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Amidino-Complexes of Iron(II) and (III)

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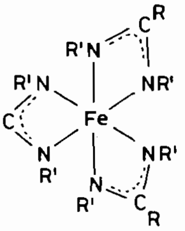
Lithioamidines $\{R'N(Li)C(R)NR'$, *I;* $R = CH_3$, $R' = C_6H_5$, $p\text{-}CH_3C_6H_4\}$ *react with iron(III) chloride*



I

in monoglyme to produce navy-blue, high spin $Fe\{R'NC(R)NR'\}_3$ *complexes which are extremely air and moisture sensitive. The corresponding reaction when* $R = R' = C_6H_5$ *produces a soluble red complex and an air-stable green complex, whereas when* $R = H$, $R' = C_6H_5$ *and* $R = R' = C_6H_5$ *and the reaction is started at* ca. *–20°, red and green complexes respectively are formed. Though all the complexes are formulated* $Fe\{R'NC(R)NR'\}_3$, *their properties reflect association through bridging amidino-groups. Iron(II) chloride reacts with* $I(R = CH_3$, $R' = p\text{-}CH_3C_6H_4)$ *to form two complexes, one crimson and soluble in organic solvents, and one brown and insoluble, which are formulated* $[Fe\{R'NC(R)NR'\}_2]_n$. *The iron(III) complexes failed to react with, or were decomposed by, a variety of reducing, electrophilic and nucleophilic reagents, though blue* $Fe\{p\text{-}CH_3C_6H_4NC(CH_3)N\text{-}p\text{-}CH_3C_6H_4\}_3$ *reacts readily with nitric oxide to form a purple addition complex from which the N-nitroso-compound* $p\text{-}CH_3C_6H_4NC(CH_3)N(NO)\text{-}p\text{-}CH_3C_6H_4$ *was obtained in high yield. Treatment of the corresponding brown iron(II) complex with nitric oxide gave no reaction.*

Binary amidino–transition metal and the isoelectronic triazenido–transition metal complexes are known for several metals, including chromium molybdenum [1, 2], cobalt [3–5], nickel [6–9], palladium, platinum [10–12], copper [7, 9, 13–19], and silver [20]. Benzamidinomolybdenum(II) [1] and –copper(II) [19] complexes have dimeric structures with four bridging amidino-groups. The short metal–metal distances in the crystal structure infer quadruple and single metal–metal bonds respectively. The 1,3-dimethyltriazenocopper(I) complex has a tetrameric structure with single amidino-bridges between adjacent coppers [17] whereas the 1,3-diphenyltriazenocopper(I) has a dimeric structure with two bridges between the metals [16]. Equilibria between dimer–tetramer have been established for related formamidino-complexes [20]. Amidino-bridges have also been established between two different transition metals, such as platinum and silver [21], rhodium and mercury [22] *etc.*, in dinuclear mixed ligand complexes. In contrast, the structures of amidino–palladium complexes depend on the amidino-substituents at the skeletal NCN carbon atom. For $Pd\{R'NC(R)NR'\}_2$ complexes, where R = H, the complexes are dimeric with amidino-bridges [12], whereas when $R = CH_3$ the complexes are monomeric with symmetrical delocalised chelate groups [11]. Interestingly the triazenidocobalt(III) complex is also monomeric and has three chelated ligand groups in a distorted octahedral arrangement [3].

Our study of binary amidino–transition metal complexes has been extended to complexes of iron, with the objective of studying the reactions at the metal whose coordination geometry, if related to $Co\{C_6H_5NNNC_6H_5\}_3$ [3], will be highly modified by the three 4-membered metallocycles. Complexes of the type $Fe\{R'NC(R)NR'\}_3$ are reported here, some of which are monomeric and others oligomeric or polymeric. The monomeric complexes are particularly reactive, though a derivative could be isolated only with nitric oxide. This complex provides a synthetic route to a N-nitrosoamidine.

Results and Discussion

A. Amidino–iron(III) Complexes

The complexes described in this paper proved to be extremely sensitive to moisture and oxygen, both

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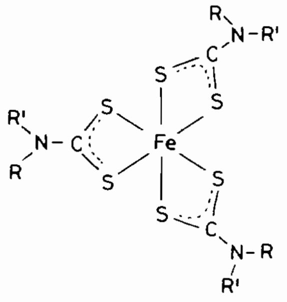
in solution and in the solid state, and great care was required to exclude both at all stages of the preparations, isolations and subsequent investigations. The reaction between LiDPAA[†] or LiDPTAA and iron(III) chloride in monoglyme proceeded smoothly to the navy-blue complexes, $Fe(DPAA)_3$ and $Fe(DPTAA)_3$ respectively, without any apparent intermediate stage. Mass spectral data indicate a monomeric structure and a structure (I) similar to that of $Co\{C_6H_5N_3C_6H_5\}_3$ [3] is consistent with the data. The complexes are soluble in most organic solvents, but decomposition is rapid with the slightest contact with air or moisture. The products are free amidine and an unidentified orange coloured hygroscopic iron hydroxy species.

