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Iron(III) Complexes of N-donor Ligands. Part II[≠]. The Reaction of $[Fe(L)_2Cl_2][FeCl_4]$* with 1,2,4-Triazole, 4-Allyl-1,2,4-triazole and 4,4'-Bipyridyl; Rearrangement of the Chelating Ligands

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Abstract

$[Fe(bpy)_2Cl_2][FeCl_4]$ and $[Fe(dmbpy)_2Cl_2][FeCl_4]$ were reacted with 1,2,4-triazole (Htrz), 4-allyl-1,2,4-triazole (Altrz) and 4,4'-bipyridyl (44-bpy). The products obtained have been characterised by elemental analyses, infrared spectroscopy and Mössbauer spectroscopy. A rearrangement of the bipyridyl ligands was found and the products obtained are probably mononuclear for Htrz, dimeric for 44bpy and dimeric or polymeric for Altrz.

Introduction

Relatively little is known about the structures and chemistry of Fe(III) complexes containing one or two bidentate nitrogen donor ligands. Only the reactions between $FeCl_3$ and ligands such as 2,2'-bipyridyl (bpy) and 1,10-phenanthroline (phen) have been studied in some detail [1–5]. A number of crystal structures of Fe(III) complexes with one or two phen or bpy ligands have recently been reported. The crystal structures of $[Fe(phen)_2Cl_2][FeCl_4]$ and of the corresponding bpy salt have been reported by White and Goodwin [6, 7]. Crystals for these determinations were grown from nitromethane or acetone. In contrast a material which has a molecular formula of $Fe(phen)Cl_3X$ (X = H_2O, MeOH) has been obtained from acetic acid [8]. Other X-ray structures reported include $[Fe(bpy)_2Cl_2][Fe(bpy)Cl_4]$ [7], the corresponding 1,10-phenanthroline complex [7], [H phen] $[Fe(phen)Cl_4]$ [9], *mer*-$Fe(phen)(DMF)Cl_3$ (DMF = dimethylformamide) [10] and *fac*-$Fe(bpy)(Htrz)Cl_3$ (Htrz = 1,2,4-triazole) [11].

The chemistry of these complexes in solution is of interest as [Fe(III)/Fe(II)] complexes of bpy and phen have been studied as solution redox couples for electrochemical energy storage [12]. Also the potential of such complexes as redox initiators in the polymerisation of acrylonitrile and acrylamide has been studied [13, 14]. Little is known however about the nature and behaviour of Fe(III) complexes of bpy and phen in solution. Only $Fe(bpy)_3^{3+}$ and $Fe(phen)_3^{3+}$ have been studied in detail. We decided to investigate the coordination chemistry of Fe(III) complexes with one or two bidentate nitrogen donors and study the behaviour of such complexes towards other ligands. In this work the reactions of $[Fe(bpy)_2Cl_2^+][FeCl_4^-]$ and $[Fe(dmbpy)_2Cl_2^+][FeCl_4^-]$ (dmbpy = 4,4'-dimethyl-2,2'-bipyridyl) with 1,2,4-triazole (Htrz) 4-allyl-1,2,4-triazole (Altrz) and 4,4'-bipyridyl (44bpy) are reported. The products were characterised by elemental analysis, infrared spectroscopy and Mössbauer spectroscopy. In part I of this series we reported the crystal and molecular structure of $Fe(bpy)(Htrz)Cl_3$, to our knowledge the first crystal structure for a neutral Fe(III) complex of bpy [11]. With these studies we hope to gain a better understanding of the criteria which determine the structure, stability and chemistry of Fe(III) complexes of N-donor ligands. This will aid the design of more stable Fe(III) redox catalysts.

Experimental

Reagent grade starting materials and solvents were used without further purification. 4-allyl-1,2,4-triazole was obtained as a gift from Dr G. Vos. (State University Leiden, The Netherlands).

Synthesis of Species with the Overall Formula of Fe(L)Cl₃ from Glacial Acetic Acid. L = bpy, dmbpy, phen

$FeCl_3$ (3 g) was dissolved in 100 ml glacial acetic acid. To this solution, 1 equivalent of L was added slowly under stirring. The yellow precipitate formed was filtered and dried *in vacuo*. The bpy and dmbpy compounds could be recrystallised from acetone/

[≠] For Part I see ref. 11.

*L = 2,2'-bipyridyl(bpy), 4,4'-dimethyl 2,2'-bipyridyl (dmbpy).

