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Solid and solution state structures of mono- and di-nuclear iron(III) complexes of related hexadentate and pentadentate aminopyridyl ligands

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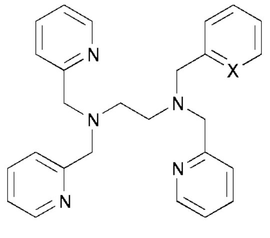
Received 26th September 2000, Accepted 20th November 2000

Two mononuclear iron(III) complexes formed with the related ligands *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine (tpen) and *N*-benzyl-*N*,*N*′,*N*′-tris(2-pyridylmethyl)ethylenediamine (bztpen) have been studied. X-Ray crystallography reveals for the complex $[Fe(tpen)][ClO_4]_3$ that tpen acts as a hexadentate ligand in the solid state. In methanol or water containing solutions it was shown by EPR and UV-Vis spectroscopy that one pyridyl arm is exchanged by a solvent molecule. In dmf solution only partial exchange of a pyridyl arm was observed. The complex with the related pentadentate ligand bztpen $[Fe(bztpen)Cl][ClO_4]_2$ showed exchange of the coordinated chloride with methanol and water, but not with dmf. In water containing solutions both complexes are slowly converted into the dimeric μ-oxo complexes $[(tpen)Fe^{III}(Cl)OFe^{III}(Cl)(tpen)]^{2+}$ or $[(bztpen)Fe^{III}(Cl)OFe^{III}(Cl)(bztpen)]^{2+}$. This reaction is accelerated by addition of an excess of chloride.

Introduction

The formation of iron(III) hydroperoxo complexes has recently been reported starting from iron(II) complexes of the aminopyridyl ligand *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine (tpen)[1] (Chart 1) and the related *N*-benzyl-*N*,*N*′,*N*′-tris(2-pyridylmethyl)ethylenediamine (bztpen)[2] (Chart 1). These are synthetic analogues of the active intermediate in the reaction cycle of bleomycin (BLM) which has been shown to be an iron(III) hydroperoxo complex.[3] From the EPR spectra of the iron(III) hydroperoxo species another low-spin iron(III) complex appeared to be present but its structure was not definitely assigned.[2] Recently, the structures of several chromium(III) complexes in which tpen acts as a hexa-, penta- or tetra-dentate ligand have been published.[4] These structures of the more robust chromium(III) complexes, where it was possible to trap the different complexes of tpen in the solid state, might be relevant for the more labile iron(III) complexes in solution. To clarify the solution structures we have therefore undertaken a spectroscopic investigation of the iron(III) complexes formed with the aminopyridyl ligands tpen and bztpen, in different solvents.



X = N (tpen)
X = CH (bztpen)

Chart 1

We present here the crystal structure of $[Fe(tpen)][ClO_4]_3$ and a study of the formation of μ-oxo bridged dimers, in the presence or absence of chloride. The produced oxo bridged dimer was independently synthesized and characterised.

Experimental

Materials

Commercially available chemicals were used without prior purification. Methanol and dmf were both Fluka puriss, water content <0.01%. The ligand tpen was synthesized according to a literature method.[4]

Physical measurements

UV-Visible absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer, FAB mass spectra on a Kratos MS50TC instrument, ES-MS spectra on a Finnigan TSQ 700 MAT triple quadrupole instrument equipped with a nano-electrospray source, and NMR spectra on a 300 MHz Varian Gemeni 2000 instrument. EPR spectra were recorded on a Bruker EMX 113 spectrometer operating at X-band and equipped with a continuous-flow liquid nitrogen cryostat. Low spin spectra were simulated using the program Bruker WINEPR Simfonia, version 1.25 and high spin spectra with the Sim program.[5] Elemental analyses were carried out by the microanalytical laboratory of the H. C. Ørsted Institute, Copenhagen.