In the mass spectrometer the complexes fragment by the loss of whole amidino-groups, and spectra are notably simple in having isotopic distribution patterns only for $Fe(Am)_3^+$, $Fe(Am)_2^+$ and $Fe(Am)^+$ ions above the peak for Am^+. Great difficulty was encountered to observe the parent ion, and it was detected only when low source temperatures (*ca.* 100°) were used. The relative ion current associated with the iron containing ions was in the order $Fe(Am)_2^+ > Fe(Am)^+ > Fe(Am)_3^+$. Because of the propensity of the amidino-group to bridge between metal centres, a search was made in the m.s. for dinuclear iron species but none were observed.

The ease with which the complexes decomposed in air prevented satisfactory i.r. spectra from being recorded. The complexes appeared to decompose when exposed to the atmosphere of a nitrogen glovebox having a combined oxygen/water level of less than 2 ppm. Resultant nujol mulls (prepared using sodium dried nujol) showed spectra only of the free amidines. The presence of paramagnetic iron(III) prevented suitable ^1H n.m.r. spectra being recorded, though n.m.r. spectroscopy did provide a useful means of determining the magnetic moments of the complexes. The method, described by Deutsch and Poling [23], gave μ_{eff} values of 5.0 and 4.7 B.M. for $Fe(DPAA)_3$ and $Fe(DPTAA)_3$ respectively, values which correspond to four rather than the five expected unpaired electrons. The values are somewhat lower than those normally associated with classical octahedral iron(III) complexes (μ_{eff} 5.9 B.M.) [24] and require further comment. Four possible explanations exist *viz.* (i) the experiment is inaccurate, (ii) a high spin–low spin crossover mechanism operates, (iii) the iron is in a + II oxidation state, or (iv) the sample has decomposed partially prior to the filling of the capillary tubes used for the ^1H n.m.r. experiments.

The accuracy of the experiment was tested by determining the magnetic moments of tris-2,4-pentanedionatoiron(III) and –chromium(III) complexes. Using freshly prepared solutions a value of μ_{eff} = 5.91 B.M. was obtained for $Fe(acac)_3$, and values of 3.86, 3.95 and 3.89 B.M. for $Cr(acac)_3$ solutions of three different concentrations. These values compare well with literature μ_{eff} values of 5.95 B.M. for $Fe(acac)_3$ [25] and 3.86 B.M. for $Cr(acac)_3$ [26], and give confidence in the method used.

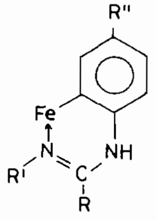
The high spin-low cross-over explanation was closely examined in view of the occurrence of such a phenomenon for the iso-electronic and possibly isostructural tris-dithiocarbamatoiron(III) complexes (II) [27]. The trigonally distorted octahedral structure does not change greatly the electronic states from those of O_h symmetry, and calculations show that the magnetic properties are insensitive to the small splittings caused by this distortion [27]. Consequently the magnetic properties are interpreted assuming O_h symmetry, and the ground states for high and low spin configurations are $^6A_{1g}(t_{2g}{}^3l_g{}^2)$ and $^2T_{2g}(t_{2g}{}^5l_g{}^0)$ respectively. With most R substituents the $^2T_{2g}$ state lies several hundred wave numbers below the $^6A_{1g}$ state, and at low temperatures μ_{eff} tends towards the value of 2.1 B.M. characteristic of the low spin state. As the temperature is raised the molecules begin to populate the high spin state and μ_{eff} rises following a sigmoidal curve which approaches an asymptotic limit. The behaviour is illustrated in Fig. 1 for a typical case where the



II

[†] The following abbreviations are used: AmH = amidine R'NHC(R)NR' (R = H, CH_3, C_6H_5; R = C_6H_5, p-$CH_3C_6H_4$); Am = amidino-group R'NC(R)NR'; *o*-met = ortho-metallated.

(*o*-met–Fe(AmH) =



DPAAH = N,N'-diphenylacetamidine, $C_6H_5NHC(CH_3)NC_6H_5$; DPAA = N,N'-diphenylacetamidino, $C_6H_5NC(CH_3)NC_6H_5$; DPTAAH = N,N'-di-p-tolylacetamidine, p-$CH_3C_6H_4NHC(CH_3)N$-p-$CH_3C_6H_4$; DPTAA = N,N'-di-p-tolylacetamidino, p-$CH_3C_6H_4NC(CH_3)N$-p-$CH_3C_6H_4$; DPBAH = N,N'-diphenylbenzamidine, $C_6H_5NHC(C_6H_5)NC_6H_5$; DPBA = N,N'-diphenylbenzamidino, $C_6H_5NC(C_6H_5)NC_6H_5$; DPFAH = N,N'-diphenylformamidine, $C_6H_5NHCHNC_6H_5$; DPFA = N,N'-diphenylformamidino, $C_6H_5NCHNC_6H_5$.

