

Molecule Matters

High Oxidation State: Fe^{VI} in an Octahedral Coordination Complex

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The synthesis of a Fe^{VI} complex in an octahedral coordination geometry has been achieved recently by Wieghardt and co-workers. This is only the second hexavalent iron complex known after the tetrahedral ferrate ion, [FeO₄]²⁻. The synthesis of the new Fe^{VI} complex involves a low temperature photolysis of an Fe^{IV}(N₃) precursor which leads to the formation of the Fe^{VI} complex containing a Fe≡N triple bond. The structural characterization of the Fe^{VI} complex has been achieved by a variety of spectroscopic techniques including Mössbauer spectroscopy and X-ray absorption spectroscopy. Experimentally it is found that the Fe^{VI} complex is diamagnetic. Theoretical calculations reveal that the Fe^{VI} complex has an electronic configuration 3d² (S = 0); the d electrons are paired in a d_{xy} orbital.

Iron is the second most abundant metal on the earth's crust after aluminum, and is present in about 6.2% natural abundance. Iron occurs naturally in the form of its ores such as hematite (Fe₂O₃), magnetite (Fe₃O₄), limonite (Fe₂O₃•1.5 H₂O), siderite (FeCO₃) and iron pyrites (FeS₂) [1]. The development of the technology for extracting iron from its ores and its routine use as a material marked a paradigm shift in the progress of human civilization. The *rust-free* iron pillar in New Delhi is a remarkable testimony to the high level of technology achieved in ancient India [2].

Iron has an exciting chemistry and biochemistry. Organometallic compounds and coordination complexes of iron are innumerable and several are quite well known. The oxidation state of iron in these compounds ranges from -2 to +4. In general, low oxidation states of iron are found in its organometallic compounds. Iron forms many carbonyl compounds such as [Fe(CO)₄]²⁻, Fe(CO)₅,

Keywords

Hexavalent iron complex, coordination complexes, Mössbauer spectroscopy.



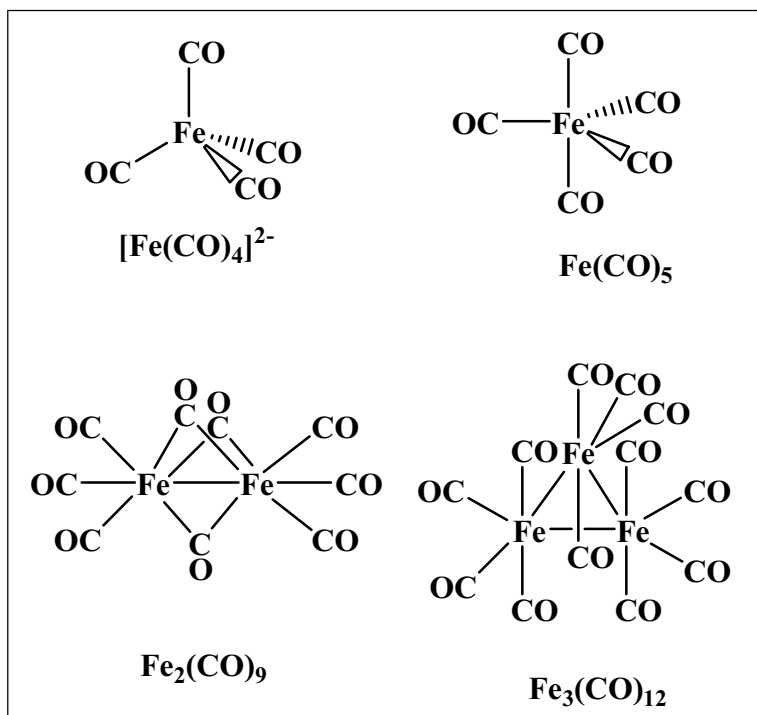


Figure 1. Examples of iron carbonyls. In $[\text{Fe}(\text{CO})_4]^{2-}$ the oxidation state of iron is -2 . In the other complexes it is zero.