Syntheses

***N*-Benzyl-*N*,*N*′,*N*′-tris(2-pyridylmethyl)ethylenediamine, bztpen.** A solution of *N*-benzylethylenediamine (2.0 g, 13.3 mmol) in CH_2Cl_2 (20 ml) was added to a solution of 2-(chloromethyl)pyridine hydrochloride (6.55 g, 40 mmol) in water (20 ml). NaOH (3.2 g, 80 mmol) in water (10 ml) was added in

DOI: 10.1039/b007799m

small portions over 5 days, keeping the reaction under an N_2 atmosphere. The reaction mixture was extracted with methylene chloride (3 × 25 ml). The combined organic phases were dried over $MgSO_4$ and evaporated to dryness to yield a white solid. It was purified by extraction in a Soxhlet apparatus using low boiling petroleum. Yield 3.2 g, 57%. ^1H NMR ($CDCl_3$): δ 8.48 (2H, m), 7.58 (3H, dt), 7.45 (3H, t), 7.19–7.32 (5H, m), 7.12 (3H, m), 3.77 (4H, s), 3.72 (2H, s), 3.59 (2H, s) and 2.74 (4H, m). ^{13}C NMR ($CDCl_3$): δ 160.09, 159.65, 148.85, 148.70, 139.11, 136.22, 128.64, 128.09, 126.79, 122.64, 122.59, 121.75, 121.69, 60.71, 60.65, 60.51, 58.91, 52.15 and 51.83. FABMS: *m*/*z* 424 (MH^+, 76), 331 ($[MH - C_6H_7N]^+$, 15), 225 ($[MH - C_{12}H_{13}N_3]^+$, 94), 212 ($[M - C_{14}H_{15}N_2]^+$, 100) and 211 ($[M - C_{13}H_{14}N_3]^+$, 95%). Calc. for $C_{27}H_{29}N_5$ (%): C, 76.56; H, 6.90, N, 16.53. Found (%): C, 76.46; H, 7.04; N, 16.65.

CAUTION! the following perchlorate compounds should be handled as potential explosives. On one occasion $[Fe(tpen)][ClO_4]_3$ exploded under handling.

$[Fe(tpen)][ClO_4]_3$. $Fe(ClO_4)_3{\cdot}9H_2O$ (147.4 mg, 0.285 mmol) in dry MeOH (10 ml) was added to a solution of tpen (60.6 mg, 0.143 mmol) and sodium acetate (24 mg, 0.293 mmol) in dry methanol (15 ml). The mustard coloured precipitate, which formed immediately, was dissolved by heating for 5 min. The product precipitated as orange crystals. Yield: 87 mg, 78%. FABMS: *m*/*z* 579 ($[Fe(tpen)(ClO_4)]^+$, 73%). Owing to the explosive nature of the complex no microanalysis was performed.

$[Fe(bztpen)Cl][ClO_4]_2{\cdot}H_2O$. bztpen (100 mg, 0.236 mmol) in abs. EtOH (5 ml) was added to a solution of $FeCl_3{\cdot}6H_2O$ (63.8 mg, 0.236 mmol) in abs. EtOH (3 ml). After stirring for 10 min, $NaClO_4{\cdot}H_2O$ (100 mg, 0.712 mmol) in abs. EtOH (3 ml) was added. The resulting yellow precipitate was isolated by filtration and washed with cold abs. EtOH (1 ml). Yield 131 mg, 76%. FABMS: *m*/*z* 613 ($[Fe(bztpen)Cl(ClO_4)]^+$, 1) and 514 ($[Fe(bztpen)Cl]^+$, 100%). Calc. for $C_{27}H_{31}Cl_3FeN_5O_9$ (%): C, 44.32; H, 4.27; N, 9.57. Found (%): C, 44.32; H, 4.13; N, 9.40.

$[(bztpen)Fe(Cl)OFe(Cl)(bztpen)][PF_6]_2{\cdot}3H_2O$. 2 M NaOH (118 mg, 0.236 mmol) in dry MeOH (1 ml) was added to a stirred solution of $FeCl_3$ (38.2 mg, 0.236 mmol) in dry MeOH (1 ml). bztpen (100 mg, 0.236 mmol) in dry MeOH (1 ml) was added and the mixture stirred for 10 min. After addition of NH_4PF_6 (50 mg, 0.307 mmol) the mustard coloured product precipitated immediately. Yield 98 mg, 60%. FABMS: *m*/*z* 514 ($[Fe(bztpen)Cl]^+$, 100%). Calc. for $C_{27}H_{32}ClF_6FeN_5O_2P$ (%): C, 46.67; H, 4.64; N, 10.08. Found (%): C, 46.16; H, 4.30; N, 10.04.