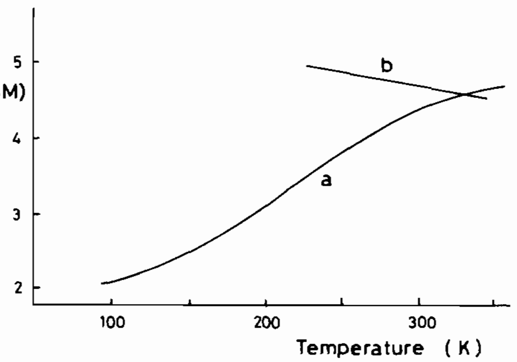


Fig. 1. Variation of the magnetic moment, μ_{eff}, with temperature for a) Fe$\{S_2CNRR'\}_3$ complexes (R = R' = C_nH_{2n+1}) [27], and b) Fe$\{p\text{-}CH_3C_6H_4NC(CH_3)N\text{-}p\text{-}CH_3C_6H_4\}_3$.

energy difference between the high and low spin states is within the range 50–150 cm^{-1} [27].

The variable temperature measurements performed on Fe(DPTAA)$_3$ showed μ_{eff} to vary to a small extent only over a 65° temperature range, and unlike the corresponding dithiocarbamato-complexes a decrease in μ_{eff} with increasing temperature was found (Fig. 1). Further a plot of molar susceptibility versus the reciprocal of temperature shows Fe(DPTAA)$_3$ to adhere closely to the Curie–Weiss law. Thus a high–low spin cross-over effect is not the reason for the low μ_{eff} values for the amidine complexes.

That the complexes Fe(DPAA)$_3$ and Fe(DPTAA)$_3$ contain iron(II) rather than (III) also appears unlikely in view of the different types of complexes produced when starting from an iron(II) precursor. Rather the low μ_{eff} values seem more likely to arise through partial decomposition of the complex. Though steps were taken to eliminate moisture and oxygen from solvents and equipment used, the high reactivity of the complexes require that this is done very efficiently. In the absence of a more plausible explanation we conclude that the low results arise from the separation of solid decomposition products in the vessel used to prepare the test solution, which were not quantitatively transferred to the capillary tube for the n.m.r. experiment. Such a conclusion is in character with the known handling problems of the complexes.

The reaction of LiDPBA with iron(III) chloride is interesting since it is the only reaction of this type which appears to give more than one product, a very reactive red complex in solution and an air-stable green solid. The latter is formulated as Fe(DPBA)$_3$ on the basis of elemental analysis, but its insolubility in organic solvents and stability to air and water suggest a different structure to that assigned to the acetamidino- and formamidino-complexes. The parent ion in the mass spectrum corresponds to Fe(DPBA)$_3^+$, with no evidence for di-iron species. The complex is paramagnetic (μ_{eff} 5.47 ± 0.50 B.M.). The lack of solubility suggests a dimeric, oligomeric or polymeric structure, and the m.s. and magnetic data are in keeping with a product having no formal Fe–Fe bond. An amidino-bridged structure is suggested for which various possibilities are shown in Fig. 2.

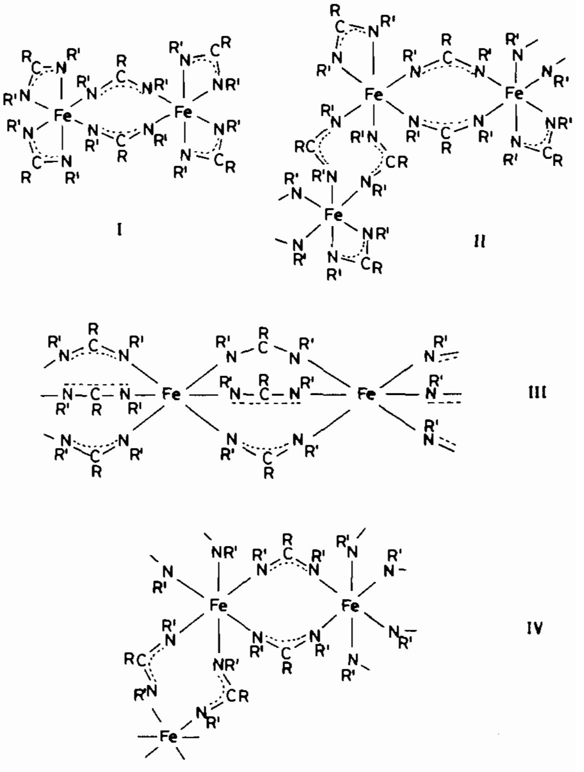


Fig. 2. Possible structures for [Fe$\{R'NC(R)NR'\}_3]_n$ complexes.

The red species formed in solution was not identified, but its solubility, deep colour and sensitivity to air suggests a close analogy with Fe(DPAA)$_3$ and Fe(DPTAA)$_3$ discussed previously. Also similar red solutions were produced when iron(III) chloride in monoglyme and lithioamidine (LiDPFA, LiDPBA) solutions were mixed at −20°. The main products from these reactions separated from solution, and though formulated as Fe(Am)$_3$, they differ in many respects from the complexes previously described. [Fe$\{C_6H_5NC(C_6H_5)NC_6H_5\}_3]_n$ is bright green and [Fe$\{C_6H_5NCHNC_6H_5\}_3]_n$ red-black. Solubility in organic solvents differs widely from complex to complex, and it is concluded that though all the complexes are formulated as Fe(Am)$_3$, the differences between the navy-blue, bright green and red or red-black complexes arise from different degrees or types of association through amidino-bridges.

