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X-Ray Investigation on a Five-Coordinated Iron(II) Complex with an Intermediate Spin State. Crystal Field and Angular Overlap Calculations

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The crystal structure of the intermediate spin complex [Fe(P$_4$)Br]BPh$_4$·CH$_2$Cl$_2$ (μ_{eff} = 1.6 BM at 298°K) where P$_4$ is the tetradentate ligand hexaphenyl-1,4,7,10-tetraphosphadecane has been determined. The crystals are of triclinic space group $P\bar{1}$ with a = 13.86 (1) Å, b = 19.29 (1) Å, c = 12.64 (1) Å, α = 71.5 (1)°, β = 81.9 (1)°, γ = 81.0 (1)°, and Z = 2. Counter methods were used to collect 3046 reflections and the structure was solved by the heavy-atom technique; least-squares refinement gave a final R factor on F of 0.081. The coordination polyhedron can be described as a distorted trigonal bipyramid. On the basis of the structural results we suggest the existence of only one type of molecule with a mixed spin state, although the presence of a mixture of two different spin states cannot certainly be ruled out. Crystal field and angular overlap calculations reasonably account for the spectral data and justify the spin equilibrium hypothesis showing the existence, for appropriate parameter values, of nearly degenerate singlet and triplet ground states.

Introduction

It has been shown that the nature of the donor atoms is an important factor in governing the spin state of five-coordinated metal complexes.[2] However the geometry of the chromophore should also play an important role in determining the spin state.[3] In fact the two recently reported[4] series of five-coordinated iron(II) complexes [Fe(PP$_3$)X]·BPh$_4$ [PP$_3$ = tris(2-diphenylphosphinoethyl)phosphine] and [Fe(P$_4$)X]BPh$_4$ [P$_4$ = hexaphenyl-1,4,7,10-tetraphosphadecane], which have the same donor set P$_4$X, show different spin multiplicities, depending on whether the ligand is linear or tripod-like. The PP$_3$ complexes have μ_{eff} values corresponding to a triplet ground state, whereas the P$_4$ complexes have μ_{eff} values which were attributed to a spin equilibrium between a singlet ground state and a thermally accessible triplet.[4] The latter complexes, together with those reported by Konig, *et al.*,[5] are the first example of five-coordinated Fe(II) complexes in a singlet ground state, since the five-coordinated Fe(II) complexes reported so far either have a triplet or quintuplet ground state[3] or are involved in a $^5E \rightleftarrows ^3A$ equilibrium.[6]

The singlet ground state in the [Fe(P$_4$)X]BPh$_4$ complexes could be indicative of a nearly square-pyramidal configuration; on the other hand the spin equilibrium suggests the existence of a thermally accessible triplet and a stereochemistry not far from a trigonal bipyramid. Therefore we have undertaken an X-ray analysis on the [Fe(P$_4$)Br]BPh$_4$·CH$_2$-Cl$_2$ complex, in order to determine the geometry of the chromophore and to contribute to the knowledge of the relationship between crystal structure and spin state. On the basis of structural results, calculations using the crystal field (CF) and angular overlap (AOM) models were performed. In spite of the model simplicity, the results of these calculations agree fairly well with the spectral data and the spin equilibrium hypothesis.

Experimental Section

Crystals of the compound were prepared as described else-

where.[4] Preliminary X-ray photographs showed no evidence of symmetry or systematic extinctions so the space group must be $P\bar{1}$ or $P1$; the former was assumed to be the space group and the successful refinement of the structure confirmed this assumption. The crystal used for data collection (0.09 × 0.17 × 0.30 mm) was mounted along the longest dimension so that the a axis was approximately parallel to the ϕ axis of a Philips computer controlled diffractometer PW 1100. Cell dimensions, determined by a least-squares refinement of 19 reflections accurately centered, are a = 13.86 (1) Å, b = 19.29 (1) Å, c = 12.64 (1) Å, α = 71.5 (1)°, β = 81.9 (1)°, and γ = 81.0 (1)°. The observed density of 1.30 g cm^{-3} (by flotation) agrees with the calculated value of 1.28 g cm^{-3} calculated for 2 molecules/cell. The intensity data were collected using Mo Kα radiation monochromatized with a flat graphite crystal. Reflections for which $2\theta \leqslant 40°$ were collected by the ω–2θ scan technique over a 2θ interval of 1.2° at a scan speed of 0.07°/sec. Stationary background counts were taken before and after each scan for a time equal to half of the scan time. Three standard reflections were monitored every 2 hr and showed partial anisotropic decomposition since their intensity decrease was from 2 to 10%. No attempt was made to take this effect into account. The total peak counts were corrected for background and the standard deviation of the resulting intensity I was estimated as described elsewhere.[7] After correction for Lorentz and polarization effects, 3046 reflections, whose intensity was greater than $3\sigma(I)$, were considered observed. No correction was applied for absorption owing to the size of the crystal and to the rather low value of the linear absorption coefficient μ = 11.5 cm^{-1}. A three-dimensional Patterson map gave the position of the bromine and iron atoms. Successive three-dimensional Fourier syntheses showed the other nonhydrogen atoms of the cation and of the tetraphenylborate anion. Moreover the presence of some diffuse peaks was attributed to the presence of solvent molecules. The four highest peaks whose electronic density was close to that of the carbon atoms were interpreted as chlorine atoms of two methylene chloride molecules with a population parameter of 0.5. Least-squares refinement was then undertaken. Because the number of parameters exceeded the capacity of the computer the parameters were divided in four blocks and the matrix was divided in four submatrices. Atoms heavier than carbon were included in the first, C(1) to C(24) in the second, C(25) to C(48) in the third, and the remaining atoms in the fourth block. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. All weights were set to unity at this stage. Three cycles of refinement with isotropic thermal parameters followed by two cycles using anisotropic thermal parameters for iron, phosphorus, and chlorine atoms and isotropic ones for the other atoms reduced the R factor to 0.092. At this point a difference Fourier map showed some diffuse peaks around the solvent molecules, but attempts to introduce and refine the carbon atoms of the methylene chloride gave very poor C–Cl bond distances. Probably our model for the solvent molecules is not fully satisfactory but no more efforts were spent, since, owing to the large number of parameters and reflections, the chemical information we could have obtained was not comparable with the computing cost. The hydrogen atoms, calculated in idealized positions

