

## Chemistry of the diphenyldithiophosphinato complexes of iron

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**Abstract.** Bis(diphenyldithiophosphinato)iron(II) (**2**) is synthesised by the action of  $(C_6H_5)_2PS_2H$  on  $FeCO_3$ . Spectroscopic data show that **2** has got a distorted tetrahedral structure. The ligand field strength in **2** ( $5748\text{ cm}^{-1}$ ) as determined from the diffuse reflectance spectrum is comparable to that in reduced rubredoxin ( $6250\text{ cm}^{-1}$ ). The isomer shift value in the Mossbauer spectrum of **2** also is quite consistent with that reported for reduced rubredoxin and other iron(II) tetrahedral compounds. In solution and in the presence of air **2** is spontaneously oxidised to the ferric complex  $[(C_6H_5)_2PS_2]_3Fe$  (**1**). The dark green **1** is reduced to the pale yellow ferrous complex **2** by the action of  $NaBH_4$  in THF solution. This redox behaviour is comparable to that of rubredoxin, although the oxidised complex differs from oxidised rubredoxin in that it has got octahedral geometry compared to the tetrahedral geometry of the oxidised rubredoxin. The reaction of **1** with 2,2'-bipyridyl,  $NH_3$ ,  $Br_2$  and NO and the Mossbauer spectra of the products are also described here.

**Keywords.** Iron in sulphur environments; rubredoxin; diphenyldithiophosphinate; iron(II) and iron(III) complexes; Mossbauer spectra; mixed ligand complexes.

### 1. Introduction

The coordination chemistry of iron in sulphur environments has attracted the attention of chemists, because many of the iron complexes of biological importance are ligated by sulphur and function as electron carriers for many of the biological reactions. The simplest among them is rubredoxin in which Fe(II) is coordinated to four cysteinyl sulphurs in an essentially tetrahedral arrangement (Eaten and Lovenberg 1970). Rubredoxin undergoes reversible one-electron oxidation and reduction with a redox potential of about  $-57\text{ mV}$ . The oxidised rubredoxin,  $Rd_{ox}$ , can be reduced with dithionite to the reduced rubredoxin,  $Rd_{rd}$ .

To understand the biological chemistry of rubredoxin in detail attempts have been made to synthesise tetrahedral complexes of iron ligated by sulphur which may be compared with the structure and properties of the active site in iron-sulphur proteins. A few tetrahedral complexes have already been synthesised. These include  $Fe[(SPR)_2N]_2$  (Davison and Switkes 1971),  $Fe[(SPR_2)_2CH]_2$  (Davison and Reger 1971) etc. However, the reversible oxidation of these complexes to the corresponding Fe(III) species as in the case of rubredoxin has not been demonstrated. Further, the magnitude of the ligand field in these complexes is much smaller than that in reduced rubredoxin. Bis(*o*-xylyl- $\alpha,\alpha'$ -dithiolato)ferrate(II) synthesised and structurally characterised by Lane *et al* (1977) represents the closest synthetic analogue reported so far which is comparable to the active site of rubredoxin protein. The reversible electrochemical redox behaviour of this

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and some tetraalkyl- and arylthiolato complexes of iron(II) have been established (Lane *et al* 1977). We describe here the chemistry of diphenyldithiophosphinato complexes of iron(II) and iron(III) which undergo chemical one-electron oxidation and reduction under mild conditions and demonstrate the points of similarities between the Fe(II) complex and the reduced rubredoxin. The ligand reactivities of the Fe(III) complex are also studied and reported here.

## 2. Experimental

### 2.1. General

Reactions were carried out in an atmosphere of nitrogen wherever necessary. Solvents were purified by standard methods.  $\text{Ph}_2\text{PS}_2\text{H}$  and its sodium salt and  $(\text{Ph}_2\text{PS}_2)_3\text{Fe}$  (**1**) were prepared according to published procedures (Higgins *et al* 1955; Cavell *et al* 1972).

### 2.2. Synthesis of $(\text{Ph}_2\text{PS}_2)_2\text{Fe}$ (**2**)

Ferrous carbonate was prepared under nitrogen by reacting an aqueous solution (20 ml) of ferrous ammonium sulphate (1.6 g, 4.08 mmol) with an aqueous solution (10 ml) of anhydrous sodium carbonate (0.5 g, 4.72 mmol). To the white suspension of ferrous carbonate alcoholic solution (20 ml) of  $\text{Ph}_2\text{PS}_2\text{H}$  (2.0 g, 8.0 mmol) was added. Ferrous carbonate dissolved slowly and the solution was filtered. The clear filtrate was stirred for five hours when pale yellow crystals of **2** separated out (1.3 g, 57.5%). The crystals were filtered, washed with absolute alcohol and dried in vacuum. Analysis: Calculated for  $\text{C}_{24}\text{H}_{20}\text{FeP}_2\text{S}_4$ : Fe 10.07; S 23.09, Found: Fe 9.84; S 22.86. Mossbauer spectrum:  $\delta = 0.85$  mm/s and  $\Delta E_Q = 2.82$  mm/s. Diffuse reflectance spectrum:  $\lambda_{\text{max}} 5748 \text{ cm}^{-1}$ .