The Fe(Am)$_3$ and [Fe(Am)$_3]_n$ complexes were involatile, and could not be sublimed when heated to 100° in a high vacuum. Above this temperature decomposition occurred, free amidine being produced which sublimed from the residue. Interestingly the possibility exists for retaining iron(III) in the decomposition process by abstraction of a proton from a coordinated amidino-group to form an *ortho*-metallated complex and the parent amidine, but a mass spectral study of blue $Fe(DPAA)_3$ showed no evidence for $[(o\text{-met})Fe(DPAA)]^+$ having particular stability. Analysis of the sublimation residue indicated the presence of the original navy-blue complex in a non-amidine iron decomposition material.

B. Amidino–iron(II) Complexes

Two products were isolated from the reaction of iron(II) chloride with the lithioamidine, LiDPTAA, an insoluble brown powder (73%) and a soluble crimson solid (21%). Both products analyse correctly for $[Fe(DPTAA)_2]_n$ and the latter product was shown by ^1H n.m.r. to be paramagnetic. Both complexes were extremely sensitive to air, and precluded study by i.r. spectroscopy. On the evidence available it seems likely that the crimson product is monomeric, or dimeric with amidine bridges, and the brown powder polymeric.

C. Reactions of $Fe\{p\text{-}CH_3C_6H_4NC(CH_3)N\text{-}p\text{-}CH_3\text{-}C_6H_4\}_3$

Because of the acute sensitivity of the blue $Fe\{R'NC(CH_3)NR'\}_3$ complexes towards air and moisture, attempts were made to produce more stable derivatives, and to discover whether the complexes were affected by reduction, electrophilic and nucleophilic reagents. Consequently, reactions with a whole variety of reagents were attempted. Triphenylphosphine, iodine, hex-1-ene, 2,2′-bipyridine failed to react with $Fe(DPTAA)_3$ in refluxing monoglyme, and ammonia failed to react at ambient temperature. Sodium amalgam caused decomposition to a yellow gum, and $Et_2O\cdot BF_3$ produced a brown gum which were not investigated further. With nitric oxide the blue solution changed to a red-brown solution, from which a brown solid separated. Recrystallisation from its purple solution in CH_2Cl_2 gave a purple solid. Solutions of this complex readily decomposed in the absence of air to form a yellow solution from which yellow crystals of $p\text{-}CH_3C_6H_4N{:}C(CH_3)N(NO)\text{–}p\text{-}CH_3C_6H_4$ were isolated. Repeated attempts to identify the purple solid by elemental analysis gave inconsistent data and daughter ions only could be identified in the m.s. The ^1H n.m.r. spectrum showed the complex to contain paramagnetic iron. The complex is believed to be of the type $Fe(DPTAA)_3(NO)_x$ where x is probably 3.

Nitrosoamines can be prepared by the action of nitric oxide on amine solutions in organic solvents, the nitrosation taking place through the intermediacy of N_2O_3 or N_2O_4 formed by the presence of oxygen or moisture in the reaction mixture [28]. Attempts to prepare the nitrosoamidine by the action of NO on DPTAAH failed, even when air and moisture were admitted. The formation of nitrosoamidine must therefore occur at the metal centre, and it is likely that initial attack occurs at the metal in solutions of $Fe(DPTAA)_3$ (see Fig. 3). Strong coordination by NO would weaken the metal-amidine bonding, and promote nucleophilic attack by an uncoordinated nitrogen of an amidino-group at the nitrosyl ligand. The $Fe(DPTAA)_2(DPTAANO)$ complex thus formed can then undergo further reaction to form $Fe(DPTAANO)_3$ and possibly $Fe(DPTAANO)_3\cdot NO$. Decomposition would produce DPTAANO.

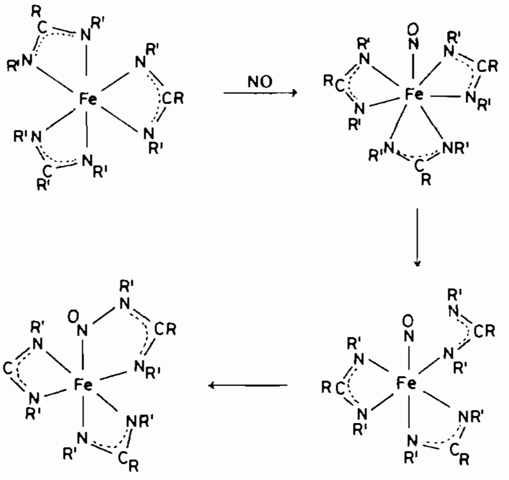


Fig. 3. Possible reaction scheme for the iron promoted nitrosation of an amidino-ligand.

Treatment of the brown powder $[Fe(DPTAA)_2]_n$ with nitric oxide did not produce a similar reaction. The brown complex was recovered unchanged.