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(C–H = 1.05 Å), were introduced in subsequent calculations with temperature factors equal to those of their own carbon atoms but were not refined. Two more cycles gave a final R of 0.081. The value of R_w is 0.096 where $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w |F_o|^2]^{1/2}$ and the standard deviation of an observation of unit weight is 2.31. In the final refinements the weights w were taken as $1/\sigma(F_{rel})^2$. Atomic scattering factors were taken from ref 8 for Br, Fe, Cl, P, N, C, and B and from ref 9 for H. Programs used were as follows: data reduction, Fourier syntheses, and structure factors were from the series of programs written for the IBM 1130 computer by the A.R.C. unit of Structural Chemistry, University College, London. Least-squares refinements were from the X-ray 70 set of programs written or adapted by J. M. Stewart and coworkers for the CDC 6600, UNIVAC 1108, and IBM 360 computers. (See Tables I and II for positional and thermal parameters.)

Results and Discussion of the Structure

The structure consists of $[Fe(P_4)Br]^+$ cations and $[BPh_4]^-$ anions. Figure 1 shows a perspective view of the cation. Bond distances with their estimated standard deviations are given in Table III. The iron atom is five-coordinated by the four phosphorus atoms of the ligand and by the bromine atom. The geometry of the coordination polyhedron, although far from the two idealized limit geometries, can be better described as a distorted trigonal bipyramid with Br, P_2, and P_4 in the equatorial plane and P_1 and P_3 in the axial positions. The distortions from the trigonal-bipyramidal geometry are significant. The axial angle is 164.1 (2)° instead of 180° and the angles between the axial and the equatorial ligands range from 97.2 (2) to 80.7 (2)°. Furthermore, although the metal atom is well in the plane of the equatorial ligands, the deviation being 0.07 Å, the equatorial angles deviate significantly from the theoretical value of 120°, the two Br–Fe–P angles being 130.5 (2) and 124.2 (2)°. As far as we know, among the few structures of five-coordinated iron(II) complexes so far reported, only two have a trigonal-bipyramidal geometry. These complexes have a donor set N_4X (X = halogen) and are both high spin: the first with the tripod-like ligand tris(2-dimethylaminoethyl)-amine has C_{3v} symmetry;[10] the second one with the macrocyclic ligand 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene shows a distorted trigonal-bipyramidal geometry.[11] In both complexes the ligand geometry has played an important role in determining a trigonal-bipyramidal rather than a square-pyramidal geometry. In the present case, the ligand is flexible enough to allow different coordination geometries; on the other hand most distortions appear to be mainly a consequence of the steric requirement of the three five-membered chelate rings formed by the tetradentate ligand. As a matter of fact the P–Fe–P bite angles, owing to the ethylene chain constraint, cannot reach 90°, their values ranging between 80.7 (2) and 84.1 (2)°. Even the value of the axial angle seems to be imposed by the strains exerted on P_1 and P_3 by the ligand. It is worth noting that two phenyl rings, c and e, are almost coplanar with the equatorial plane of the coordination polyhedron (Table IV) and that two hydrogen atoms of these phenyl rings, H(24) and H(32) [numbered according to the atom to which they are attached], point toward the bromine atom, the Br–H contact distances being 2.80 and 2.72 Å, respectively. Steric repulsions between the bromine and the hydrogen atoms (the sum of the van der Waals radii is 3.15
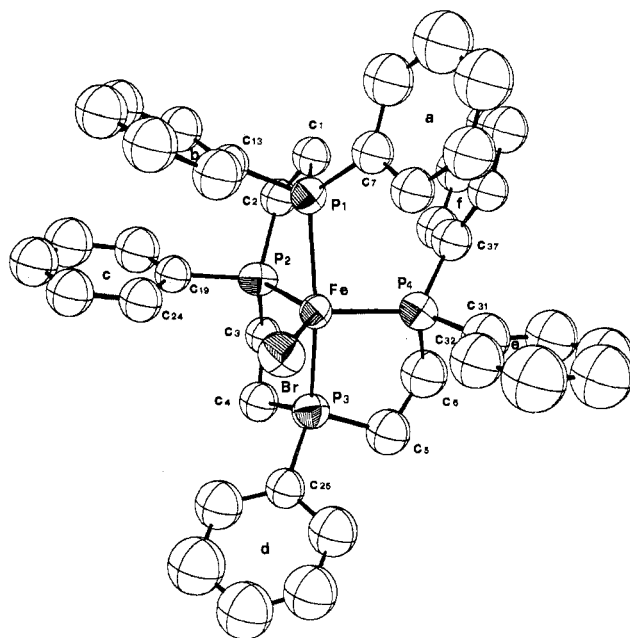
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Figure 1. Perspective view of the $[Fe(P_4)Br]^+$ cation (ORTEP diagram, showing 30% probability ellipsoids). Only the atoms mentioned in the paper are numbered.