X-Ray crystallography

Experimental and crystal data are collected in Table 1. The crystal structure of $[Fe(tpen)][ClO_4]_3$ was solved by direct methods (SIR 92).[6] Two of the perchlorate groups are disordered, and the following constraints were applied in order to get the best possible determination of the rest of the structure: all perchlorate groups are identical, regular tetrahedra; two groups were each allowed two orientations with refined occupancy, the most populated in both cases about 65%. Atomic displacement parameters for each perchlorate group were modelled by the TLS approximation.[7]

CCDC reference number 186/2274.

See http://www.rsc.org/suppdata/dt/b0/b007799m/ for crystallographic files in .cif format.

Results and discussion

Ligand synthesis

Synthesis of the ligand bztpen is by nucleophilic substitution of 2-(chloromethyl)pyridine with *N*-benzylethylenediamine. The product was isolated in acceptable yields as an off-white, crystalline solid, which is stable for months at room temperature.

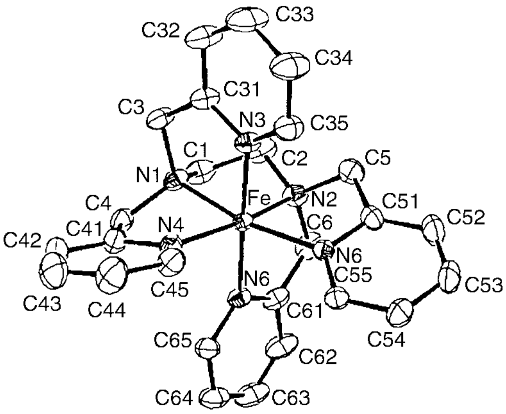


Fig. 1 An ORTEP[11] drawing of the $[Fe(tpen)]^{3+}$ cation. Ellipsoids at 30% probability and hydrogens omitted for clarity.

Synthesis of iron(III) complexes

$[Fe(tpen)][ClO_4]_3$ was isolated from the reaction of tpen with $Fe(ClO_4)_3{\cdot}9H_2O$ (1 : 2) in the presence of two equivalents of acetate. A mustard coloured impure precipitate was formed initially, which redissolved by heating to give an orange solution from which the orange monomeric product could be isolated. ES-MS spectra of acetone solutions of the mustard coloured intermediate support formulations of the type $[(tpen)Fe]_2O(X)(Y)^{2+}$ (X = Y = Cl or ClO_4 or X = Cl, Y = ClO_4). Chloride is probably introduced with the tpen or as an impurity from the ES-MS experiment. Dominant peaks were identified as the dimeric $\{(tpen)_2Fe_2OCl_2\}^{2+}$ (*m*/*z* 523), $\{(tpen)_2Fe_2OCl(ClO_4)\}^{2+}$ (555) and $\{(tpen)_2Fe_2O(ClO_4)_2\}^{2+}$ (587) and monomeric $[(tpen)Fe]^{2+}$ (*m*/*z* 240) and $\{(tpen)FeClO_4\}^+$ (579). This indicates that the μ-oxo dimer may be an intermediate for the formation of $[Fe(tpen)][ClO_4]_3$. No peaks containing acetate could be identified in the ES-MS, and substitution of acetate by triethylamine in the synthesis had no influence on the yield and purity of the product. This shows that a base is crucial for the formation of $[Fe(tpen)]^{3+}$, possibly to aid formation of the above mentioned μ-oxo dimer.

$[Fe(bztpen)Cl][ClO_4]_2$ was synthesized by a 1 : 1 reaction of bztpen with anhydrous $FeCl_3$ followed by precipitation with $NaClO_4{\cdot}H_2O$. No product could be obtained in the absence of Cl^- ions from reaction of bztpen with $Fe(ClO_4)_3{\cdot}9H_2O$ in various solvents.