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toluene mixtures. The phen compound was obtained from ethanol. *Anal.* for $[Fe(bpy)_2Cl_2][FeCl_4]$ (**1**). Calc.: C, 37.71; H, 2.51; N, 8.80; Cl, 33.42%. Found: C, 37.5; H, 2.3; N, 8.8; Cl, 34.4%. $[Fe(dmbpy)_2Cl_2][FeCl_4]$ (**2**). Calc.: C, 41.58; H, 3.47; N, 8.09; Cl, 30.7%. Found: C, 41.5; H, 3.5; N, 8.2; Cl, 31.1%.

Reaction of Fe(L)Cl₃ with 1,2,4-Triazole, 4-Allyl-1,2,4-triazole and 4,4′-Bipyridyl. L = bpy, dmbpy

500 mg of $Fe(L)Cl_3$ was dissolved in 25 ml acetone and an excess of the N-donor ligand was added, dissolved in acetone. When needed, some toluene was added to cause the formation of crystals. The yellow crystals were filtered and dried *in vacuo*. *Anal.* $Fe(bpy)(Htrz)Cl_3$, (**3**). Calc.: C, 37.19; H, 2.84; N, 18.07. Found: C, 37.3; H, 2.8; N, 17.3%. $Fe(dmbpy)(Htrz)Cl_3$ (**4**). Calc.: C, 40.44; H, 3.61; Cl, 25.60%. Found: C, 40.1; H, 3.8; Cl, 25.5%. $Fe(bpy)(Altrz)Cl_3$ (**5**). Calc.: C, 42.13; H, 3.51; N, 16.39; Cl, 24.89%. Found: C, 42.4; H, 4.0; N, 16.4; Cl, 25.6%. $Fe(dmbpy)(Altrz)Cl_3$ (**6**). Calc.: C, 44.79; H, 4.17; Cl, 23.35%. Found: C, 44.5; H, 4.1; Cl, 23.4%. $Fe(bpy)(44bpy)_{1/2}Cl_3$ (**7**). Calc.: C, 45.50; H, 3.02; N, 10.60; Cl, 26.82%. Found: C, 45.1; H, 3.2; N, 10.3; Cl, 27.2%.

Equipment

Infrared spectra were recorded on a Perkin-Elmer 1330 Spectrophotometer. Mössbauer spectra were recorded at the physics department, Trinity College Dublin as reported elsewhere [15].

Results and Discussion

General

The product obtained when $FeCl_3$ is reacted with 1 equivalent of a chelating ligand such as bpy or phen depends strongly on the solvent used for the reaction. For a material with the overall formula $Fe(phen)Cl_3$ two different molecular structures have been identified by X-ray techniques: $[Fe(phen)_2Cl_2][FeCl_4]$ (crystals obtained from acetone or nitromethane [6] and $Fe(phen)Cl_3{\cdot}X$ (X = H_2O, CH_3OH) (crystals obtained from glacial acetic acid and methanol [7]. For the corresponding bpy material the crystal structure of $[Fe(bpy)_2Cl_2][FeCl_4]$ has been reported [8] (crystals from nitromethane). We reacted $FeCl_3$ with one equivalent of bpy, dmbpy and phen in acetic acid which yielded the products **1**, **2** and **8**. The phen complex **8** has a Mössbauer spectrum identical to that reported by Berrett *et al.* [5]. As the preparation method used by Berrett is the same as the one used by White *et al.*, in their crystal structure determination of $Fe(phen)Cl_3{\cdot}X$ we assume the material obtained in this manner to have the last structure and not the dimeric structure proposed by Berrett. When $FeCl_3$ was reacted with bpy in the same solvent, a compound was obtained which also analysed as $Fe(L)Cl_3$ but with a quite different infrared spectrum (see Table I). The far-infrared region shows clearly the presence of the $FeCl_4^-$ anion (νFe–Cl = 380 cm^{-1}). This together with the Mössbauer spectrum (*vide infra*) suggests that the molecular structure for the bpy complex is $[Fe(bpy)_2Cl_2][FeCl_4]$ rather than the mononuclear structure found for $Fe(phen)Cl_3X$. $[Fe(bpy)_2Cl_2][FeCl_4]$ could be recrystallised from acetone without a change in spectroscopic properties. When $FeCl_3$ and bpy were reacted in diethyl ether $[Fe(bpy)_2Cl_2][FeCl_4]$ was obtained, and in acetone two products crystallised. The first fraction analyses as $[Fe(bpy)_2Cl_2][Fe(bpy)Cl_4]$ while the second fraction appears to be $[Fe(bpy)_2Cl_2][FeCl_4]$. It is perhaps surprising that the products obtained in acetic acid with bpy and phen do not have the same structure. It is also clear that when $FeCl_3$ is reacted with ligands such as bpy or phen the solvent used plays an important role.