Å)[12] could force the equatorial Br–Fe–P angles to be larger than 120°.

An examination of Table III shows that the Fe–P bond distances range between 2.299 (5) and 2.181 (5) Å and that the equatorial Fe–P bond distances are shorter than the axial ones. In this connection it is probably interesting to note that the peculiar arrangement of the phenyl rings c and e could be responsible for the shortening of the equatorial Fe–P bond. In fact this arrangement might allow for the formation of a partially conjugated system.

The Fe–Br bond distance of 2.361 (4) Å is significantly shorter than the value of 2.482 (3) Å reported for the high-spin five-coordinated tris(2-dimethylaminoethyl)amineiron(II) bromide cation.[10] This difference is probably related to the different spin states of the two complexes. Contraction of the metal–ligand distances on going from high spin to low spin have been noticed for iron(II)[13] and iron(III)[14-16] six-coordinated complexes and for five-coordinated cobalt(II) complexes.[7] However a rigorous comparison perhaps is not possible because in the latter complex the bromine atom occupies an axial position while in the present case it lies in the equatorial plane.

As regards the tetraphenylborate anion, the B–C bond distances appear to be normal and the angles in the phenyl rings show a trend already noticed:[17] the angles at the carbon atom bonded to the boron atom are less than 120°, mean 114.3°, and the contiguous angles are all larger than 120°, the mean being 122.9°. There are not significant contact distances between the ions.

The anomalous magnetic behavior of this complex could

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Table I. Positional Parameters and Isotropic Thermal Parameters, with Estimated Standard Deviations in Parentheses