Reaction of $FeCl_3$ with bztpen in the presence of two equivalents of NaOH, followed by addition of PF_6^-, resulted in precipitation of the μ-oxo product, $[(bztpen)Fe(Cl)OFe(Cl)(bztpen)][PF_6]_2$. The metpen (*N*-methyl-*N*,*N*′,*N*′-tris(2-pyridylmethyl)ethane) analogue, $[(metpen)Fe(Cl)OFe(Cl)(metpen)]Cl[OH]{\cdot}7H_2O$ has been isolated from a reaction of $[Et_4N]_2[Cl_3FeOFeCl_3]$ with metpen in acetone solution.[8] However the preparation of $[Et_4N]_2[Cl_3FeOFeCl_3]$[9] is quite lengthy and extensive purification is necessary. Here we are able to synthesize the oxo-dimer directly in a one-step reaction, albeit in slightly lower yields.

The crystal structure of $[Fe(tpen)][ClO_4]_3$ shows that in the solid state tpen acts as a hexadentate ligand. The complex forms a distorted octahedron with the iron–nitrogen bond distance typical of low-spin (LS) iron(III) complexes[10] (Fig. 1 and Table 2). The major distortion from an ideal octahedron is the angle N4–Fe–N5 which is large, 111.2°. The structure of the iron(III) complex differs significantly from that of the iron(II) complex of tpen, $[Fe(tpen)][ClO_4]_2$, which is a spin cross-over compound.[12] The low-spin iron(II) complex has slightly longer bond distances than the LS iron(III) complex (Fe–N(pyridine)

1.99 and 1.97 Å respectively and Fe–N(amine) 2.03 and 1.99 Å) and the angle N4–Fe–N5 is only 91°.[12] In the corresponding chromium(III) complex, $[Cr(tpen)][ClO_4]_3$, the angle N4–Fe–N5 is 116°. The difference in the angle N4–M–N5 could stem from the ligand-field stabilisation energy (LFSE) (equal to −1.2 for Cr^{III}, −2.0 for Fe^{III} and −2.4 for Fe^{II}.[13]

Table 1 Crystal and experimental data for $[Fe(tpen)][ClO_4]_3$

Formula	$C_{26}H_{23}Cl_3FeN_4O_{12}$
Formula weight	778.78
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	9.816(2)
b/Å	18.486(2)
c/Å	18.156(2)
β/°	93.702(7)
V/Å^3	3288(1)
Z	4
T/K	295
Wavelength, λ(Mo-Kα)/Å	0.71073
Diffractometer	Huber four-circle diffractometer
μ/cm^{-1}	0.771
Absorption correction	None
Reflections collected	6279
Independent reflections	5793
R_{int}	0.029
Reflections with $I > 3\sigma(I)$	4371
R	0.045
wR	0.055
Data/parameters	4371/392

Table 2 Selected bond distances (in Å) and angles (in °) for $[Fe(tpen)][ClO_4]_3$

Fe–N1	1.989(3)	Fe–N4	1.971(3)
Fe–N2	1.986(3)	Fe–N5	1.973(3)
Fe–N3	1.970(3)	Fe–N6	1.977(3)
N1–Fe–N2	87.2(1)	N2–Fe–N6	84.5(1)
N1–Fe–N3	84.5(1)	N3–Fe–N4	86.5(1)
N1–Fe–N4	81.2(1)	N3–Fe–N5	90.7(1)
N1–Fe–N5	166.5(1)	N3–Fe–N6	177.8(1)
N1–Fe–N6	97.5(1)	N4–Fe–N5	111.2(1)
N2–Fe–N3	96.4(1)	N4–Fe–N6	93.0(1)
N2–Fe–N4	167.7(1)	N5–Fe–N6	87.6(1)
N2–Fe–N5	80.7(1)		