Little is known about the chemistry of complexes such as $[Fe(bpy)_2Cl_2][FeCl_4]$. Their behaviour towards other N-donor ligands has not been investigated. We reacted $[Fe(bpy)_2Cl_2][FeCl_4]$ and $[Fe(dmbpy)_2Cl_2][FeCl_4]$, obtained from acetic acid, with N-donor ligands 1,2,4-triazole, 4-allyl-1,2,4-triazole and 4,4′-bipyridyl in acetone. It

TABLE I. Far-infrared Data of some Fe(III) Complexes.

Compounds	Metal–ligand vibrations (cm^{-1})	Other bands
$Fe(bpy)Cl_3$	378(s);330(s);268(m)	410(m);360(w)
$Fe(bpy)(Htrz)Cl_3$	310(s);282(br,s)	415(m);364(w)
$Fe(bpy)(Altrz)Cl_3$	322(s);300(s);282(s)	415(m);350(w)
$Fe(bpy)(44bpy)_{1/2}Cl_3$	320(sh);303(s);284(s)	415(m);360(w)
$Fe(dmbpy)Cl_3$	380(s);328(s)	420(m)
$Fe(dmbpy)(Htrz)Cl_3$	315(s);270(br,s)	420(m);385(w)
$Fe(dmbpy)(Altrz)Cl_3$	306(sh);294(br,s);280(sh)	419(m);380(w)
$Fe(phen)Cl_3$	334(s);310(m)	420(m)

was found from elemental analyses and spectroscopic data (*vide infra*) that with Htrz and Altrz complexes are formed as in eqn. 1:

$$[Fe(L)_2Cl_2][FeCl_4] + Htrz \longrightarrow 2Fe(L)(Htrz)Cl_3 \quad (1)$$

with 44bpy a reaction is taking place as in eqn. 2:

$$[Fe(L)_2Cl_2][FeCl_4] + 44bpy \longrightarrow 2Fe(L)(44bpy)_{0.5}Cl_3 \quad (2)$$

yielding a 44bpy bridged dimeric species. It is important to notice that a rearrangement is taking place. One of the ligands L (L = bpy, dmbpy) is transferred to the $FeCl_4^-$ anion, this being emphasised by the 90% yield of the reactions (based on iron). The fact that bpy (and dmbpy) is so easily transferred from one metal centre to another has important consequences. It means that: (i) by looking at the products little or no information can be obtained about the structure of the starting materials; (ii) the structure of the compounds in solution is not necessarily the same as the structure found in the solid state. It was for example found that a 10^{-3} M/l solution of $Fe(bpy)(Htrz)Cl_3$, which according to its X-ray structure is a neutral, mononuclear complex in the solid state, shows roughly the same conductivity as a similar $[Fe(bpy)_2Cl_2][FeCl_4]$ solution. This makes measurements in solution, such as conductivity and solution UV/VIS rather questionable for these compounds. The compounds obtained were therefore only characterised using solid state techniques such as infrared Mössbauer spectroscopy.

Crystal Structure and Molecular Structure of fac-Fe(bpy)(Htrz)Cl$_3$

The interpretation of the spectroscopic data is greatly facilitated by the crystal and molecular structure reported earlier for $Fe(bpy)(Htrz)Cl_3$ [11]. This compound has been shown to be a mononuclear neutral Fe(III) complex (see Fig. 1). Only a few of such compounds exist and to our knowledge this is the first bpy complex with such a structure. Fe–Cl distances in the complex vary between 2.32 and 2.29 Å, Fe–N distances are 2.168 and 2.184 Å for the bpy nitrogen atoms and 2.195 Å for the triazole nitrogen. These values fall in the range expected for high spin Fe(III) complexes of this type [6–10]. 2,2′-Bipyridyl is as expected acting as a bidentate ligand while 1,2,4-triazole is bound via the N^4-atom as a monodentate ligand. The geometry around the metal ion is distorted octahedral. The N–Fe–N angle of 146° shows the largest deviation from a regular octahedral angle. All Cl–Fe–Cl angles are about 96°. The Cl ions in a *fac*-arrangement occupy more space than they would in a regular octahedral coordination.