Atom	x/a	y/b	z/c	B, Å^2	Atom	x/a	y/b	z/c	B, Å^2
		[Fe(P$_4$)Br]$^+$					[BPh$_4$]$^-$		
Br	0.2135 (1)	0.1223 (1)	−0.0336 (1)		C(43)	−0.241 (1)	0.391 (1)	−0.344 (1)	5.3 (4)
Fe	0.2493 (2)	0.2043 (1)	−0.2138 (2)		C(44)	−0.234 (1)	0.423 (1)	−0.462 (1)	5.6 (4)
P(1)	0.3968 (3)	0.2303 (2)	−0.1813 (4)		C(45)	−0.210 (1)	0.383 (1)	−0.538 (1)	5.8 (4)
P(2)	0.2253 (3)	0.3242 (2)	−0.2748 (4)		C(46)	−0.187 (1)	0.305 (1)	−0.498 (2)	6.7 (5)
P(3)	0.1007 (3)	0.2124 (2)	−0.2714 (4)		C(47)	−0.194 (1)	0.274 (1)	−0.386 (2)	5.9 (5)
P(4)	0.3035 (3)	0.1695 (3)	−0.3647 (4)		C(48)	−0.218 (1)	0.313 (1)	−0.309 (1)	5.6 (4)
C(1)	0.429 (1)	0.311 (1)	−0.296 (1)	5.0 (4)	C(49)	−0.251 (1)	0.389 (1)	−0.130 (1)	5.1 (4)
C(2)	0.339 (1)	0.364 (1)	−0.338 (1)	4.9 (4)	C(50)	−0.320 (1)	0.343 (1)	−0.065 (2)	6.6 (5)
C(3)	0.131 (1)	0.358 (1)	−0.371 (1)	4.7 (4)	C(51)	−0.308 (1)	0.301 (1)	0.048 (2)	8.2 (5)
C(4)	0.049 (1)	0.310 (1)	−0.321 (1)	5.6 (4)	C(52)	−0.227 (2)	0.306 (1)	0.097 (2)	8.7 (6)
C(5)	0.110 (1)	0.180 (1)	−0.392 (1)	7.0 (5)	C(53)	−0.156 (1)	0.346 (1)	0.035 (2)	7.6 (5)
C(6)	0.205 (1)	0.194 (1)	−0.460 (2)	7.9 (5)	C(54)	−0.170 (1)	0.387 (1)	−0.077 (1)	5.9 (4)
C(7)	0.500 (1)	0.163 (1)	−0.171 (1)	5.3 (4)	C(55)	−0.385 (1)	0.475 (1)	−0.258 (1)	4.0 (3)
C(8)	0.489 (1)	0.090 (1)	−0.142 (1)	5.7 (4)	C(56)	−0.444 (1)	0.484 (1)	−0.343 (1)	5.1 (4)
C(9)	0.573 (2)	0.037 (1)	−0.137 (2)	7.6 (5)	C(57)	−0.541 (1)	0.515 (1)	−0.338 (1)	5.7 (4)
C(10)	0.665 (2)	0.058 (1)	−0.162 (2)	9.9 (6)	C(58)	−0.585 (1)	0.540 (1)	−0.249 (1)	5.4 (4)
C(11)	0.680 (2)	0.128 (1)	−0.187 (2)	10.5 (6)	C(59)	−0.530 (1)	0.532 (1)	−0.162 (1)	5.7 (4)
C(12)	0.597 (2)	0.182 (1)	−0.195 (1)	7.7 (5)	C(60)	−0.430 (1)	0.500 (1)	−0.166 (1)	4.9 (4)
C(13)	0.397 (1)	0.255 (1)	−0.055 (1)	4.8 (4)	C(61)	−0.202 (1)	0.508 (1)	−0.297 (1)	4.2 (4)
C(14)	0.400 (1)	0.328 (1)	−0.057 (1)	6.2 (4)	C(62)	−0.227 (1)	0.574 (1)	−0.276 (1)	4.7 (4)
C(15)	0.401 (1)	0.342 (1)	0.046 (2)	7.7 (5)	C(63)	−0.162 (1)	0.627 (1)	−0.299 (1)	6.3 (4)
C(16)	0.400 (1)	0.289 (1)	0.144 (2)	7.8 (5)	C(64)	−0.069 (1)	0.617 (1)	−0.347 (1)	5.2 (4)
C(17)	0.400 (1)	0.220 (1)	0.145 (2)	8.2 (5)	C(65)	−0.038 (1)	0.551 (1)	−0.370 (1)	5.4 (4)
C(18)	0.395 (1)	0.201 (1)	0.045 (2)	7.1 (5)	C(66)	−0.104 (1)	0.499 (1)	−0.345 (1)	5.7 (4)
C(19)	0.181 (1)	0.366 (1)	−0.167 (1)	4.6 (4)	B	−0.269 (1)	0.442 (1)	−0.260 (2)	4.4 (4)
C(20)	0.175 (1)	0.441 (1)	−0.194 (2)	7.4 (5)					
C(21)	0.143 (1)	0.476 (1)	−0.108 (2)	8.6 (6)			Solvent		
C(22)	0.115 (1)	0.438 (1)	−0.001 (2)	8.0 (5)	Cl(1)	0.033 (1)	0.204 (1)	0.286 (1)	
C(23)	0.120 (1)	0.362 (1)	0.022 (2)	7.2 (5)	Cl(2)	0.206 (2)	0.079 (1)	0.321 (2)	
C(24)	0.150 (1)	0.325 (1)	−0.058 (2)	6.2 (4)	Cl(3)	−0.081 (2)	0.087 (1)	0.270 (2)	
C(25)	0.007 (1)	0.164 (1)	−0.180 (1)	5.1 (4)	Cl(4)	−0.128 (1)	0.085 (1)	0.556 (2)	
C(26)	−0.053 (1)	0.193 (1)	−0.104 (2)	7.6 (5)					
C(27)	−0.122 (2)	0.152 (1)	−0.023 (2)	10.4 (6)					
C(28)	−0.129 (2)	0.082 (1)	−0.024 (2)	9.7 (6)					
C(29)	−0.073 (2)	0.052 (1)	−0.095 (2)	8.9 (6)					
C(30)	−0.004 (1)	0.093 (1)	−0.177 (2)	7.7 (5)					
C(31)	0.331 (1)	0.072 (1)	−0.341 (2)	7.5 (5)					
C(32)	0.314 (1)	0.021 (1)	−0.240 (2)	8.8 (6)					
C(33)	0.341 (2)	−0.057 (1)	−0.218 (2)	12.4 (7)					
C(34)	0.379 (2)	−0.076 (1)	−0.316 (2)	11.6 (7)					
C(35)	0.389 (2)	−0.029 (1)	−0.412 (2)	10.6 (7)					
C(36)	0.369 (1)	0.045 (1)	−0.430 (2)	8.9 (6)					
C(37)	0.408 (1)	0.203 (1)	−0.455 (1)	5.8 (4)					
C(38)	0.502 (1)	0.167 (1)	−0.434 (1)	5.6 (4)					
C(39)	0.587 (1)	0.203 (1)	−0.498 (2)	7.3 (5)					
C(40)	0.569 (1)	0.272 (1)	−0.586 (1)	6.5 (5)					
C(41)	0.480 (1)	0.305 (1)	−0.606 (1)	6.9 (5)					
C(42)	0.396 (1)	0.273 (1)	−0.542 (1)	6.7 (5)					

Table II. Thermal Parameters for the Atoms Refined Anisotropically, with Estimated Standard Deviations in Parentheses[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	6.1 (1)	4.5 (1)	5.2 (1)	−1.0 (1)	0.0 (1)	0.0 (1)
Fe	3.9 (1)	2.8 (1)	4.2 (1)	−0.5 (1)	−0.1 (1)	−0.9 (1)
P(1)	4.4 (3)	3.0 (2)	4.5 (3)	−0.3 (2)	−0.4 (2)	−0.8 (2)
P(2)	3.8 (3)	3.4 (2)	5.0 (3)	−0.3 (2)	−1.2 (2)	−0.1 (2)
P(3)	4.4 (3)	4.5 (3)	5.1 (3)	−0.8 (2)	−0.4 (2)	−1.3 (2)
P(4)	4.7 (3)	6.7 (3)	6.4 (3)	−1.2 (2)	0.3 (2)	−2.9 (3)
Cl(1)	26 (2)	8 (1)	8 (1)	−9 (1)	0 (1)	0 (1)
Cl(2)	28 (2)	29 (2)	19 (1)	−14 (2)	5 (1)	−16 (1)
Cl(3)	25 (2)	28 (2)	32 (2)	7 (2)	−17 (2)	−19 (2)
Cl(4)	16 (1)	22 (2)	37 (2)	−1 (1)	4 (1)	−20 (2)

[a] The temperature factor is defined as $\exp(-\frac{1}{4}\Sigma_{i=1}\Sigma_{j=1}B_{ij}h_ih_ja_i{}^*\cdot a_j{}^*)$.

arise from the presence in the lattice of two molecules: one in a singlet ground state and the other in a triplet ground state differing in bond distances and angles of the coordination polyhedron. In fact it is known that different coordination geometries correspond to different spin states.[7,13-16] The presence of two such molecules should cause disorder in the crystal. Furthermore thermal parameters could be in-

dicative of whether or not the time-averaged structure is oscillating between two different distortions. Analysis of a difference Fourier map did not show evidence of disorder and, although the temperature factors of the carbon atoms are rather high, those of the donor atoms appear to be normal (Table V).