Solution species

EPR and UV-Vis spectroscopy show that $[Fe(tpen)][ClO_3]_4$ and $[Fe(bztpen)Cl][ClO_4]_2$ are labile towards solvent attack. The reactions observed are summarised in Charts 3 and 4. In the solid state at 100 K $[Fe(tpen)][ClO_3]_4$ shows a rhombic EPR spectrum, typical of LS iron(III) centres,[14] with $g = 2.36$, 2.15 and 1.92 (Table 3). In a frozen dmf solution at 100 K we find two overlapping rhombic LS spectra. The minor signal, with $g = 2.38$, 2.17, 1.93, is assigned to the six-coordinated $[Fe(tpen)]^{3+}$ species in which tpen acting as a hexadentate ligand. The major signal with $g = 2.34$, 2.15, 1.93 is assigned to a complex in which one pyridyl arm has been replaced by a dmf molecule (the spectrum of $[Fe(bztpen)(dmf)]^{3+}$ is similar, see later). Exchange of a pyridyl ligand for a dmf molecule can take place at two different sites. One site is *trans* to another pyridyl group (N3 or N6 in Fig. 1) and the other is *trans* to a secondary amine (N4 or N5 in Fig. 1). In the corresponding chromium(III) complex, $[Cr(tpen)][ClO_4]_3$, an exchange of a pyridyl arm for an hydroxide ion is observed at the position *trans* to the secondary amine (see Chart 2).[4] By analogy to this complex we therefore suggest that the exchange at Fe^{III} also takes place at this position. The structures of complexes with linear tetradentate ligands related to tpen furnish support for this argument. For example those of *cis*-$[Fe(LBzl_2)Cl_2][PF_6]$[10] ($LBzl_2$ = *N*,*N′*-bis(benzyl)-*N*,*N′*-bis(2-pyridylmethyl)-ethane-1,2-diamine) and *cis*-$[Fe(bispicen)Cl_2][ClO_4]$ (bispicen =

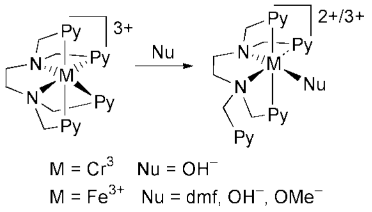


Chart 2

Table 3 EPR and UV-Vis data of the complexes

Complex	Spin state	EPR Characteristic Solvent, E/D (HS) or g values (LS)	UV-Vis Solvent and λ_{max}/nm	Reference
$[Fe(bztpen)Cl][ClO_4]_2$	HS	Solid ≈0.15	Not determined	This work
$[Fe(bztpen)Cl][ClO_4]_2$	HS	dmf 0.15	dmf 300, 368	This work
$[Fe(bztpen)(dmf)]^{3+}$	LS	dmf 2.35, 2.15, 1.93	Not determined	
$[Fe(bztpen)(OMe)]^{2+}$	LS	MeOH–dmf 2.325; 2.140; 1.933	MeOH 358	This work
$[Fe(bztpen)(OH)]^{2+}$	LS	MeOH–dmf–water 2.39, 2.19, 1.91	Not determined	This work
$[Fe(tpen)][ClO_4]_3$	LS	Solid 2.36, 2.15, 1.92	Not determined	This work
$[Fe(tpen)]^{3+}$	LS	dmf 2.385, 2.175, 1.930	Not determined	This work
$[Fe(tpen)(dmf)]^{3+}$	LS	dmf 2.34, 2,15, 1.93	Not determined	This work
$[Fe(tpen)(OMe)]^{2+}$	LS	MeOH–dmf 2.336, 2.140, 1.934	MeOH 358	This work
$[Fe(tpen)(OH)]^{2+}$	LS	MeOH–dmf–water 2.39, 2.19, 1.91	Not determined	This work
$[Fe(N4Py)(OMe)][ClO_4]_2$[a]	LS	MeOH 2.29, 2.12, 1.96	MeOH 255, 360	17
$[Fe(LBzl2)Cl_2][PF_6]$[b]	HS	MeCN–dmf (2 : 1) 0.115	MeCN 256, 300, 370	10

[a] N4Py = (bis-2-pyridylmethyl)bis(2-pyridylmethyl)amine. [b] LBzl2 = *N*,*N′*-bis(benzyl)-*N*,*N′*-bis(2-pyridylmethyl)ethane-1,2-diamine.