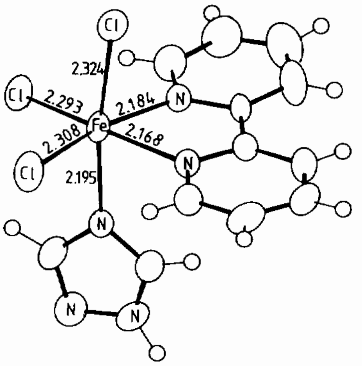

Fig. 1. Molecular structure of *fac*-Fe(bpy)(Htrz)Cl$_3$.

Infrared Spectra

All compounds were characterised by infrared spectra and showed in the 4000–600 cm^{-1} region the vibrations expected for the various ligands. Infrared spectra have been used to determine the coordination mode of 1,2,4-triazoles. The out-of-plane ring vibrations which can be found between 600–700 cm^{-1} can be used to differentiate between monodentate and bidentate coordination of the ligand. They can also be used to investigate the coordination mode for Htrz and the position of the N–H proton [16]. For $Fe(bpy)(Htrz)Cl_3$ 3 vibrations at 631, 651 and 668 cm^{-1} are observed between 600–700 cm^{-1}. For the corresponding dmbpy complex 4 two vibrations are observed in this region at 636 and at 672 cm^{-1}. These data suggest that the bands at about 630 and 670 cm^{-1} are triazole ring vibrations while the band at 651 cm^{-1} in the bpy complex is a bpy vibration. Dmbpy has no infrared absorptions in this area. The position of the triazole ring torsion vibrations suggests that that 1,2,4-triazole is bound through the N^4-nitrogen with the N–H proton on the 1-position [16] and this is in fact confirmed by the molecular structure of $Fe(bpy)(Htrz)Cl_3$.

For the corresponding Altrz complexes two bands are found in the 600–700 cm^{-1} region for the bpy complex, 634 and 650 cm^{-1} and for the dmbpy complex **6** one strong vibration is found at 635 cm^{-1}. The presence of a single band at 635 cm^{-1} indicates a bidentate bridging coordination of Altrz. [16, 17], and this suggests a dimeric or polymeric structure for these compounds.

In the far-infrared region (measured between 600–250 cm^{-1}) strong vibrations were observed for all compounds between 250 and 460 cm^{-1}. In this region metal–ligand stretching vibrations are expected [18]. The strong bands have been attributed to Fe–Cl stretching vibrations. Fe–N stretching vibrations are expected to be much weaker and only few data concerning Fe(III)–N vibrations are available [18]. At this stage of the work the identification of the ν_{Fe-N} bands was not attempted but experiments with Fe(III) complexes of different anions are in progress.

For starting materials with formula Fe(L)Cl$_3$ **1** and **2** a strong band at 380 cm^{-1} shows the presence of the [FeCl$_4$]$^-$ anion, and a molecular structure of [FeL$_2$Cl$_2$][FeCl$_4$] is therefore proposed for these materials. The $\nu_{\text{Fe—Cl}}$ bands of the cation are found at 330 cm^{-1} in agreement with an octahedral coordination of Fe(III) (see Table I). In contrast, the infrared spectrum of Fe(phen)Cl$_3$ (also obtained from acetic acid) shows only strong bands at 335 and 310 cm^{-1}, which is in agreement with the reported mononuclear, octahedral molecular structure of the compound. Compounds 3–7 all exhibit a strong infrared absorption (which is sometimes split) at about 300 cm^{-1}. This band has been attributed to Fe–Cl stretching vibrations in octahedral Fe(III) complexes. The number of $\nu_{\text{Fe—Cl}}$ vibrations can be indicative for the stereochemistry round the metal-ion. At present the uncertainty about the position of the Fe–N vibrations prohibits a detailed analysis.

Mössbauer Spectra

It was hoped that Mössbauer spectra would yield additional information about the structure of the complexes obtained. Mössbauer spectra do indeed differentiate between [FeL$_2$Cl$_2$][FeCl$_4$] and FeLCl$_3$·H$_2$O. The spectrum obtained for Fe(phen)Cl$_3$ agrees with that reported by Berrett *et al.* The spectrum of **1** taken at 100 K can be fitted as a singlet (isomer shift of 0.27 mm/sec) and a doublet (quadrupole splitting of 0.45; isomer shift of 0.30 mm/sec) in a 1:1 ratio. (Isomer shifts relative to iron metal). This suggests that the singlet can be assigned to (FeCl$_4^-$) while the doublet is possibly due to the octahedral [Fe(bpy)$_2$Cl$_2$]$^+$. For all the other compounds a broad featureless spectrum is obtained, with an isomershift of about 0.3–0.4 mm/sec and the spectra therefore do not yield any additional information about the structure of these compounds.

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