In conclusion, although the presence of a mixture of two different spin states cannot certainly be ruled out, we suggest the existence of only one type of molecule with a mixed spin state.

CF and AOM Approach

Since the X-ray investigation shows the absence of any symmetry in the [Fe(P$_4$)Br]$^+$ chromophore, we have performed some calculations on the basis of a model which was simple and nearest, as possible, to the above complex geometry: a FeL$_5$ chromophore, having C_{2v} symmetry and oriented as in Figure 2.

The calculations were executed using the crystal field (CF) and the angular overlap (AOM) models: both satisfactorily explain the spectral data and show that, for suitable values of the parameters, a singlet state can exist together with a

Table III. Distances (A) and Angles (deg)

About the Metal Atom

(a) Distances

Fe–Br	2.361 (4)	Fe–P(2)$_{eq}$	2.181 (5)
Fe–P(1)$_{ax}$	2.299 (5)	Fe–P(4)$_{eq}$	2.215 (6)
Fe–P(3)$_{ax}$	2.248 (5)		

(b) Angles

P(1)–Fe–P(3)	164.1 (2)	P(3)–Fe–P(4)	84.1 (2)
P(1)–Fe–P(2)	80.7 (2)	P(3)–Fe–Br	95.6 (2)
P(1)–Fe–P(4)	97.2 (2)	P(2)–Fe–P(4)	105.0 (2)
P(1)–Fe–Br	96.7 (2)	Br–Fe–P(2)	130.5 (2)
P(3)–Fe–P(2)	83.7 (2)	Br–Fe–P(4)	124.2 (2)

In the Ligand Molecule

(c) Distances

P(1)–C(1)	1.83 (2)	P(3)–C(25)	1.78 (2)
P(1)–C(7)	1.77 (2)	P(4)–C(6)	1.86 (2)
P(1)–C(13)	1.80 (2)	P(4)–C(31)	1.80 (2)
P(2)–C(2)	1.83 (2)	P(4)–C(37)	1.78 (2)
P(2)–C(3)	1.82 (2)	C(1)–C(2)	1.53 (2)
P(2)–C(19)	1.78 (2)	C(3)–C(4)	1.51 (2)
P(3)–C(4)	1.85 (2)	C(5)–C(6)	1.47 (3)
P(3)–C(5)	1.80 (2)		

(d) Angles

Fe–P(1)–C(1)	106.8 (5)	C(4)–P(3)–C(5)	104.9 (7)
Fe–P(1)–C(7)	119.3 (6)	C(4)–P(3)–C(25)	106.9 (7)
Fe–P(1)–C(13)	116.1 (5)	C(5)–P(3)–C(25)	103.0 (8)
C(1)–P(1)–C(7)	106.9 (7)	Fe–P(4)–C(6)	109.5 (6)
C(1)–P(1)–C(13)	105.2 (7)	Fe–P(4)–C(31)	115.7 (7)
C(7)–P(1)–C(13)	101.4 (7)	Fe–P(4)–C(37)	122.1 (6)
Fe–P(2)–C(2)	112.1 (5)	C(6)–P(4)–C(31)	101.9 (8)
Fe–P(2)–C(3)	112.7 (5)	C(6)–P(4)–C(37)	103.3 (8)
Fe–P(2)–C(19)	113.6 (6)	C(31)–P(4)–C(37)	101.9 (8)
C(2)–P(2)–C(3)	110.6 (7)	P(1)–C(1)–C(2)	112.3 (10)
C(2)–P(2)–C(19)	104.4 (7)	P(2)–C(2)–C(1)	111.4 (10)
C(3)–P(2)–C(19)	102.8 (7)	P(2)–C(3)–C(4)	106.1 (10)
Fe–P(3)–C(4)	109.6 (5)	P(3)–C(4)–C(3)	109.8 (10)
Fe–P(3)–C(5)	110.8 (6)	P(3)–C(5)–C(6)	111.1 (12)
Fe–P(3)–C(25)	120.5 (5)	P(4)–C(6)–C(5)	108.5 (12)

In the Anion

(e) Distances

B–C(43)	1.63 (2)	B–C(55)	1.64 (2)
B–C(49)	1.66 (3)	B–C(61)	1.61 (2)

(f) Angles

C(43)–B–C(49)	108.7 (13)	C(49)–B–C(55)	106.5 (13)
C(43)–B–C(55)	111.5 (13)	C(49)–B–C(61)	110.5 (13)
C(43)–B–C(61)	110.0 (13)	C(55)–B–C(61)	109.7 (13)

Table IV. Least-Squares Planes in Triclinic Coordinates[a]

1: $13.57x + 4.34y + 4.30z - 3.28 = 0$

Br (0.00), P(2) (0.00), P(4) (0.00), Fe (0.07)

2: $13.57x + 4.30y + 4.31z - 3.35 = 0$

Br (−0.08), Fe (−0.01), P(2) (−0.09), P(4) (−0.08), C(19) (−0.03), C(20) (0.07), C(21) (0.18), C(22) (0.12), C(23) (−0.07), C(24) (−0.17), C(31) (−0.03), C(32) (−0.02), C(33) (0.14), C(34) (0.09), C(35) (0.02), C(36) (−0.03)

[a] Distances (A) of atoms from plane are given in parentheses.