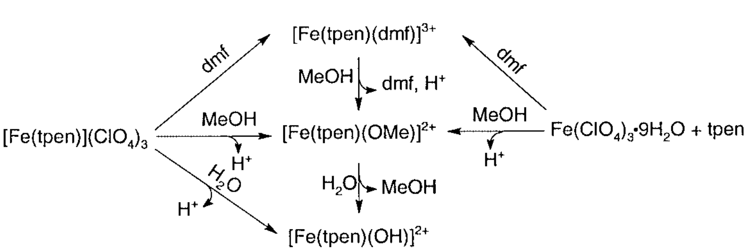


Chart 3

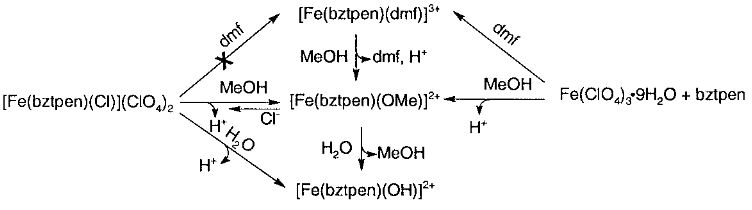


Chart 4

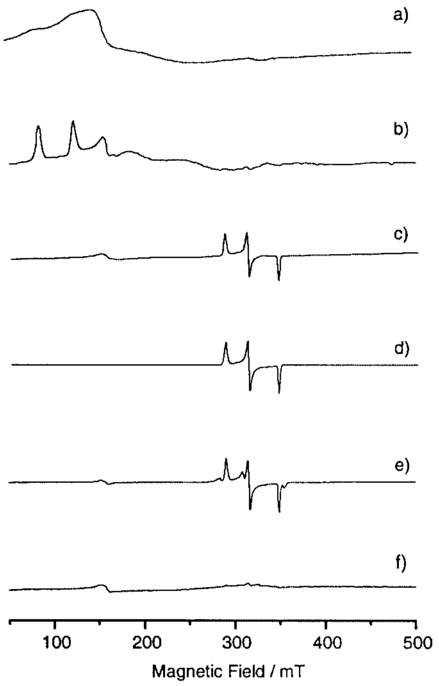


Fig. 2 EPR spectra of the bztpen complexes: (a) solid state [Fe(bztpen)Cl][ClO$_4$]$_2$, (b) [Fe(bztpen)Cl]$^{2+}$ generated by *in situ* reaction of Fe(ClO$_4$)$_3$·9H$_2$O, bztpen and tetrabutylammonium chloride, (c) [Fe(bztpen)(OMe)]$^{2+}$ in MeOH–dmf (3 : 1), (d) simulation of (c), (e) after addition of water to [Fe(bztpen)(OMe)]$^{2+}$ in MeOH–dmf (3 : 1) and (f) after addition of an excess of chloride to (e).

N,*N*′-bis(2-pyridylmethyl)-ethane-1,2-diamine)[15] show that the two halide ligands are found *cis* to each other (*trans* to the secondary amines) and thus the pyridyl donors are *trans* to each other. The alternate structures, halide *trans* and the pyridyl donors *cis* or both the pyridyl donors and the halides *cis*, have not been observed thus far.