$\text{Fe}_2(\text{CO})_9$, and $\text{Fe}_3(\text{CO})_{12}$ (Figure 1). In these compounds iron is present in low oxidation states. Notice that in these compounds the carbonyl ligand can be either *terminal* or *bridging*. Notice also, the presence of Fe-Fe bonds in $\text{Fe}_2(\text{CO})_9$ and $\text{Fe}_3(\text{CO})_{12}$. Historically the most important organometallic compound of iron is ferrocene (Figure 2). This compound was first discovered accidentally by Pauson and Kealy who were unable to deduce its

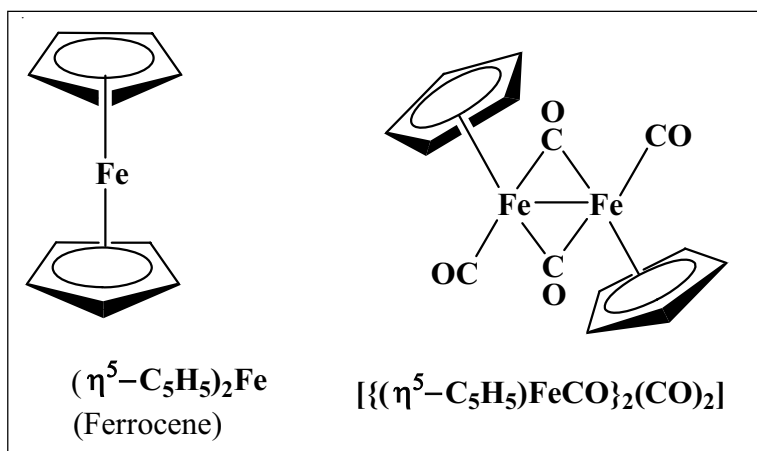


Figure 2. Cyclopentadienyl organometallic complexes of iron. In ferrocene the oxidation state of iron is $+2$. In $[\{(\eta^5-\text{C}_5\text{H}_5)\text{FeCO}\}_2(\text{CO})_2]$ the oxidation state of iron is $+1$.

Iron-containing proteins are essential for several biochemical transformations.

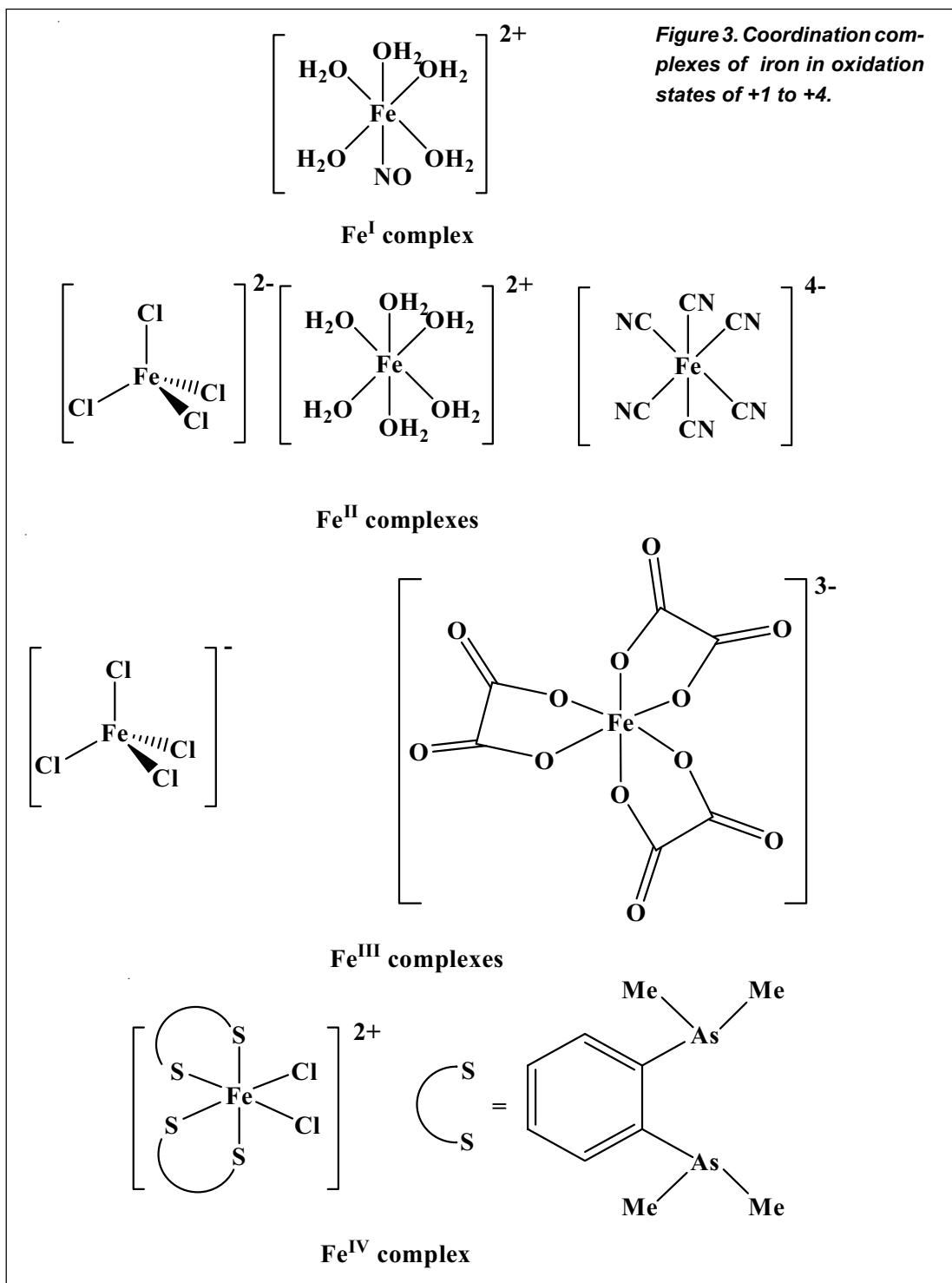
structure correctly. Wilkinson and Woodward [1] discovered the correct structure wherein the central iron atom is sandwiched between two planar aromatic cyclopentadienyl ligands, all the carbon atoms being equidistant from the iron and bonding with it. Each cyclopentadienyl ligand is formally anionic and contributes 6e towards bonding with the iron. Because of this the iron atom is formally in +2 oxidation state in ferrocene. The discovery of ferrocene is a historical milestone in the development of organometallic chemistry. Today organometallic chemistry is a burgeoning science and is an important interface area between the traditional realms of organic and inorganic chemistry. Iron compounds containing one cyclopentadienyl ligand and other carbonyl ligands are also known. In these compounds iron possesses an oxidation state of +1 (*Figure 2*).