Alternative pathways to preparing amidino–iron complexes were explored, and included refluxing $Fe(acac)_3$ with DPTAAH in monoglyme, and a series of Carius tube reactions of DPTAAH with $Fe(acac)_3$, $FeCl_3$, $(\eta^5\text{-}C_5H_5)_2Fe$ and $FeCl_2$. Starting materials were recovered from all reactions except for that with $FeCl_2$ which led to the isolation of an orange powder formulated as $FeCl_3(DPTAAHHCl)_3$ and a grey powder believed to be metallic iron. The material decomposes at a low temperature (65°) and interestingly, the i.r. spectrum of the product is considerably simpler than those of DPTAAH and the hydrochloride salt, indicating a higher symmetry. The ratio of Fe:Cl of 1:6 is not the usual ratio for a chloroiron(III) complex, though in the solid state of $FeCl_3$ the iron occupies octahedral holes in a chloride ion lattice. Since the colour of the present compound and $FeCl_3$ are very similar, it is conceivable that a related geometry about the iron is achieved in an inclusion type complex as shown in Fig. 4. This type of structure is consistent with the low decomposition temper-

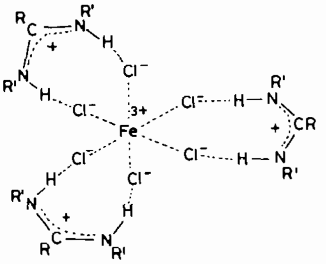


Fig. 4. Possible structure for $FeCl_3 \cdot 3\{p\text{-}CH_3C_6H_4NHC(CH_3)\text{-}NH\text{-}p\text{-}CH_3C_6H_4\}^+Cl^-$.

ature (65°) and its ready decomposition to DPTAAH. Various attempts at preparing such materials directly from iron(III) chloride and amidinium hydrochlorides in the presence or absence of a solvent proved unsuccessful.

Experimental

The acetamidines and benzamidines were prepared by standard methods, and the formamidine purchased commercially. Anhydrous iron(II) and iron(III) chlorides, n-butyllithium in hexane solution and nitric oxide were used as supplied by the chemical companies without further purification. All solvents were dried and rigorously degassed before use. Reactions were undertaken under an atmosphere of nitrogen.

I.r. spectra were recorded on a Perkin-Elmer 456 spectrometer, and ^1H n.m.r. spectra on a Bruker HX90E spectrometer modified for F.T. operation using a Nicolet B.N.C. 12 computer. Carbon, hydrogen and nitrogen contents were determined using a Perkin-Elmer 240 Elemental Analyser, and iron contents determined using a Perkin-Elmer 403 Atomic Absorption Spectrophotometer.

Reaction of Iron(III) Chloride with $\{C_6H_5N(Li)C(CH_3)NC_6H_5\}$ *in a 1:3 Molar Ratio*

A solution of the lithio-reagent was prepared by dissolving DPAAH (3.91 g, 18.6 mmol) in monoglyme (20 ml), freezing to −196°, and then adding n-butyllithium (18.6 mmol) in hexane. The mixture was warmed to room temperature and stirred for about 15 m. The pale yellow solution thus formed, was slowly added to a stirred solution of anhydrous $FeCl_3$ (1.00 g, 6.20 mmol) in monoglyme (10 ml), cooled to *ca.* −20°. The iron solution darkened as soon as the lithio-reagent was added, gradually changing colour from yellow to blue-green and finally to navy-blue. After all the lithio-reagent had been added, the solution was stirred at room temperature for 1/2 h. to ensure complete reaction. The monoglyme was removed *in vacuo* and the residue extracted with toluene (40 ml). Filtration of the solution, followed by reduction to small bulk (15 ml) *in vacuo*, addition of hexane and cooling to −10°, gave navy-blue plate-like crystals of $Fe\{C_6H_5NC(CH_3)NC_6H_5\}_3$ (m. 134° (dec.); yield 3.12 g, 74%). Found C, 74.0; H, 5.74; N, 12.3; Fe, 7.96; $C_{42}H_{39}N_6Fe$ requires C, 73.8; H, 5.76; N, 12.3; Fe, 8.17%. M.s.: The parent ion was observed at $^m/e$ 683 with daughter ions at $^m/e$ 464 $[Fe(DPAA)_2]^+$, and $^m/e$ 209 $[DPAAH]^+$. Metastable ions were not observed.

Reaction of Iron(III) Chloride with $\{p\text{-tolyl}\text{-}N(Li)\text{-}C(CH_3)N\text{-}p\text{-tolyl}\}$ *in a 1:3 Molar Ratio*

The experimental procedure was identical to the reaction described above. The navy-blue crystalline product $Fe\{p\text{-}CH_3C_6H_4NC(CH_3)N\text{-}p\text{-}CH_3C_6H_4\}_3$ (m. 110° dec.) was obtained in 75% yield. Found: C, 74.9; H, 6.65; N, 10.9; Fe, 7.60; $C_{48}H_{51}N_6Fe$ requires C, 75.1; H, 6.70; N, 10.9; Fe, 7.27%. M.s.: The parent ion was observed at $^m/e$ 767 with daughter ions at $^m/e$ 530 $[Fe(DPTAA)_2]^+$, $^m/e$ 293 $[Fe(DPTAA)]^+$ and $^m/e$ 238 $[DPTAAH]^+$. Metastable ions were not observed.

