FE (II) - FE (III) ELECTRONIC AND MAGNETIC INTERACTION THROUGH A THIOPYRIDINE BRIDGE.

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In memoriam of Doctor Guido S. Canessa C.

ABSTRACT

Reaction of CpFe(dppe)I with dithiopyridine in methanol and in presence of NH_4PF_6 affords the new mixed valence complex {[CpFe(dppe)]$_2$ - μ - S - Py}(PF$_6$)$_2$ (1). Observation of an intervalence electron transfer affords the Hush parameters that permit to classify this compound as a type II Robin Day complex. The electron transfer across the pyridinethiolate ligand occurs at a rate estimated to be about 10^6 seg^{-1}. Variable - temperature magnetic susceptibility measurements have been carried out in the range of 5-300 °K. Results can be interpreted as principally due to weak intermolecular antiferromagnetic interactions between Fe (II) - Fe (III) dimers in the solid state.

KEYWORDS: iron complexes, magnetic interaction, electronic interaction, thiopyridine bridge. Interacción Fe (II) – Fe (III) electrónica y magnética a través de un puente Tiopiridina.

RESUMEN

La reacción de CpFe(dppe) con ditiopiridina en metanol y en presencia de NH_4PF_6 da como producto el nuevo complejo de valencia mixta {[CpFe(dppe)]$_2$ - μ - S - Py} (PF$_6$)$_2$ (1). La observación de una transferencia electrónica de intervalencia permite la evaluación de los parámetros de Hush los cuales están de acuerdo con una clasificación tipo II de Robin Day. La transferencia de electrones a través del ligando tiolatopiridina ocurre a una velocidad estimada de 10^6 seg^{-1}. Mediciones de susceptibilidad magnética a temperatura variable se han realizado en el rango 5-300 °K. Los resultados pueden ser interpretados como debidos principalmente a interacciones antiferromagneticas intermoleculares entre los dimeros Fe (II) – Fe (III) en estado sólido.

PALABRAS CLAVES: complejos de hierro, interacción magnética, interacción electrónica, puente Tiopiridina.

INTRODUCTION

Mixed valence complexes are a useful model for electron transfer processes in biological systems as well as in molecular electronic devices [1-4]. On the other hand, magnetic interactions between metal centers are of great interest in material science [5]. The development of new materials in which magnetic properties are combined with optical and electrical properties is a new and interesting field. We have

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previously reported the oxidative addition of disulphides to the complex CpFe(dppe)I to give the thiolate iron (III) complexes [CpFe(dppe) SR]PF$_6$ [6]. Recently we have found that the reaction of dithiopyridine PySSPy with CpFe(dppe)I affords different products depending on the solvent and the halide abstractor used [7]. With 4,4´-dithiopyridine and MeOH as solvent, in the presence of NH$_4$PF$_6$, a new mixed valence complex was obtained.
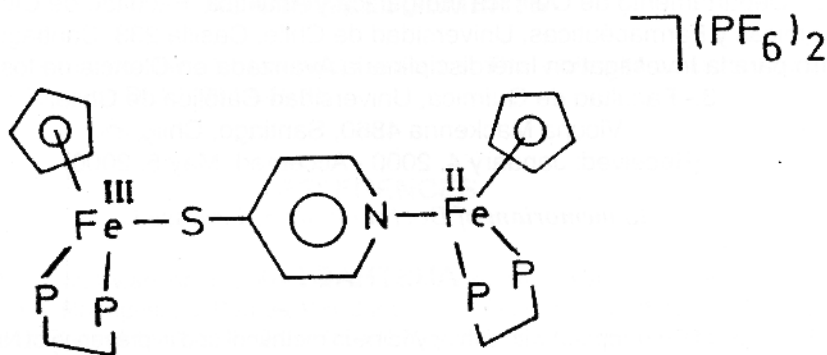
To our knowledge this is the first Fe (III) - Fe (II) complex containing a thiolate bridging ligand. In this complex the Fe(III) iron is bonded to the sulphide moiety, while the Fe(II) center is linked to the nitrogen atom of the bridging ligand.

RESULTS AND DISCUSSION

Observation of a metal - metal intervalence transition at 787 nm. for complex 1 allows the estimation of the Hush parameters [4] , using the equations:

$$\alpha^2 = \frac{(4.2 \cdot 10^{-4}) \, \varepsilon_{max} \Delta \nu_{1/2}}{\nu_{max} \, d^2} \tag{1}$$

$$\Delta \bar{\nu}_{1/2} = (2.31 \cdot 10^3 \, \nu_{max})^{1/2} \tag{2}$$

$$H_{ab} = \frac{2.06 \cdot 10^{-2} \, (\varepsilon_{max} \nu_{max} \Delta \nu_{1/2})^{1/2}}{d} \tag{3}$$

$$k_{th} = [(H_{ab})^2/h] \bullet [\pi/kT\lambda]^{1/2} \bullet \exp[-E_a/RT] \tag{4}$$

