 N1-M-N2 (bite) 81.0(1)	2.060 (3) 2.088 (3) 2.078 (3) 2.075 2.091 (3) 2.112 (3) 2.118 (3) 2.107 2.107 (1)	2.109(3) 2.109(3) 2.109 2.164(3) 2.139(3) 2.152 76.08(11)	1.978 (4) 1.978 1.937 (4) 1.937 80.61 (18)	1.987(2) 1.979(2) 1.978(2) 1.981 1.941(2) 1.936(2) 1.945(2) 1.941 81.11(7)	2.2693 (15) 2.2521 (14) 2.2740 (15) 2.2651 2.2534 (15) 2.2928 (15) 2.2963 (14) 2.2808 73.51(5)	2.2499 (14) 2.2552 (15) 2.2647 (15) 2.2566 2.2850 (15) 2.3046 (16) 2.3278 (15) 2.3058 73.40(5)	2.3001 (15) 2.3026 (15) 2.3145 (15) 2.3057 2.3471 (16) 2.3517 (16) 2.3767 (15) 2.3586 71.75(6)
Average N1-M- N2' (trans)	81.0(1) 80.5(1) 80.8 176.0 (1) 171.8 (1) 173.9 (1) average 173.9 N1-M-N1 98.8(1) 99.4(1) 99.4(1) Average 99.2 N2-M-N2 90.9(1)	76.2(1) 76.5(1) 76.5 165.2 (1) 161.5 (1) 163.8 (1) 163.5 107.1 (1) 106.0 (1) 105.8 (1) 106.3 85.9(1)	75.85(12) 75.97 157.08(12) 159.29(12) 158.19 108.91(9) 106.74(9) 107.83 81.68(12)	80.61 173.54 (19) 173.54 99.14 (16) 99.14 92.94 (18)	81.39(7) 81.56(8) 81.35 174.38 (7) 175.94 (8) 175.58 (8) 175.30 96.35(8) 96.88(7) 96.28(7) 96.50 93.64(7)	73.17(5) 73.46(5) 73.38 159.34 (6) 165.54 (6) 158.55 (5) 161.14 101.31 (5) 102.70 (5) 100.99 (6) 101.67 87.03(6)	73.69(5) 72.59(5) 73.23 161.05 (5) 160.33 (6) 156.06 (5) 159.15 104.41 (5) 105.12 (5) 104.32 (6) 104.62 87.76(5)	71.36(5) 71.56(5) 71.56 157.94 (6) 157.60 (6) 159.90 (6) 158.38 117.05 (6) 114.05 (6) 112.70 (5) 114.60 88.50(6)
average C1-N-C1	93.1 118.8 (2) 117.7 (2) 118.9 (2) average 118.5	87.4 113.3 (3) 113.1 (4) 114.8 (4) 113.7	82.63 111.32(19) 112.7(2) 112.0	92.94 117.9 (2) 117.9	94.36 119.9(2) 119.9(2) 119.0(2) 119.6	89.00 113.52 (15) 114.11 (15) 113.41 (15) 113.68	86.28 112.52 (15) 112.78 (15) 112.81 (14) 112.70	90.76 107.92 (15) 108.35 (15) 108.05 (14) 108.11

^a 4-fim is 4-imidazole carboxaldehyde

^b Data from reference ³²

^c this work

^d two values are given for this compound as there are two independent cations each of which has 3 fold symmetry

^e the iron cation has three fold symmetry

^f Data from reference ^{6a}