The solid state EPR spectrum of [Fe(bztpen)Cl][ClO$_4$]$_2$ at 100 K consists of three very broad absorptions with effective *g* values of *ca.* 8.0, 5.7 and 4.4 (Fig. 2a) indicative of a HS iron(III) complex. The EPR spectra of HS d^5 systems are usually described by the spin Hamiltonian parameter *D*, which results from axial zero field splitting, and *E*/*D*, describing the rhombicity of the complex ($0 \le E/D \le 1/3$).[14] In a frozen dmf solution, a nitromethane glass and by *in situ* mixing of equivalent amounts of Fe(ClO$_4$)$_3$·9H$_2$O, bztpen and tetrabutylammonium chloride in dmf at 100 K four lines are observed (Fig. 2b) at *g* equal to 8.16, 5.58, 4.3 and 3.67 at 100 K. The intensity of the signal at $g = 4.3$ varies between samples and its position is typical of an HS iron(III) complex with $E/D = 1/3$. This signal has been seen for other HS polypyridyl complexes and attributed to an impurity.[10] The rest of the present spectrum can be simulated using $E/D = 0.15$ and $D = 0.3$ cm^{-1}. The complex [Fe(bztpen)(dmf)]$^{3+}$ is prepared by *in situ* mixing of equivalent amounts of Fe(ClO$_4$)$_3$·9H$_2$O, and bztpen in dmf. It yields a rhombic LS signal with $g = 2.35$, 2.15 and 1.93 at 100 K. This *in situ* experiment supports assignment of the signal observed in solution to the [Fe(bztpen)Cl]$^{2+}$ ion and indicates that dmf is not capable of replacing the coordinated chloride. The UV-Vis spectrum of [Fe(bztpen)Cl][ClO$_4$]$_2$, in dmf solution at room temperature, shows two absorption bands at 300 and 368 nm (Fig. 3a) which may be attributed to ligand to metal charge transfer (LMCT) transitions.[16]

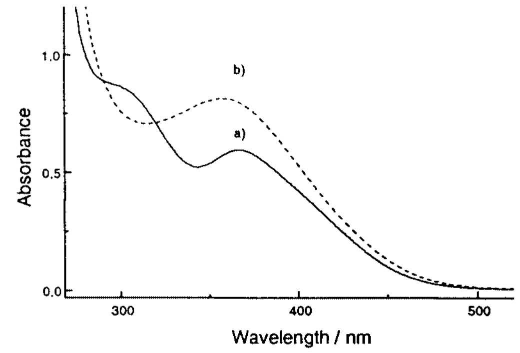


Fig. 3 UV-Vis spectra of (a) [Fe(bztpen)(dmf)]$^{2+}$ in dmf and (b) [Fe(bztpen)(OMe)]$^{2+}$in MeOH at room temperature.

In a MeOH–dmf (3 : 1) glass at 100 K both [Fe(tpen)][ClO$_4$]$_3$ and [Fe(bztpen)Cl][ClO$_4$]$_2$ show a new rhombic low-spin signal with $g = 2.32$, 2.14 and 1.93 (Fig. 2c). The same signal is also seen on *in situ* mixing of equivalent amounts of Fe(ClO$_4$)$_3$·9H$_2$O and bztpen in methanol. This leads us to the conclusion that the one pyridyl arm (for tpen) or a chloride (for bztpen) has been replaced by a methoxo ligand, forming an LS species. The UV-Vis spectrum in methanol reveals a band at 358 nm (Fig. 3) which is similar to the band observed for [Fe(N4Py)(OMe)][ClO$_4$]$_2$ (N4Py = (bis-2-pyridylmethyl)bis(2-pyridylmethylamine) in methanol.[17] If water then is added to the MeOH–dmf (3 : 1) solution at room temperature and the spectrum subsequently measured at 100 K we observe a new rhombic EPR signal with slightly different *g* values at 2.39, 2.18 and 1.91 (Fig. 2d). The intensity of this signal can be correlated with the amount of water added. We assign this signal to a complex in which the methoxo ligand has been replaced by a hydroxo ligand. Despite several attempts we were not able to isolate any hydroxo or methoxo complexes of either tpen or bztpen.