### 2.3. Reaction of **1** with $\text{NaBH}_4$

Dry THF (20 ml) was added to a mixture of **1** (0.8 g, 0.99 mmol) and  $\text{NaBH}_4$  (0.04 g, 1.06 mmol) in a dry flask under nitrogen. On stirring the dark green solution turned pale green and finally a pale yellow precipitate settled down which was filtered, washed with deoxygenated alcohol and dried. The product was identified as **2** by comparison of the electronic and Mossbauer spectra.

### 2.4. Reaction of **1** with 2,2'-bipyridyl

Dry benzene (20 ml) was added to a mixture of **1** (0.6 g, 0.742 mmol) and 2,2'-bipyridyl (bp), (0.35 g, 2.24 mmol) under nitrogen and stirred. The dark red  $[\text{Fe}(\text{bp})_3][(\text{S}_2\text{PPh}_2)_3]$  precipitated immediately. It was filtered, washed with benzene and dried. (0.9 g, 93.9%) Analysis: Calculated for  $\text{C}_{66}\text{H}_{54}\text{FeN}_6\text{P}_3\text{S}_6$ : Fe 4.39; S 15.11; N 6.61, Found: Fe 4.46; S 14.86; N 6.70. Mossbauer spectrum:  $\delta = 0.27$  mm/s and  $\Delta E_Q = 0.36$  mm/s.

### 2.5. Reaction of **1** with $\text{NH}_3$

To nearly 25 ml of liquid ammonia, **1** (0.4 g, 0.49 mmol) was added and stirred. The deep green solution turned yellow and then dark brown. On complete evaporation of ammonia, a brownish yellow mass was obtained. The product was washed with benzene

and dried in vacuum. While drying ammonia was evolved from the product giving back the starting material.

### 2.6. Reaction of 1 with bromine

A dichloromethane solution of bromine (0.189 g in 7 ml) was added dropwise to a solution of 1 (0.8 g, 0.99 mmol) in dichloromethane (20 ml) and kept stirred overnight. After removal of the solvent the brown mass obtained was dissolved in a minimum quantity of benzene and filtered. On cooling  $[(\text{Ph}_2\text{PS}_2)_2\text{FeBr}]$  crystallised out which was filtered, washed with benzene and dried (0.4 g, 63.5%). Analysis: Calculated for  $\text{C}_{24}\text{H}_{20}\text{BrFeP}_2\text{S}_4$ : Br 12.61; Fe 8.81; S 20.18, Found: Br 13.29, Fe 8.83; S 19.46. Mossbauer spectrum:  $\delta = 0.31$  mm/s and  $\Delta E_Q = 0.11$  mm/s.

### 2.7. Reaction of 1 with NO

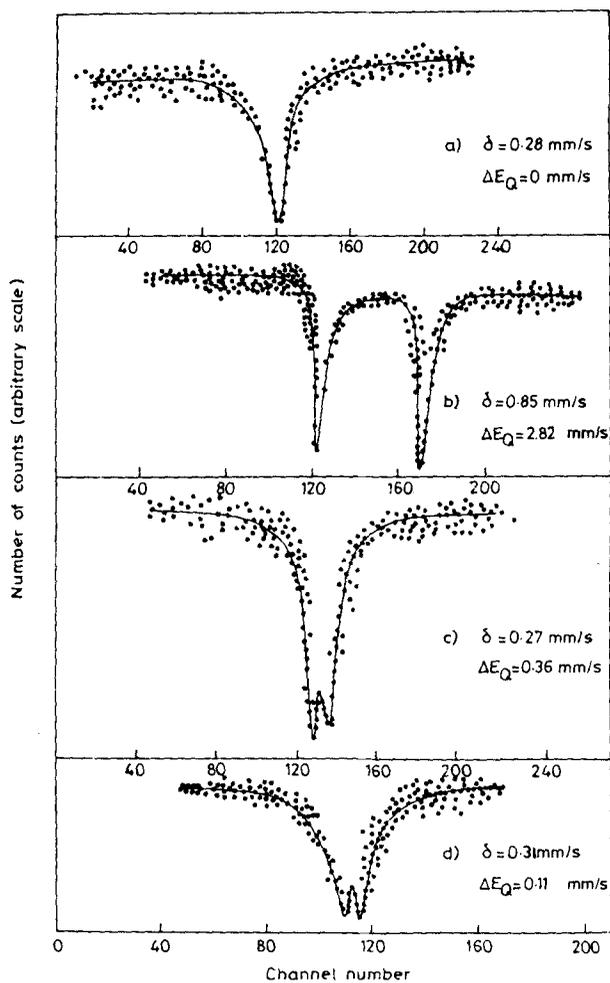
Dry NO was bubbled through a solution of 1 (0.4 g, 0.49 mmol) in dry dichloromethane (20 ml) for 1 hour. The deep green solution was changed to dark chocolate brown slowly. The formation of nitrosyl complex was indicated by the IR spectrum ( $\nu_{\text{NO}} 1705 \text{ cm}^{-1}$ ). The product, however, decomposes easily and could not be isolated.