Table V. Root-Mean-Square Displacements (A) along the Principal Axes of Thermal Ellipsoids for the Atoms of the Coordination Polyhedron

	Axis 1	Axis 2	Axis 3
Br	0.212	0.278	0.303
Fe	0.186	0.206	0.244
P(1)	0.195	0.236	0.247
P(2)	0.191	0.219	0.279
P(3)	0.228	0.243	0.256
P(4)	0.236	0.258	0.308
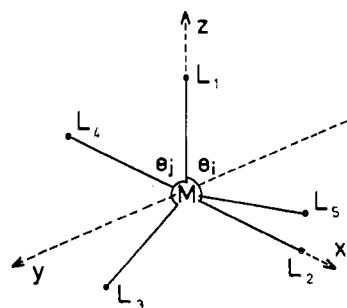
Figure 2. Coordinate system for the FeL$_5$ chromophore. θ_i = L$_1$–M–L$_2$ = L$_1$–M–L$_4$ = 90°; θ_j = L$_1$–M–L$_3$ = L$_1$–M–L$_5$ = 130°.

In the AOM the d-orbital energies are expressed by the e_σ and e_π parameters[19,20] and calculated by the matrices $\mathbf{A}_\sigma = \mathbf{D}_\sigma \cdot \mathbf{E}_\sigma \cdot \tilde{\mathbf{D}}_\sigma$ and $\mathbf{A}_\pi = \mathbf{D}_\pi \cdot \mathbf{E}_\pi \cdot \tilde{\mathbf{D}}_\pi$, where $\mathbf{E}_\sigma$ and $\mathbf{E}_\pi$ are diagonal matrices in e_σ and e_π, respectively, and $\mathbf{D}_\sigma$ and $\mathbf{D}_\pi$ are the angular overlap matrices reported in ref 20.

Since in C_{2v} symmetry the monoelectronic $d(z^2)$ and $d(x^2 - y^2)$ functions (a_1 species) mix, their suitable linear combinations $d(z^2)'$ and $d(x^2 - y^2)'$ have been considered.

For the model we have considered, the order of energies of the monoelectronic levels is (the order of the b_1 and a_2 levels may invert for some parameters values; however the results are not altered)

———	$(x^2 - y^2)'$	a_1
———	yz	b_2
———	$(z^2)'$	a_1
———	xy	b_1
———	xz	a_2

The functions and the energy matrices were obtained as described in ref 18 considering the hole formalism. Only the more stable levels have been considered, since it was verified that the introduction of more excited states does not alter appreciably the energy of the functions considered (see Appendix). In our calculations it was assumed $C = 4B$. The energy levels are plotted in Figures 3 and 4 as a function of the relevant parameters for CF and AOM, respectively.

The $^1A_1$ state is stabilized with respect to $^3B_2$ by low B

thermally accessible triplet state. In fact in the proximity of a crossover point pure spin states do not exist, states of different spin multiplicity being mixed *via* spin-orbit coupling. However, as we intend to perform an approximate calculation, the spin-orbit coupling was neglected and only pure spin states were considered. The Hamiltonian $\mathcal{H} = V_{lig} + \Sigma_{i>j} e^2/r_{ij}$, where V_{lig} is the potential produced by the ligands, was used to calculate transition energies.

In the crystal field method the d-orbital energies are expressed as a function of the radial integrals

$$G_2 = \frac{e^2 Z}{a^3} \langle r^2 \rangle$$

$$G_4 = \frac{e^2 Z}{a^5} \langle r^4 \rangle = 6Dq$$

applying the potential

$$V_{(r)} = \Sigma_{n,m} V_n{}^m = \Sigma_{n,m} A_n{}^m r^n P_n{}^m (\cos \theta) \exp(im\phi)$$

for a C_{2v} symmetry, as described in ref 18.

(18) R. M. Golding, "Applied Wave Mechanics," Van Nostrand, London, 1969.

(19) C. E. Schaffer and C. K. Jorgensen, *Mol. Phys.,* 9, 401 (1965).