Values are shown in Table1. A value of 7.6Å was used for the intermetallic distance estimated from X –ray data for similar compounds and standard tables [4] This intervalence transition disappears upon reduction with Red Al (sodium bis (2-methoxyethoxy) aluminium) (See figure 1) .As expected the intense bands around 559 nm typical of the CpFe(III)-S chromophores [6a,6b] decrease upon reduction. The only absorptions that remain at 450nm are assigned to a characteristic transition of the CpFe(II)-S chromophore [6h].
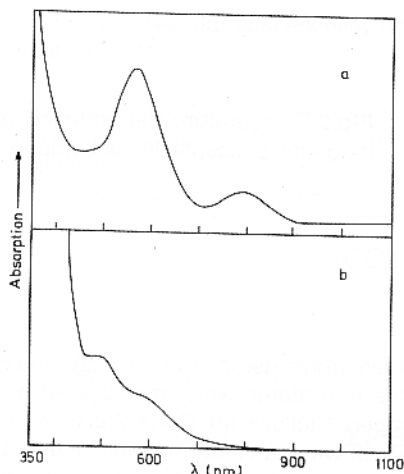

Fig.1. Uv-visible electronic spectrum of 1 (a) and upon reduction (b)

The α delocalization parameter obtained indicates that the studied complex is a partially delocalized class II species in the mixed valence complexes Robin - Day description [8]. On the other hand the coupling parameters H_{ab} suggest the existence of a moderate electronic interaction between the metal centers similar to that found in mixed-valence complexes with large bridging ligands containing pyridine groups linked to metals [4]. This value is also close to that observed for some metalloproteins [9]. The thermal first order electron transfer rate constant is $k_{th} \approx 10^6$ seg^{-1} , of the order magnitude of for rate constants for other mixed valence complexes containing pyridine bridging ligands [4].

Table I. Intervalence Transition Parameter[a] for $[\{Cp(dppe)Fe\}_2\text{-}\mu\text{-}S(Py)](PF_6)_2$ in Several Solvents.

Solvent	E_{op} (cm^{-1})	α	$\Delta\nu_{1/2}$ (cm^{-1})	Hab (cm^{-1})	E_a (cm^{-1})	k_{th}(s^{-1})
Acetonitrile	12682.3	0.028	1615	362	3170.6	6.3·10^6
Ethylmethylketone	12674.3	0.030	1689	388	3168.5	9.1·10^6
Acetone	12674.3	0.030	1592	385	3168.6	7.2·10^6
Dichloromethane	12698.4	0.028	1616	361	3174.6	6.5·10^6
Methanol	12690.4	0.026	2233	331	3172.6	2.4·10^6

[a] Calculated using the Hush formalism given in references 4(a-b).

The good solubility of the complex in several organic solvents permits to study the solvent dependence on the intervalence transition which, gives information about reorganizational energy arising from rearrangements of the inner and outer coordination spheres [4,10]. The intercept of a plot of E_{op} vs $(1/D_{op} - 1/D_S)$ for the solvents displayed in Table 1 affords the λ_i value, (λ_i = 12470 cm^{-1}). From equation E_{op} = λ = $\lambda_i + \lambda_o$, the λ_o value can be calculated (λ_o = 227 cm^1), assuming a symmetrical bridge (this approximation is frequently used when the oxidation potentials are not known in all the solvents;for a treatment for asymmetrical ligands see ref.[4a,4b]). Thus the small but not null solvent dependence confirm

the class II Robin –Day classification .The high inner - sphere reorganization contribution respect to the outer - sphere reorganization may be associated to a considerable participation from the vibrational modes of the bridging ligand. Appreciable contribution to the inner-sphere reorganization of the cyanide as a bridging ligand in dinuclear mixed valence complexes has been previously reported [11].
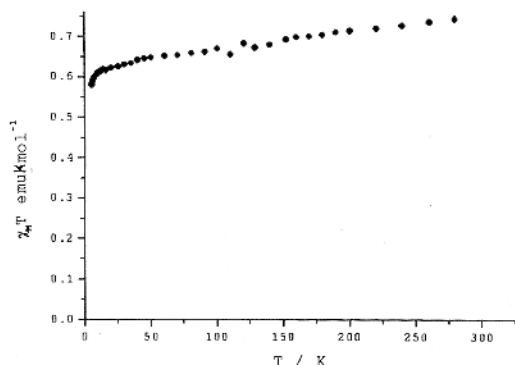

Fig.2.Temperature dependence of molar magnetic susceptibility of complex **1**

Taking in consideration that there is a degree of electronic delocalization in the mixed valence complex, the possible magnetic interactions between the iron atoms were investigated by variable - temperature magnetic susceptibility measurements. Complex 1 follows the Curie-Weiss law with θ= -7.5 °K. The negative value of the Weiss constant is indicative of weak antiferromagnetic interactions. Data shown in Figure 2 can be interpreted as a nearly normal paramagnetism, such as the magnetic behavior of complexes $[CoCp_2{}^*]^+[TCNE]^-$; $[FeCp_2{}^*]^+[C_6(CN)_4Cl]^-$; $[FeCp_2{}^*]^+[C_3(CN)_5]^-$; $[NiCp_2{}^*]^+[C_4(CN)_6]^-$ and $[NiCp_2{}^*]^+ [TCNE]^-$ with θ values -1; -1; -1.2; -6.0; and -11.5 respectively [12,13].