## 3. Results and discussion

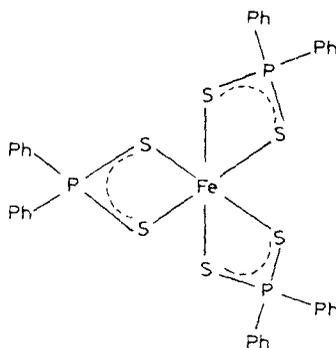
The ferric complex, tris(diphenyldithiophosphinato)iron(III), 1, was prepared by a metathesis reaction as reported by Cavell *et al* (1972). It is insoluble in water and ethanol, but soluble in common organic solvents except petroleum ether. The solutions in presence of air undergo decomposition slowly. The Mossbauer spectrum of 1 is reported here for the first time (figure 1a). The spectrum shows no quadrupole splitting indicating the undistorted octahedral configuration of 1 (figure 2). The isomer shift occurs at  $\delta = 0.28$  mm/s relative to iron metal which confirms the +3 oxidation state of iron and the high spin nature of the complex. The Mossbauer spectral studies of tris(dialkyldithiocarbamate)iron(III) complexes at room temperature indicate that there is a thermal equilibrium between the high and low spin states of iron(III) (Frank and Abeledo 1966). Accordingly in those cases, a quadrupole splitting is observed. The absence of quadrupole splitting in the Mossbauer spectrum of 1 confirms the absence of similar high-low spin equilibrium at room temperature.

The most important reaction undergone by 1 is that on treatment with  $\text{NaBH}_4$  in THF solution, it is reduced to the pale yellow iron(II) complex  $[(\text{C}_6\text{H}_5)_2\text{PS}_2]_2\text{Fe}$  (2). The formation of 2 is confirmed by comparison of the electronic and Mossbauer spectra with those of  $[(\text{C}_6\text{H}_5)_2\text{PS}_2]_2\text{Fe}$  prepared by direct reaction *viz* by the action of  $(\text{C}_6\text{H}_5)_2\text{PS}_2\text{H}$  on a freshly prepared aqueous alcoholic suspension of  $\text{FeCO}_3$ . In solution and in presence of air 2 is spontaneously oxidised to the dark green 1. This redox behaviour is comparable to that of rubredoxin, although the oxidised complex differs from oxidised rubredoxin in that it has octahedral geometry compared to the tetrahedral geometry of the oxidised rubredoxin.

Although a tetrahedral structure has been proposed for 2 (Cavell *et al* 1972), no spectroscopic data have been reported. In the diffuse reflectance spectrum of the



**Figure 1.** Mössbauer spectra at room temperature of (a)  $[(Ph_2PS_2)_3Fe]$ , (b)  $[(Ph_2PS_2)_2Fe]$ , (c)  $[Fe(bp)_3](S_2PPh_2)_3$  and (d)  $[(Ph_2PS_2)_2FeBr]$ .



**Figure 2.** Structure of  $[(Ph_2PS_2)_3Fe]$  (1).

complex, there is a single peak in the near infrared region corresponding to the  ${}^5T_2 \leftarrow {}^5E$  transition. The absorption maximum occurs at  $5748\text{ cm}^{-1}$  as is characteristic of iron(II) tetrahedral complexes. This is comparable to the ligand field in reduced rubredoxin (Eaton and Lovenberg 1970) which occurs at  $6250\text{ cm}^{-1}$  and in the thiolato complex, bis(*o*-xylyl- $\alpha$ - $\alpha'$ -dithiolato)ferrate(II) anion (Lane *et al* 1977) at  $5560\text{ cm}^{-1}$ . The peak at  $5748\text{ cm}^{-1}$  is split indicating the tetragonal distortion from the perfect tetrahedral structure. The large splitting observed indicates that the degeneracy of the  $T_2$  state is removed not only by spin orbit coupling but also by the Jahn-Teller effects.