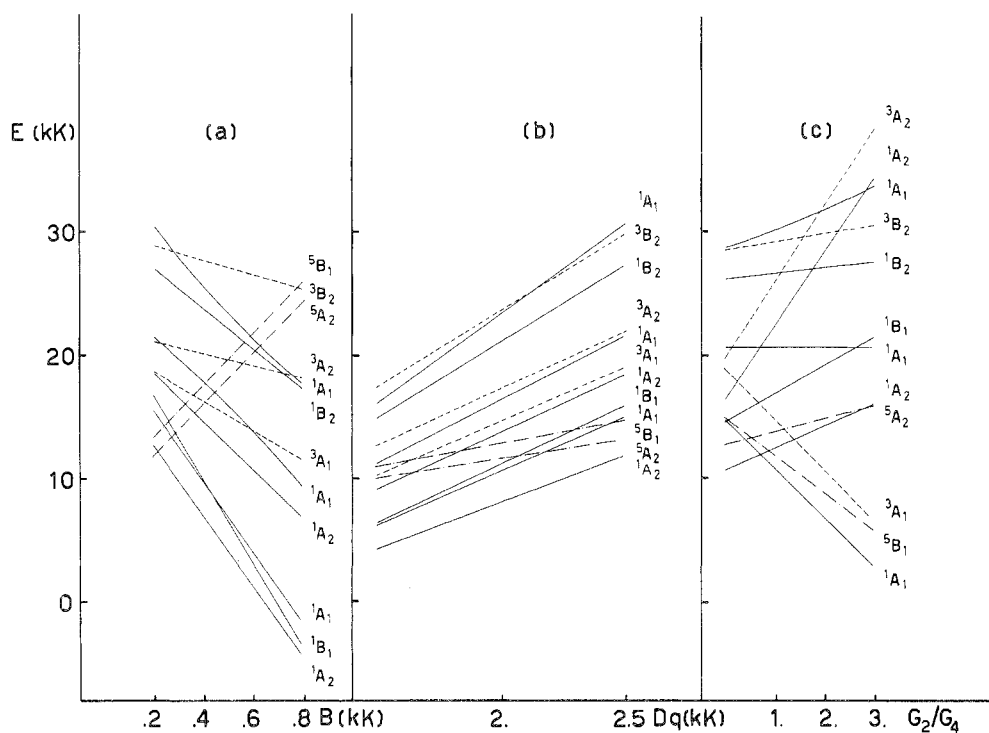(20) C. E. Schaffer, *Struct. Bonding (Berlin),* 5, 68 (1968).

Figure 3. Energy level diagram in the CF approximation: (a) $G_2/G_4 = 0.2$, $Dq = 2.4$ kK; (b) $G_2/G_4 = 0.2$, $B = 0.25$ kK; (c) $B = 0.25$ kK, $Dq = 2.4$ kK. The highest level is indeed the ground level, as we have considered the hole formalism.
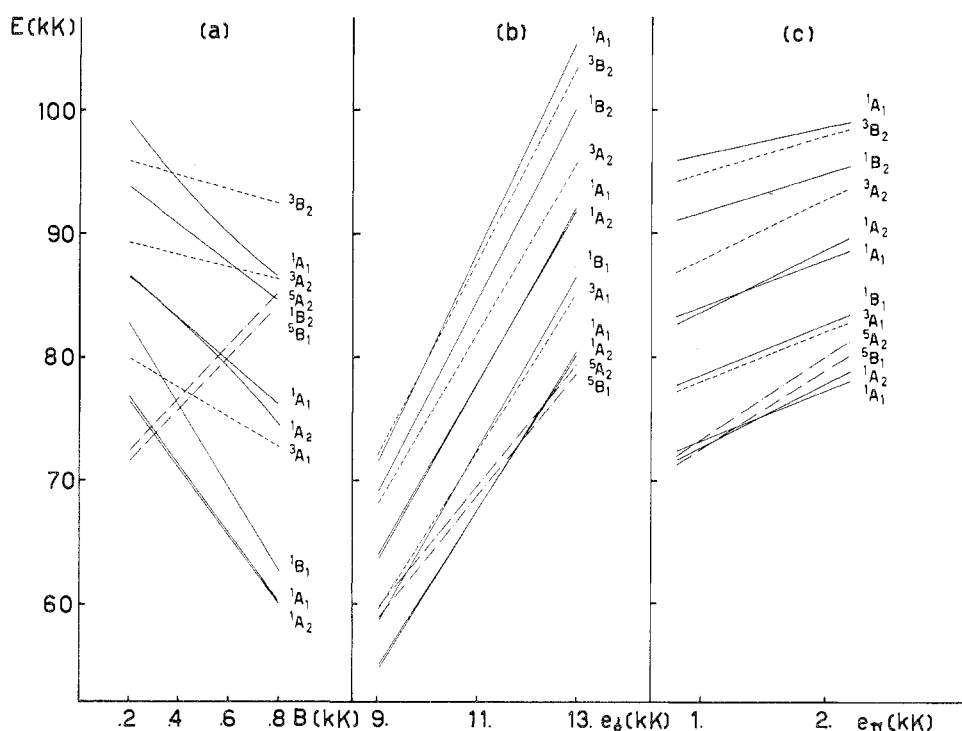

Figure 4. Energy level diagram in the AOM approximation: (a) $e_\sigma = 12.0$ kK; $e_\pi = 1.2$ kK; (b) $e_\pi = 1.2$ kK, $B = 0.3$ kK; (c) $e_\sigma = 12.0$ kK, $B = 0.3$ kK. The highest level is indeed the ground level, as we have considered the hole formalism.

values (B for the free ion Fe^{2+} is 0.917 kK);[21] at $B = 0.3$–0.4 kK the two levels are nearly degenerate; a pronounced nephelauxetic effect is not unexpected if one considers the soft character of the coordinated atoms.

As expected the $^1A_1$ state is stabilized at strong fields and Figures 3 and 4 show that $^1A_1$ and $^3B_2$ levels are nearly energetic for a large range of field strengths. Moreover

(21) Y. Tanabe and S. Sugano, *J. Phys. Soc. Jap.*, **9**, 766 (1954).

Figure 4c shows that, though the π bond does not affect dramatically the energy of the most stable levels, an increase of the π character stabilizes the triplet state.