Formation of oxo-bridged dimer complexes

The integrations of the EPR spectrum of [Fe(bztpen)(OMe)]$^{2+}$ in dry MeOH–dmf (3 : 1) solution kept at room temperature remained unchanged after 48 h. In a MeOH–dmf (3 : 1) solution containing *ca.* 5% water the integrals changed significantly with time. After 48 h the concentration of the methoxo complex was reduced to approximately 15% of the starting concentration. In the presence of both water and an excess of chloride the signal was lost rapidly and after two days only 0.1% was left. The UV-Vis spectra of aged solutions (48 h) containing both water and an excess of chloride show an absorption band at 320 nm and a stronger band at 374 nm, as found in the UV-Vis spectra of the μ-oxo complexes [{(bztpen)FeCl}$_2$O}]$^{2+}$, [{(metpen)FeCl}$_2$O}]$^{2+}$ [8] and [{(TPA)FeCl}$_2$O]$^{2+}$ (TPA = tris(2-pyridylmethyl)amine)[18] dimers. Furthermore ES-MS experiments on the aged solution showed the presence of [{(bztpen)FeCl}$_2$O}]$^{2+}$ (*m*/*z* 522). This indicates that the EPR silent product formed is a μ-oxo complex. Analogous reactions were observed with [Fe(tpen)][ClO$_4$]$_3$.

Although no detailed kinetic study was undertaken, our results show that the formation of the μ-oxo dimer is accelerated by the presence of chloride ions. This is understandable when considering the fact that an HS dimer is stabilised through π donation from the O^{2-} bridge and therefore the dimerisation of HS iron(III) monomeric complexes will proceed much faster than that of LS monomers. The addition of chloride will shift the equilibrium towards HS species, which will then form HS dimers. The reactions are summarised in Chart 5.

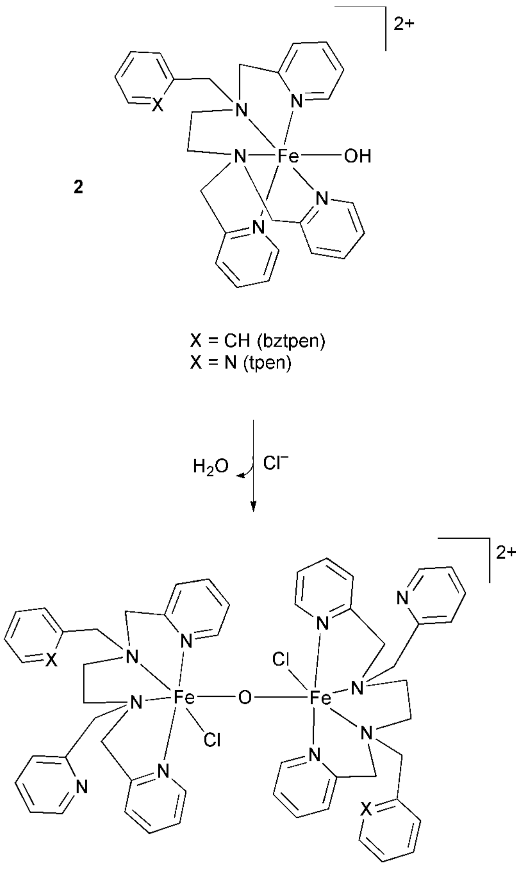


Chart 5

Conclusion

tpen acts as a hexadentate ligand toward iron(III) in the solid state. This was shown by X-ray crystallography where a distorted octahedra structure was observed. In solution we found by EPR, UV-Vis and ES-MS that one pyridyl was exchanged by a solvent molecule. In the case of dmf the exchange did not go to completion, but in methanol and water it was total. We found an analogous behaviour for the complex [Fe(bztpen)Cl)][ClO$_4$]$_2$. Thus in dmf solution no exchange of chloride was observed, whereas in methanolic and water containing solution the chloride was exchanged with either a methoxo or a hydroxo ligand, respectively.

Both the tpen and the bztpen complexes react further in solution and form an oxo bridged dimer which we were able to identify by comparison of the UV-Vis spectral characteristics with those of the deliberately synthesized complex [{Fe(bztpen)Cl}$_2$O]$^{2+}$ and of previous published μ-oxo dimers. We have observed a difference in the dimerisation rates for the monomers depending on the presence of chloride ion. Excess of chloride makes the dimerisation process proceed much faster and this can be explained by the fact that dimerisation of HS iron(III) complexes is favoured and the excess of chloride increases the concentration of the HS monomer.

Acknowledgements

Dr K. B. Jensen, University of Southern Denmark, Odense Campus is thanked for assistance with the ES-MS experiment. The Danish Natural Science research council is thanked for a grant (C. J. M.).

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