The Mossbauer spectrum of **2** (Figure 1b) shows a quadrupole splitting ( $\Delta E_Q = 2.82\text{ mm/s}$ ) centred at  $\delta = 0.85\text{ mm/s}$  relative to iron metal. The isomer shift value is quite consistent with that reported for other iron(II) tetrahedral compounds and for reduced rubredoxin (Lane *et al* 1977). The observed quadrupole splitting confirms the distorted tetrahedral configuration. In perfect cubic symmetry, tetrahedral iron(II) complexes cannot exhibit quadrupole splitting since the electric field gradient at the nucleus due to the *d* orbitals are equal and opposite in sign. In a tetrahedral ligand field, the free ion  ${}^5D$  term splits into a lower  ${}^5E$  and an upper  ${}^5T_2$  states. The energy separation between  ${}^5E$  and  ${}^5T_2$  states is of the order of  $5748\text{ cm}^{-1}$ . This splitting is sufficiently large that one may ignore the effect of the population of the  ${}^5T_2$  state when considering the electric field gradient at the nucleus. If  $[(C_6H_5)_2PS_2]_2Fe$  were exactly cubic, then the sixth *3d* electron outside the  $3d^5$  shell would be distributed equally among the degenerate  ${}^5E$  orbitals. This would produce zero quadrupole splitting, since the electric field gradient for the  $d_{z^2}$  and  $d_{x^2-y^2}$  states are  $-(4/7)\langle r^{-3} \rangle 3d$  and  $+(4/7)\langle r^{-3} \rangle 3d$  respectively (Edwards *et al* 1967). The observation of large quadrupole splitting shows that these levels must be split by a distortion of the iron.

The reaction of **1** with 2,2'-bipyridyl (bp) in 1 : 3 molar ratio gives a dark red product, tris(bipyridyl)iron(III) diphenyldithiophosphinate. The Mossbauer spectrum of the complex (figure 1c) shows a quadrupole splitting ( $\Delta E_Q = 0.36\text{ mm/s}$ ) centred at  $\delta = 0.27\text{ mm/s}$  relative to iron metal. These values confirm that iron is in the +3 oxidation state and that the complex is low spin. In the IR spectrum of this complex there is a medium intensity band at  $1025\text{ cm}^{-1}$  with a shoulder at  $1065\text{ cm}^{-1}$  due to the  $\nu_{as}(P-S)$  and  $\nu_s(P-S)$  vibrations. Further the absence of a band characteristic of Fe-S linkage expected in the region  $350-380\text{ cm}^{-1}$  is due to the non-bonded nature of the  $(C_6H_5)_2PS_2$ -moiety. The reaction of **1** with liquid ammonia gives a brownish yellow product, probably the hexamine complex,  $[Fe(NH_3)_6](S_2PPh_2)_3$ . However, while drying in vacuum, the product gives off ammonia giving back the original complex. The reaction of **1** with NO was carried out to obtain the nitrosyl complex  $[(C_6H_5)_2PS_2]_2FeNO$ . The formation of a chocolate brown nitrosyl complex is indicated by the IR spectrum ( $\nu_{NO} 1705\text{ cm}^{-1}$ ). The product, however, decomposes easily and could not be isolated.

A mixed ligand complex,  $[(C_6H_5)_2PS_2]_2FeBr$ , is formed by the action of bromine on **1** in methylenechloride in a 1 : 1 molar ratio. The Mossbauer spectrum of the new complex (figure 1d) shows a two-line quadrupole pattern ( $\Delta E_Q = 0.11\text{ mm/s}$ ) centred at  $\delta = 0.31\text{ mm/s}$  relative to iron metal. The splitting arises due to the electric field gradient produced by different ligands. In the IR spectrum of the complex, the band at  $310\text{ cm}^{-1}$  can be assigned to the Fe-Br vibration. The stretching frequency of Fe-S is shifted to higher frequency compared to that in  $Fe(S_2PPh_2)_3$  and occurs at  $380\text{ cm}^{-1}$ . A distorted square pyramidal structure is proposed for the complex  $[(C_6H_5)_2PS_2]_2FeBr$  with the iron atom lying above the basal plane formed by the four sulphur atoms

analogous to bromobis(N,N'-dialkyldithiocarbamato)iron(III) complexes (Martin and White 1967).

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