Figure 2 depicts the $\chi_m T$ vs T dependence for the binuclear Fe(II)-Fe(III) complex. From this plot it is possible to infer the decrease of the magnetic moment from a value of 2.44 BM at 280°K to μ_{eff} = 2.15 BM at 5.3°K. The latter calculated according to eq.5.

$$\mu_{eff}= [3k/N\beta^2(\chi_M T)]^{1/2} \qquad (5)$$

The magnetic moment was calculated assuming that both metal centers have regular octahedral geometry and therefore correspond, assuming high crystal field, to a diamagnetic Fe(II) d^6 system (S=0) and a low spin Fe(III) d^5 system (S=1/2). Therefore only the Fe(III) center was considered to be paramagnetic. This model permits to propose that the decrease of the magnetic moment with the lowering in temperature is due in part to intermolecular interactions. The room temperature magnetic moment of complex 1 is higher than the spin-only values due to one electron (μ_{eff} =1.73 BM). The low spin complexes with $t^5{}_{2g}$ configurations usually have orbital contributions to their moments at room temperature; values of approximately 2.3BM have been observed. These moments are intrinsically temperature dependent decreasing as the temperature is lowered. Mononuclear Fe(III) complexes $[CpFe(dppe)-SR]PF_6$ with a low spin d^5 configuration have been reported to exhibit magnetic moments in the range 1.6-2.3 BM (6a) .

Although $[CpFe(dppe)L]PF_6$ complexes usually exhibit a singlet state (S=0)[6g] structural modifications of the fragment CpFe(dppe) can generate triplet states (S=1) [14,15], thus leading to paramagnetic Fe(II) species [16]. There are a few complexes in which the symmetry is very low and the intermediate S=1 state is the adopted ground state [17]. On the other hand, it can not be excluded that the experimental data could result from the coexistence of species with Fe(II) centers with S=0 and S=2 (from unpaired electrons due to low crystal field generated in an octahedral environment) [18].

If the two metal centers are assumed to present a high spin state, the Fe(II) iron can be described by a S=2 term ,and the Fe(III) iron by S=5/2. The magnetic analysis was carried out using the susceptibility

equation (6) based on the following set of energies corresponding to the dimer: 3/4J, 15/4J, 35/4J, 63/4J, 99/4J, which were introduced into the Van Vleck equation [19]

$$\chi_M = \frac{[Ng^2/3Kt](\ 3/2exp3x + 15exp15x + 105/2exp35x + 126exp63x + 495/2\ [exp99x]}{(2exp3x + 4exp15x + 6exp35x + 8exp63x + 10exp99x)} \quad (6)$$

x=J/4kt

χ_M denotes the molar molecular susceptibility per binuclear complex, while the remaining symbols have their usual meaning.

The best fit of the experimental data was obtained with magnetic parameters g=2.5 and J=123cm^{-1}. However these do not account for the observed magnetic behavior, since a positive value of J corresponds to a ferromagnetic interaction. The failure of this fit to account the observed magnetic behavior permits to assess the high crystal field of the ligand involved in complex 1.

CONCLUSION

The mixed valence Fe(II)-Fe(III) complex 1 exhibits a moderate strong electron delocalization between the iron centers, whilst the weak antiferromagnetism observed appears to arise in part from an intermolecular interaction rather than to some intramolecular spin interaction in the dimeric complex.

EXPERIMENTAL

Details about experimental procedures and spectroscopic routine (IR, UV-Visible, EPR, etc.) measurements have been previously reported (4-6). Temperature dependent magnetic susceptibilities of a powdered sample were recorded on a SHE SQUID susceptometer in the range 5 - 300 K with an applied field of 1 Koe. Pascal's constants were used to estimate the correction for the underlying diamagnetism of the sample.

Synthesis of {[CpFe(dppe)$_2$] μ - S- Py}(PF$_6$)$_2$
Cp(dppe)FeI 0.15 g (0.23 mmol) was stirred with 4,4-dithiobispyridine 0.08 g (0.36 mmol) in presence of NH$_4$PF$_6$ 0.06 g (0.37 mmol) in CH$_3$OH (30 ml) for 24 h. at room temperature. The solvent was evaporated under vacuo and the black solid residue was extracted with dichloromethane (15 ml). Upon addition of a 1:1 mixture of n-hexane-diethyl ether blue-black microcrystals precipitated which were washed with diethyl ether for several times and dried under reduced pressure. Yield c.a. 70%. Anal. Found. : C 55.98, H 4.17. N. 1.1 Calc. for C$_{67}$H$_{62}$NF$_{12}$SP$_6$Fe$_2$.
C 55.93, H 4.31. N 0.97. Full detail of the spectroscopic characterization of this complex has been previously given [6f].

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