Reaction of Iron(III) Chloride with $\{C_6H_5N(Li)C(C_6H_5)NC_6H_5\}$ *in a 1:3 Molar Ratio*

A solution of the lithio-reagent was prepared by dissolving DPBAH (1.51 g, 5.55 mmol) in monoglyme (25 ml), freezing it to −196° and then n-BuLi solution (5.55 mmol in hexane) was added. The mixture was allowed to warm slowly to ambient temperature, then stirred for 15 m. The resulting yellow solution was slowly added to a solution of anhydrous $FeCl_3$ (0.300 g, 1.85 mmol) in monoglyme (10 ml) at −20°. The pale blue solution which formed immediately changed to a green solution after 30 sec; a green precipitate was then deposited. The mixture was stirred at room temperature for 1/2 h., then filtered to give a red solution and a bright green precipitate. The precipitate was washed with toluene (4 X 10 ml), dried *in vacuo*, washed with water (4 X 5 ml), and finally dried *in vacuo* to yield the product, $Fe\{C_6H_5NC(C_6H_5)NC_6H_5\}_3$, as a bright green powder (m. 95° dec.; yield 1.20 g, 75%). Found: C, 78.4; H, 5.02; N, 9.60; Fe, 5.23; $C_{57}H_{45}N_6Fe$ requires C, 78.4; H, 5.06; N, 9.62; Fe, 6.28%. M.s.: The parent ion was observed at $^m/e$ 869 with the daughter ions given below. The major peak in the spectrum was due to $DPBA^+$ at $^m/e$ 271. Magnetic moment: μ_{eff} 5.4 B.M.

Ion	$^m/e$	Relative peak height
$Fe(DPBA)_3^+$	869	28
$Fe(DPBA)_2^+$	598	100
$Fe(DPBA)\{PhNC(Ph)NH_2\}^+$	523	7

(continued overleaf)

(continued)

Ion	${}^{m}/e$	Relative peak height
$Fe(DPBA)(Ph_2N)^+$	495	16
$Fe(DPBA)(PhN)^+$	418	10
$Fe(DPBA)(Ph)^+$	404	17
$Fe(DPBA)^+$	327	73

Reaction of Iron(III) Chloride with $C_6H_5N(Li)CHNC_6H_5$ in a 1:3 Molar Ratio

A solution of LiDPFA was prepared from DPFAH (3.55 g, 18.6 mmol) in monoglyme (30 ml) as described above. The pale yellow lithio-reagent was slowly added to a stirred solution of anhydrous $FeCl_3$ (1.00 g, 6.20 mmol) in monoglyme (10 ml) at −20°. An immediate colour change from yellow to dark red occurred on mixing but no further changes occurred on stirring the solution at room temperature for 1/2 h. After removing the solvent *in vacuo*, the red-black residue was extracted with CCl_4 (40 ml). The solution was filtered, reduced in volume to 10 ml *in vacuo*, and hexane (10 ml) added. The red-black solid, $Fe\{C_6H_5NCHNC_6H_5\}_3$ (dec. 85°) was collected by filtration (yield 3.07 g, 77%). Found: C, 73.1; H, 5.19; N, 13.2; Fe, 8.65; $C_{39}H_{33}N_6Fe$ requires C, 73.0; H, 5.14; N, 13.1; Fe, 8.74%. M.s.: The parent ion was not observed, the peak of highest ${}^{m}/e$ value corresponding to an iron containing ion at ${}^{m}/e$ 252 $[Fe(DPFA)]^+$.

Reaction of Iron(II) Chloride with $C_6H_5N(Li)C(CH_3)NC_6H_5$ in a 1:2 Molar Ratio

n-Butyllithium (1.85 mmol in hexane) was added to anhydrous $FeCl_3$ (0.300 g, 1.84 mmol) in monoglyme, forming an oily brown deposit. A solution of LiDPAA, prepared by the addition of n-BuLi (3.70 mmol in hexane) to DPAAH (0.776 g, 3.70 mmol) in monoglyme (10 ml) at −96°, was added to the iron solution, and the brown mixture stirred at 20° for 18 h. The solvent was removed *in vacuo* and the bown residue extracted with toluene (10 ml). A navy-blue solution and brown gummy residue were produced. The blue solution yielded $Fe(DPAA)_3$ which was identified by m.s. The brown gum failed to yield a pure product.

Reaction of Iron(II) Chloride with $\{p\text{-}CH_3C_6H_4N(Li)C(CH_3)NC_6H_4\text{-}p\text{-}CH_3\}$ in a 1:2 Proportion

A solution of the lithio-reagent was prepared by the addition of n-BuLi (27.9 mmol in hexane) to a solution of DPTAAH (6.61 g, 27.9 mmol) in monoglyme (40 ml) at −196°. The mixture was warmed to room temperature and stirred for 15 m. This solution was added slowly to a suspension of anhydrous $FeCl_2$ (1.77 g, 13.9 mmol) in monoglyme (10 ml) at −20°. A brown precipitate formed immediately, and after stirring the mixture for 18 h. the solution was filtered. The brown solid was washed with toluene and monoglyme, then dried *in vacuo*. Attempts to recrystallise the material from boiling monoglyme failed because of lack of solubility.