Coordination complexes of iron, where the metal is surrounded by classical Werner-type ligands, are well known. Compounds occur with diverse geometries and coordination numbers. Examples of compounds where the oxidation state of iron varies from +1 to +4 and where the number of ligands around iron varies from 4 to 6 are given in *Figure 3*.

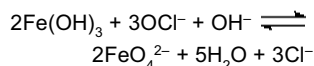
The above introduction to the chemistry of iron will not be complete without mentioning the role of iron in biological systems, which is extremely important and is crucial to life processes. Living organisms have to obtain iron from nature, store it, transport it and incorporate it in many iron-containing proteins which are essential for several biochemical transformations. Two main types of iron-containing proteins are known based on the type of ligands complexing iron at the active site – heme proteins with porphyrin ligands and non-heme proteins with a multitude of other ligands. Examples of heme proteins are hemoglobin and myoglobin while important examples of non-heme proteins are the iron-sulfur proteins. Both these classes of proteins are essential to perform important biological functions including oxygen transport, oxygen storage and electron transfer [1].

Even though a large number of iron complexes are known as





¹ Ferrate ion is an unstable species and is normally prepared in strongly alkaline solution, using chlorine as the oxidizing agent.



It is precipitated using an appropriate cation such as Ba^{2+} . The central iron atom is surrounded by four oxide ligands in a tetrahedral environment. Ferrate ion is a good oxidizing agent and is used in various oxidation processes.

shown in *Figure 3*, most of them contain iron in low oxidation states like +2 or +3, and just a handful are known with iron in +4 oxidation state. There are very few examples where iron is present in a *very high* oxidation state. Until 2006, the ferrate ion $[\text{FeO}_4]^{2-}$ was the only known example of a hexavalent iron complex¹. In 2006, Wieghardt and coworkers reported the second iron(VI) coordination complex [3]. This article deals with this remarkable discovery.