On the contrary the G_2/G_4 ratio strongly affects the stability of the levels and only low values of this ratio ($G_2/G_4 < 2$) can stabilize the $^1A_1$ level. Unfortunately we have not found in the literature many results to compare with our values of the parameters.[22]

Our calculations, however, satisfactorily justify the elec-

Table VI. Observed and Calculated Transition Energies (kK) of the $[Fe(P_4)Br]^+$ Chromophore

$Obsd^a$	Calcd $(CF)^b$	Transition	Calcd $(AOM)^c$	Transition
8.5	8.3	$^3B_2 \rightarrow {}^3A_2$ or $^1A_1 \rightarrow {}^3A_2$	8.0	$^3B_2 \rightarrow {}^3A_2$ or $^1A_1 \rightarrow {}^3A_2$
	8.6	$\rightarrow {}^1A_1$		
11.8	11.7	$\rightarrow {}^1A_2$	12.0 / 12.1	$\rightarrow {}^1A_1$ / $\rightarrow {}^1A_2$
15.0	14.2 / 15.2	$\rightarrow {}^1B_1$ / $\rightarrow {}^1A_1$	17.5	$\rightarrow {}^1B_1$
23.0	18.2	$\rightarrow {}^1A_2$	22.9 / 23.1	$\rightarrow {}^1A_1$ / $\rightarrow {}^1A_2$

^{a} Reference 4. ^{b} Calculated for $G_2/G_4 = 0.2$; $Dq = 2.4$ kK; $B = 0.25$ kK. ^{c} Calculated for $e_\sigma = 12.0$ kK; $e_\pi = 1.2$ kK; $B = 0.30$ kK.

tronic spectra of the $[Fe(P_4)X]^+$ chromophores. In Table VI are reported the observed[4] and calculated absorption frequencies for the $[Fe(P_4)Br]^+$ chromophore.

The first three bands at low energy certainly must be attributed to d–d transitions. The intensity of the 8.5-kK band is temperature dependent and vanishes at liquid nitrogen temperature.[4] This fact seems to indicate that a triplet level is involved in the transition. It is likely that the above band corresponds either to a spin-forbidden singlet–triplet transition, whose intensity, at room temperature, is enhanced by the high degree of mixing of the triplet and singlet functions in the ground state;[23] or, as suggested by a reviewer, to a triplet–triplet transition, as the triplet is not populated at the lower temperatures. CF calculations however do not exclude a singlet–singlet transition at that frequency.

On the basis of our calculations in the C_{2v} model, the bands at 11.8 and 15.0 kK may well be assigned to the $^1A_1 \rightarrow {}^1A_1$ and/or $^1A_2$ and $^1A_1 \rightarrow {}^1B_1$ and/or $^1A_1$ transitions, respectively.

The strong intensity of the 23.0-kK band would suggest a charge-transfer mechanism, although the AOM calculations are consistent with a d–d transition ($^1A_1 \rightarrow {}^1A_1$ and/or $^1A_2$); in this case the band intensity could be enhanced by a charge-transfer band at higher energy.

Acknowledgments. Thanks are expressed to Professor L. Sacconi for his continued interest and helpful discussion.

(22) M. J. Norgett, J. H. M. Thornley, and L. M. Venanzi, *J. Chem. Soc. A,* 540 (1967).

(23) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, Chapter 8.

Appendix

Singlet functions

$$|^1A_1\ 0\ a_1\rangle = |(x^2-y^2)'^+(x^2-y^2)'^- yz^+yz^-\rangle$$
$$= |(x^2-y^2)'^+(x^2-y^2)'^-(z^2)'^+(z^2)'^-\rangle$$
$$= (1/\sqrt{2})|(x^2-y^2)'^+(z^2)'^- yz^+yz^- -$$
$$(x^2-y^2)'^-(z^2)'^+ yz^+yz^-\rangle$$

$$|^1A_2\ 0\ a_2\rangle = (1/\sqrt{2})|(x^2-y^2)'^+(x^2-y^2)'^- yz^+xz^- -$$
$$(x^2-y^2)'^+(x^2-y^2)'^- yz^-xz^+\rangle$$
$$= (1/\sqrt{2})|(x^2-y^2)'^+(x^2-y^2)'^-(z^2)'^+ xy^- -$$
$$(x^2-y^2)'^+(x^2-y^2)'^-(z^2)'^- xy^+\rangle$$

$$|^1B_1\ 0\ b_1\rangle = (1/\sqrt{2})|(x^2-y^2)'^+(x^2-y^2)'^- yz^+xy^- -$$
$$(x^2-y^2)'^+(x^2-y^2)'^- yz^-xy^+\rangle$$

$$|^1B_2\ 0\ b_2\rangle = (1/\sqrt{2})|(x^2-y^2)'^+(x^2-y^2)'^- yz^+(z^2)'^- -$$
$$(x^2-y^2)'^+(x^2-y^2)'^- yz^-(z^2)'^+\rangle$$

Triplet functions

$$|^3A_1\ 1\ a_1\rangle = |yz^+yz^-(x^2-y^2)'^+(z^2)'^+\rangle$$
$$|^3A_2\ 1\ a_2\rangle = |(x^2-y^2)'^+(x^2-y^2)'^- yz^+xz^+\rangle$$
$$|^3B_2\ 1\ b_2\rangle = |(x^2-y^2)'^+(x^2-y^2)'^- yz^+(z^2)'^+\rangle$$

Quintuplet functions

$$|^5A_2\ 2\ a_2\rangle = |(x^2-y^2)'^+ yz^+(z^2)'^+ xz^+\rangle$$
$$|^5B_1\ 2\ b_1\rangle = |(x^2-y^2)'^+ yz^+(z^2)'^+ xy^+\rangle$$