The red mother liquor was concentrated *in vacuo* and hexane (10 ml) added slowly. A crimson solid separated, which was separated by filtration, washed with hexane and dried *in vacuo* (yield 1.56 g).

Data for Red Product

Found: C, 71.3; H, 8.86; N, 11.2; $Fe\{CH_3C_6H_4NC(CH_3)NC_6H_4CH_3\}_2$ requires C, 72.4; H, 6.41; N, 10.6%. $Fe\{DPTAA\}_2\cdot(C_4H_{10}O_2)$ requires C, 69.67; H, 7.10; N, 9.03%. M.p. 108° dec. M.s. The peak of highest ${}^{m}/e$ value was at 237, corresponding to $[DPTAA]^+$. The sample was introduced at several source temperatures (80 – 200°) but a parent ion peak could not be detected.

Data for Brown Product

Found: C, 71.8; H, 7.20; N, 9.89; $Fe(DPTAA)_2$ requires C, 72.4; H, 6.41; N, 10.6%. M.p. 109° dec. M.s.: The spectrum was identical to that for the red product described above.

Reaction of $Fe\{p\text{-}CH_3C_6H_4NC(CH_3)NC_6H_4\text{-}p\text{-}CH_3\}_3$ with NO

Nitric oxide was bubbled through a solution of $Fe(DPTAA)_3$ (0.400 g, 0.52 mmol) in monoglyme (20 ml) causing the colour to change from navy-blue to orange-brown. Concentration of the solution *in vacuo*, followed by the addition of hexane, produced a red-brown solid. Further concentration produced a yellow solid which was recrystallised from a monoglyme/hexane mixture to give yellow crystals (yield 0.213 g).

The red-brown solid, which decomposed in air to produce NO_2, was washed with CCl_4, then recrystallised from its purple solution in CH_2Cl_2 to give an air-sensitive purple solid (yield 0.102 g). Solutions of the purple solid decomposed slowly, even under nitrogen, giving a yellow solution from which yellow crystals were obtained. These crystals were identical in all respects with the yellow crystals obtained from the mother liquor.

Data for the Yellow Crystals

Found: C, 71.3; H, 6.46; N, 15.4; $C_{16}H_{17}N_3O$ requires C, 71,9; H, 6.41; N, 15.7%. ${}^1H$ n.m.r. spectrum: $\delta(CD_2Cl_2)$: 2.30s, 2.38s, 2.63s (1:1:1) 7.24, 7.08, 6.90, 6.81, 6.64, 6.50 (2:2:2:1:2:1). M.s. The parent ion $[DPTAA(NO)]^+$ was observed at ${}^{m}/e$ 267. Loss of NO produced the daughter ion $[DPTAA]^+$ at ${}^{m}/e$ 237. I.r. spectrum (nujol mull): 1668m, 1605sh, 1490m, 1243w, 1212w, 1190s, 1172s, 1108w, 1066s, 1056s, 1020m, 965w, 942s, 849w, 824m, 809w, 753m, 732m, 719m, 695w, 552w, 522w, 510w cm^{-1}.

Data for the Purple Solid

Analytical data were inconsistent, typical data being as follows. Found: C, 65.5; H, 3.63; N, 14.2; Fe, 4.80; Fe(DPTAA)$_3$NO requires C, 72.3; H, 6.40; N, 12.30; Fe, 7.03%. Fe(DPTAA)$_3$(NO)$_4$ requires C, 64.9; H, 5.75; N, 15.8; Fe, 6.13%. Fe(DPTAA)$_2$-NO requires C, 68.6; H, 6.07; N, 12.50; Fe, 10.0%. M.s.: A peak at $^m/e$ 413 was detected in one spectrum together with peaks at $^m/e$ 267 and 237 corresponding to [DPTAA(NO)]$^+$ and [DPTAA]$^+$ respectively. The $^m/e$ 413 peak, assigned to either [Fe(DPTAA)-(NO)$_4$]$^+$ or [Fe(DPTAA)(NO)(monoglyme)]$^+$, could not be detected in subsequent spectra.

Attempted Reaction of p-$CH_3C_6H_4NHC(CH_3)NC_6H_4$-p$CH_3$ with NO

No reaction was achieved in monoglyme solution at 20° over 1 h. on bubbling NO through the solution. The amidine was recovered unchanged.

Attempted Reaction of Fe(DPTAA)$_2$ with NO

A suspension of the brown complex in monoglyme failed to react at 20° over 1 h. when NO was bubbled through the suspension. The complex was recovered unchanged.