The journey of Wieghardt and coworkers began with the preparation of Fe(III) complexes using cyclam-type ligands possessing a pendant carboxylate group [4]. Cyclam ligands are tetrazamacrocycles and can bind very tightly to a metal ion by means of four nitrogen atoms. Wieghardt and coworkers used modified cyclam ligands. An additional carboxylate group that can bind through an oxygen atom was tethered to the cyclam ligand at one of the nitrogen atoms through a 'CH₂' spacer group. Two examples of these modified cyclam ligands, L(1) and L^{Me}(2) are shown in *Figure 4*. Both these ligands would be able to provide five coordinating atoms to a metal ion (four nitrogens and one oxygen). Reaction of 1 and 2 with $[\text{NEt}_4][\text{FeCl}_4]$ afforded an Fe^{III}-Cl complex which was not isolated. Substitution of chloride by azide (by a reaction with sodium azide) followed by an anion exchange lead to the complexes $[\text{LFe}^{\text{III}}\text{N}_3](\text{PF}_6)$ (3) and $[\text{L}^{\text{Me}}\text{Fe}^{\text{III}}\text{N}_3](\text{PF}_6)$ (4) (*Figure 5*). In these complexes iron is present in +3 oxidation state. Interestingly while 3 is a low-spin complex (one unpaired electron, $S=1/2$) 4 is a high-spin complex (five unpaired electrons, $S=5/2$).

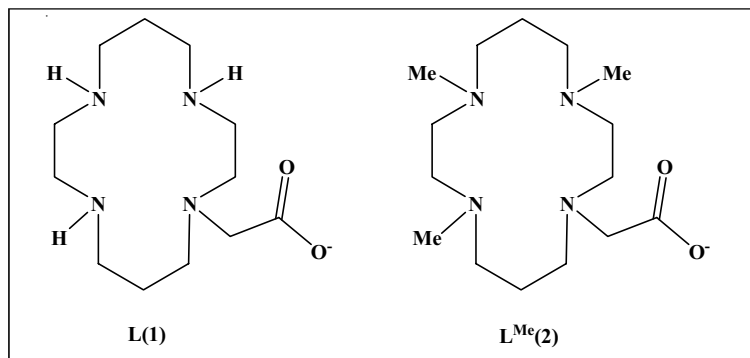


Figure 4. Cyclam ligands L(1) and L^{Me}(2).

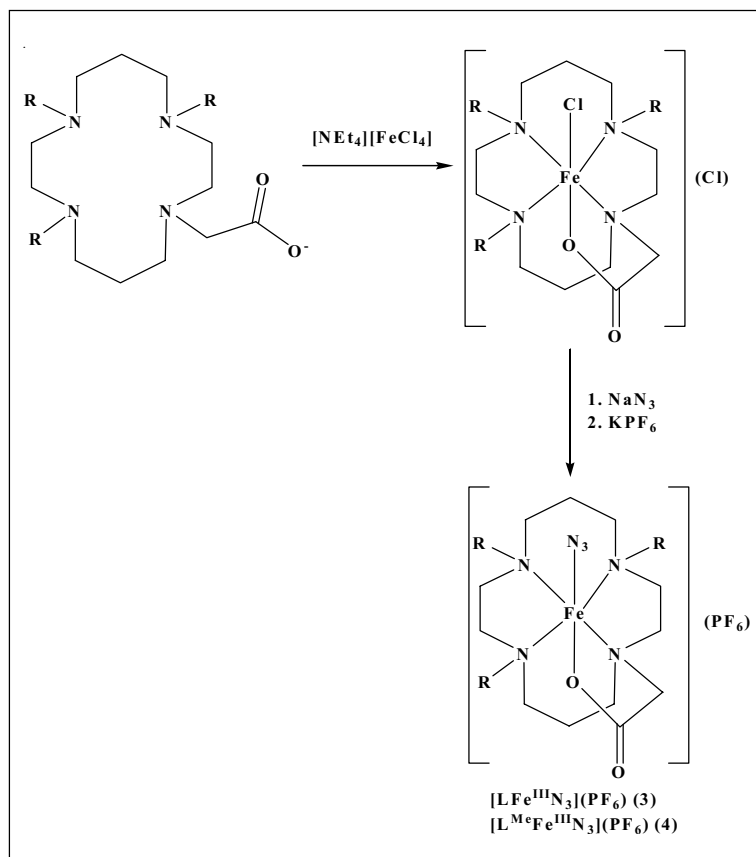


Figure 5. Synthesis of $[\text{LFe}^{\text{III}}\text{N}_3](\text{PF}_6)$ and $[\text{L}^{\text{Me}}\text{Fe}^{\text{III}}\text{N}_3](\text{PF}_6)$.

In addition to differences in the magnetic properties, **3** and **4** also have different chemical reactivity. While **4** can be oxidized readily to $[\text{L}^{\text{Me}}\text{Fe}^{\text{IV}}\text{N}_3](\text{PF}_6)_2$, **3** does not lead to a stable product. At this juncture Wieghardt and coworkers decided to utilize the photo reactivity of the azido group. In principle the photolysis of these Fe-N₃ compounds can proceed in two ways (*Figure 6*).

The following events can occur in the first pathway involving homolytic Fe-N bond scission:

- 1) Loss of the azide group from the coordination sphere of iron through a Fe-N bond scission.
- 2) Formal reduction at the iron center.
- 3) Formal oxidation of the azide moiety to molecular dinitrogen.

Figure 6. Possible pathways in the photolysis of $[LFe^{III}N_3](PF_6)$ and $[L^{Me}Fe^{III}N_3](PF_6)$. Pathway 1 leads to a Fe-N bond cleavage and reduction at iron. Pathway 2 leads to N-N bond scission and oxidation at iron.

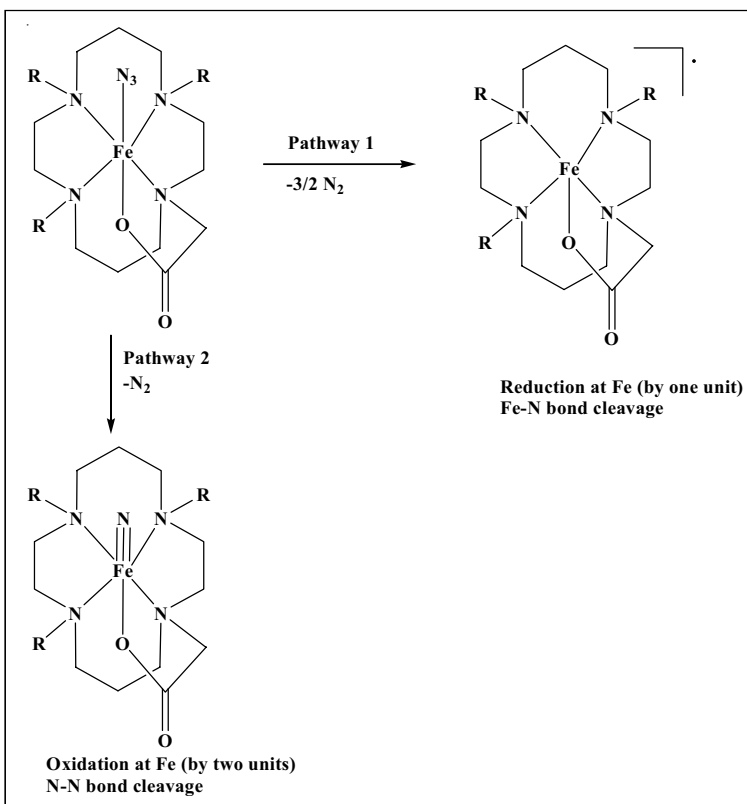
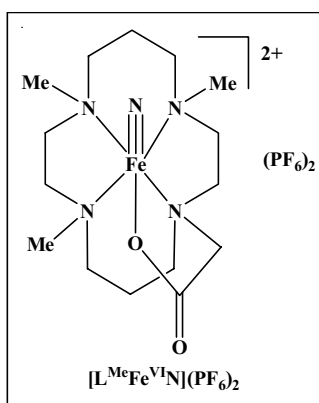


Figure 7. The hexavalent iron complex $[L^{Me}Fe^{VI}N](PF_6)_2$ formed in a low temperature photolysis of $[L^{Me}Fe^{IV}N_3](PF_6)_2$.



The second pathway is characterized by the following events:

- 1) In contrast to a Fe-N bond cleavage of pathway 1, a N-N bond cleavage can occur. This means that one of the nitrogen atoms of the azide unit is retained in the form of a Fe-N triple bond.
- 2) This pathway is characterized by a formal oxidation of iron by two units.