Attempted Reactions of Fe(DPTAA)$_3$ with Sodium Amalgam, PPh$_3$, Bipyridine, Hex-1-ene, Iodine, Ammonia and Et$_2$OBF$_3$

With Na/Hg: Attempted reduction of the complex in THF resulted in decomposition and the formation of an orange gum which was not studied further. With PPh$_3$: In monoglyme at the reflux temperature over four hours no reaction was detected. In refluxing toluene decomposition to a yellow gum occurred, but a product could not be isolated. With 2,2′-bipyridine: No reaction in refluxing monoglyme over 3 h. With hex-1-ene: No reaction in refluxing monoglyme over 4 h. With iodine: No reaction in monoglyme at ambient temperature over 1 h. With NH$_3$: No reaction in monoglyme on saturating the solution at ambient temperature. With BF$_3$·OEt$_2$: In a 1:1 molar reaction in monoglyme, the colour of the solution changed from navy-blue to red-brown, but attempts to isolate a pure product failed.

Attempted Reaction of tris-2,4-pentanedionatoiron-(III) with DPAAH

No reaction occurred when the reagents in a 1:1 molar ratio were heated in boiling monoglyme for 4 h.

Attempted Reactions of DPTAAH with Fe(acac)$_3$, (η^5-C_5H_5)$_2$Fe, FeCl$_3$ in Carius Tubes

Products were not obtained from these attempted reactions undertaken in the absence of a solvent at 95° over 8 h. Reaction occurred with FeCl$_3$ to form a red solid, but a pure product could not be isolated by recrystallisation or chromatography.

Reaction of Iron(II) Chloride with DPTAAH

FeCl$_2$ (0.135 g, 1.06 mmol) and DPTAAH (1.01 g, 4.25 mmol) were ground together forming an off-white powder which was placed in a Carius tube, evacuated, sealed and heated to 95° for 4 h. After cooling to ambient temperature an orange glass-like solid was formed, which was extracted with CH$_2$Cl$_2$ (30 ml) over 18 h. An unidentified grey residue remained. The orange extract, after filtration, was reduced *in vacuo* to form an orange solid which was subsequently extracted with hexane (to remove the excess amidine (0.203 g), then with ether. On cooling the ether solution, an orange solid separated which when recrystallised from monoglyme/hexane mixtures gave a white solid (identified as DPTAAH(HCl)) and an orange powder (65° dec.). Data for the orange powder: Found: C, 57.06; H, 5.64; N, 8.52; Cl, 21.09; Fe, 6.62. [DPTAAH$_2$]$_3$FeCl$_6$ requires C, 58.43; H, 5.83; N, 8.52; Cl, 21.56; Fe, 5.66%. Severe broadening of the signals prevented the recording of a suitable ^{1}H n.m.r. spectrum, and a m.s. study gave the highest $^m/e$ peak at 238 corresponding to [DPTAAH]$^+$. No iron containing species was identified.

Attempted Sublimation of Fe{$C_6H_5NC(CH_3)NC_6H_5$}$_3$

The navy-blue solid was heated to 110° *in vacuo* for 16 h. during which time a white crystalline solid collected on a water cooled cold finger. This product was identified by elemental analysis and i.r. spectroscopy as DPAAH. The residue, a dark blue solid, appeared on the basis of analytical data and colour to be mainly the unchanged iron(III) complex.

Magnetic Measurements

1. Fe{C$_6$H$_5$NC(CH$_3$)NC$_6$H$_5$}$_3$. A capillary tube was filled with an aliquot of a solution of the complex (0.1014 g) in CH$_2$Cl$_2$ (10.0 ml), and sealed with an oxygen flame. A similar tube containing neat CH$_2$-Cl$_2$ was prepared, and the two sample tubes inserted into a n.m.r. tube (5 mm) to which CCl$_4$ was added to hold the samples in position. N.m.r. spectra were measured and the difference in frequency ($\Delta\nu$) of the proton resonance of CH$_2$Cl$_2$ in the solution and the pure solvent determined using a 60 MHz instrument. Temp. 308 K; density of CH$_2$Cl$_2$ = 1.327 g cm^{-3}; density of solution = 1.131 g cm^{-3}; diamagnetic susceptibility of complex = 366 × 10^{-6} cgs. $\Delta\nu$ = 16.8, 16.9, 16.8, 16.8, 16.7 Hz, average $\Delta\nu$ = 16.8 Hz. μ_{eff} = 5.0 B.M.

2. Fe $\{p\text{-}CH_3C_6H_4NC(CH_3)N\text{-}p\text{-}CH_3C_6H_4\}_3$: sample weight = 0.1408 g; density of solution = 1.314 g cm^{-3}; temperature = 298 K; instrument used = 90 MHz; $\Delta\nu$ = 29.34; 29.35; 29.34; 29.34; 29.34, average $\Delta\nu$ = 29.34 Hz; μ_{eff} = 4.8 B.M.

Standard errors have not been calculated for measurements involving solutions of the air and moisture sensitive complexes, because of the large uncertainty about the extent of decomposition (see discussion section). Indeed, the magnetic moment data may be the best method for estimating the degree of decomposition arising from the reaction with residual oxygen in the solvent and nitrogen atmosphere, and with traces of moisture on the surface of the glassware.

3. $[Fe\{C_6H_5NC(C_6H_5)NC_6H_5\}_2]_n$: The Gouy method was used for a small sample of this complex. Found μ_{eff} = 5.47 (±0.5) B.M.

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