Which pathways are preferred in the photolysis of **3** and **4**? Wieghardt and coworkers found that **3** can be photolyzed efficiently to afford the Fe(V) complex, $[LFe^V N](PF_6)$ whereas photolysis of **4** affords only an Fe(II) complex. Surprisingly, however, $[L^{Me}Fe^{IV}N_3](PF_6)_2$ (which was obtained by the electrochemical oxidation of **4**) upon photolysis using laser irradiation (650 nm) at 77 K afforded predominantly the Fe(VI) complex, $[L^{Me}Fe^{VI}N](PF_6)_2$ ending the long quest for a second example of a hexavalent iron complex (Figure 7).

How does one characterize these complexes and determine their oxidation states? Mössbauer spectroscopy (see *Box 1* for the principles of Mössbauer spectroscopy) is an excellent structural characterization technique for iron complexes. Two parameters viz., isomer shifts (symbol : δ ; units: mm s^{-1}) and quadrupole splitting parameters (symbol : ΔE_Q ; units : mm s^{-1}) can provide

Box 1. Mössbauer Spectroscopy

Mössbauer Effect, the phenomenon of *recoilless* gamma ray emission and absorption, was discovered by Rudolph Mössbauer in 1957. He received the Nobel Prize in Physics in 1961 for this discovery. Mössbauer spectroscopy is based on the *Mössbauer Effect*.

The basis of Mössbauer spectroscopy is that nuclei in atoms can undergo a variety of energy level transitions involving emission or absorption of gamma rays.

However, as nuclei absorb or emit the high energy gamma rays, they suffer recoil which causes a loss of energy (this is similar to the situation when a bullet is fired from a gun) blurring the resonance condition for the absorption of gamma rays and detection of nuclear transitions. Mössbauer discovered that *recoilless* gamma ray emission and absorption occurs when atoms are present in a solid matrix.

The nuclear energy levels depend on the surrounding environment of the nucleus and hence Mössbauer spectroscopy is an extremely useful analytical tool. For example, in iron complexes, the nuclear energy levels of ^{57}Fe (having long-lived low-energy excited state) depend on the coordination number, the types of ligands attached and the coordination geometry around iron.

How is this technique implemented for iron compounds?

A ^{57}Co source upon electron capture gives a ^{57}Fe in an excited (nuclear) state. A vast majority of these species decay to give 14.4 keV gamma radiation. This is then absorbed by the ^{57}Fe present in the sample.

The variation of gamma ray energy, which is required to be used as a spectroscopic probe, is achieved by taking advantage of the Doppler shift. The energy of the gamma beam can be varied by moving the source. For example, moving the source at a velocity of 1 mm/sec toward the sample will increase the energy of the photons by 14.4 keV $(v/c) = 4.8 \times 10^{-8}$ eV. Consequently, in Mössbauer spectroscopy, the unit of energy is quite peculiar and is mm sec^{-1} . This is equal to 4.8×10^{-8} eV for Fe^{57} .

Mössbauer spectrometer consists of a source which can be moved relative to the sample. A counter is placed after the sample to monitor the intensity of the gamma ray beam after it has passed through the sample. The Mössbauer spectrum is a plot of the intensity of the exiting gamma ray (given by the number of counts) vs. the velocity of the source (energy of the gamma ray beam). Quantitative data is obtained in the form of *Isomer shifts* and *Quadrupole splitting parameters*.



| Compound | Coordination environment/ Coordination | Oxidation state of iron | Isomer shift (δ) (mm s ⁻¹) | Quadrupole splitting ΔE_Q (mm s ⁻¹) |
|---|---|-------------------------|--|--|
| [L ^{Me} Fe ^{VI} N](PF ₆) ₂ | [5N,1O]; Octahedral | +6 | -0.29 | 1.53 |
| [L ^{Me} Fe ^{IV} N ₃](PF ₆) ₂ | [5N,1O]; Octahedral | +4 | 0.11 | 1.92 |
| [L ^{Me} Fe ^{III} (CH ₃ CN)](PF ₆) ₂ | [5N,1O]; Octahedral | +3 | 0.53 | 1.13 |
| [L ^{Me} Fe ^{III} N ₃](PF ₆) (high spin) | [5N,1O]; Octahedral | +3 | 0.53 | 0.84 |
| [L ^{Me} Fe ^{III} N ₃](PF ₆) (low spin) | [5N,1O]; Octahedral | +3 | 0.33 | 2.21 |

Table 1. Isomer shifts and quadrupole splitting parameters of a series of iron complexes where the oxidation state of iron is varied systematically from +3 to +6 (adapted from [3] and [4]).

structural information. In particular, isomer shifts can be used for ascertaining the oxidation state of iron in its coordination complexes. This is particularly valid if the general coordination environment around iron is kept constant. A collection of the isomer shifts for various complexes discussed in this article are given in Table 1. It can be clearly seen that as the oxidation state of the iron in the complex varies from +3 to +6 the isomer shift value becomes more negative. Thus, for the hexavalent iron complex, [L^{Me}Fe^{VI}N](PF₆)₂, the isomer shift is -0.29 mm s⁻¹.

The results obtained from Mössbauer spectroscopy can be confirmed by X-ray absorption spectroscopy. An intense *pre-edge* peak corresponding to the energy (7115.1 eV) and an edge peak at 7125.0 eV are seen for [L^{Me}Fe^{VI}N](PF₆)₂. These energies of absorption are higher than those observed for the iron complexes with a lower oxidation state and confirms the assignment of the oxidation state of +6 for the iron in [L^{Me}Fe^{VI}N](PF₆)₂. What about the structural parameters of the iron complex? In general, if we can grow suitable crystals, X-ray diffraction techniques can be used to obtain precise information about the molecular structure. But, suitable crystals of [L^{Me}Fe^{VI}N](PF₆)₂ could not be obtained, presumably because of its thermal instability; while it is stable at 77K, it decomposes above 40K readily. However, by using EXAFS (Extended X-ray Absorption Fine Structure) the gross structural parameters of [L^{Me}Fe^{VI}N](PF₆)₂ were obtained. From this data it was found that one of the Fe-N bonds was very short (1.57 Å); this value agrees well with a theoretical value for a Fe-N triple bond in a hexavalent iron. Infrared spectroscopy was

The existence of hexavalent iron in [L^{Me}Fe^{VI}N](PF₆)₂ is confirmed by Mössbauer and X-ray absorption spectroscopies.

used to determine the Fe≡N stretching frequency in $[L^{Me}Fe^{VI}N](PF_6)_2$ (1064 cm^{-1}).

An iron (VI) complex should have a d^2 electronic configuration. The ferrate ion $[FeO_4]^{2-}$ is a d^2 system and is paramagnetic with $S = 1$ (two unpaired electrons). In contrast, $[L^{Me}Fe^{VI}N](PF_6)_2$, also a d^2 system, is diamagnetic ($S = 0$). This means that the two electrons present in the d orbitals must be paired. An energy level calculation was carried out to determine the relative energy levels of the five 3d orbitals of iron in $[L^{Me}Fe^{VI}N](PF_6)_2$. This indicates that the two electrons of Fe^{VI} are paired in a d_{xy} orbital which is described as a non-bonding orbital. The d_{xz} and d_{yz} orbitals suffer destabilization and are higher in energy. The $d_{x^2-y^2}$ is the next higher energy orbital. The highest energy 3d orbital is found to be d_{z^2} (Figure 8).

In conclusion, a novel high-oxidation state Fe^{VI} octahedral complex has been obtained through an innovative synthetic strategy. The characterization of this complex was carried out by a multitude of sophisticated spectroscopic techniques. Apart from its obvious academic interest, high-oxidation state iron complexes have implications in biological systems. Clearly this area involving the synthesis, structure and reactivity of high-valent iron complexes will continue to interest chemists for some time. Proof of such interest comes from two recent papers which report non-heme $Fe(IV)=O$ and $Fe(V)=O$ complexes [5,6].

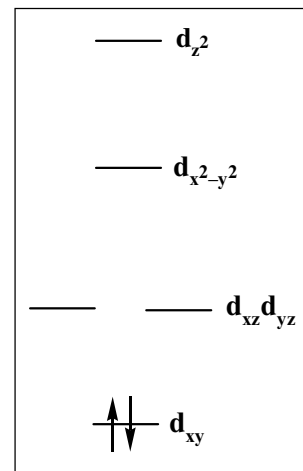


Figure 8. 3d energy level diagram of $[L^{Me}Fe^{VI}N](PF_6)_2$ with an $S=0$ ground state.

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Suggested Reading

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