is similarly believed to be uncoordinated.[35]

This interpretation is supported by the ESR spectrum (Figure 5), which shows the formation of a new complex of axial symmetry (Table VI). A decrease of $g_{\parallel}$ and an increase in $A_{\parallel}$ are to be expected if the charge on the complex decreases.[36] For Cu(TCD)$^{2+}$ the changes in $g_{\parallel}$ from 2.263 to 2.175 and in $A_{\parallel}$ from 162 to 186 G are the ones anticipated for a charge decrease of 2 units. Both the ESR and optical spectra indicate that, with less than 2 equiv of added cyanide ion, a mixture of Cu(TCD)$^{2+}$ and the cyano complex is present. Thus, a dicyano complex forms preferentially with no significant amount of an intermediate monocyano species.

With Cu(dien)$^{2+}$, a shift from 620 to 550 nm occurs upon the addition of 1 equiv of CN$^-$. The second equivalent shifts the d–d band back to 625 nm, and spontaneous reduction occurs.[34] The blue shift upon the addition of one cyanide indicates coordination in the basal plane, and the subsequent shift reversal is consistent with apical binding,[34] a well-known phenomenon for copper(II) amine complexes.[17]

Relevance to the Chemistry of Copper Protein Active Sites. Connecting the terminal nitrogen atoms of the diethylenetriamine ligand with a pentamethylene chain produces several important consequences for its 1:1 copper(II) complex. Owing to the constrained N–Cu–N angle of 138.7°, it is easier to reduce Cu(TCD)$^{2+}$ than Cu(dien)$^{2+}$ and the electrochemical redox reaction is more reversible. Both high redox potentials and reversible redox behavior are features characteristic of copper centers in biology,[37] and the present study demonstrates how the protein environment might use stereochemistry to tune a CuN$_3$ center to achieve these characteristics. It is interesting, moreover, that Cu(TCD)$^{2+}$ takes up two cyanide ligands into its principal coordination plane, presumably with loss of one of the amine donor atoms of the TCD minicycle and relief of the steric constraint, compared with Cu(dien)$^{2+}$ which only binds one CN$^-$ ligand in the basal plane. These results may be compared with those for met apo hemocyanin.[38] Here the so-called "endogenous" ligand is tightly bound to copper, and only one cyanide ion coordinates strongly. A second such ligand binds only in the presence of 100-fold excess cyanide, presumbly in an apical position. Thus, Cu(dien)$^{2+}$ more closely mimics the copper site in this protein derivative than does Cu(TCD)$^{2+}$. Had met apo hemocyanin bound tightly to two cyanide ligands, however, this information could not have been used to argue that two in-plane sites were unoccupied by a strong donor ligand (e.g., histidine), as the present results demonstrate.

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Registry No. [Cu(TCD)(NO$_3$)](NO$_3$), 90790-08-2; [Cu(dien)(NO$_3$)](NO$_3$), 90790-10-6; Cu(TCD)$^{2+}$, 90790-11-7; Cu(dien)$^{2+}$, 45520-77-2; Cu(TCD)$^{2+}$/2CN$^-$, 90790-12-8.

Supplementary Material Available: Listings of atomic thermal parameters and observed and calculated structure factors (Tables S1 and S2) for [Cu(TCD)(NO$_3$)](NO$_3$) (6 pages). Ordering information is given on any current masthead page.

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Contribution from the Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione,
CNR, 50132 Firenze, Italy, and Istituto Ricerca Onde Elettromagnetiche, CNR, 50127 Firenze, Italy

Low-Temperature Crystal Structure of a Five-Coordinate Iron(II) Complex Exhibiting Singlet–Triplet Spin Equilibrium

MAURO BACCI,[1b] CARLO A. GHILARDI,*[1a] and ANNABELLA ORLANDINI[1a]

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The [Fe(P$_4$)Br]BPh$_4$·CH$_2$Cl$_2$ complex (P$_4$ = hexaphenyl-1,4,7,10-tetraphosphadecane) shows a smooth variation of the magnetic moment between 86 K (μ_{eff} = 0.89 μ_B) and 376 K (μ_{eff} = 2.26 μ_B) and is a rare example of singlet–triplet equilibrium in iron(II) complexes. At room temperature this compound has an intermediate-spin state (μ_{eff} = 1.60 μ_B), and its structural parameters have been previously reported. The crystal and molecular structure at 150 K has been determined in order to detect the structural changes associated with the spin transition. The space group does not change on cooling. Crystal data: C$_{67}$H$_{64}$BBrCl$_2$FeP$_4$, triclinic system, space group $P\bar{1}$, a = 13.549 (9) Å, b = 19.058 (12) Å, c = 12.475 (8) Å, α = 72.0 (1)°, β = 82.4 (1)°, γ = 81.2 (1)°, Z = 2. The structure was refined by full-matrix least-squares methods to the conventional R factor value of 0.079 for 3500 observed reflections. The variation in the cell parameters is accompanied by significant decrease in distortions from the idealized C_{2v} symmetry. Angular-overlap model calculations well account for the smooth variation of the magnetic moment and support the hypothesis that the spin equilibrium is due to a general increase of the mean ligand field by decreasing temperature.

Introduction

Depending upon the strength of the ligand field (LF), high-spin or low-spin ground states can occur in octahedral transition-metal complexes having electronic configurations d^4, d^5, d^6, and d^7. When the restriction of O_h symmetry is released, ground states of different spin multipicities are theoretically allowed also for electronic configurations d^2, d^3, and d^8. For intermediate LF's an anomalous magnetic behavior is observed, which often has been named spin crossover or spin equilibrium.

By now many examples of such a phenomenon have been described,[2,3] particularly in the chemistry of iron(II), iron(III),

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and cobalt(II), and its widespread occurrence has given rise to a large interest in solid-state physics, inorganic chemistry, and biochemistry as well.[4-19]

For the temperature dependence of the magnetic moment in these complexes, two different behaviors are observed: (i) a smooth increase of the magnetic moment with temperature or (ii) an abrupt change in a very short range of temperature from the low-spin to the high-spin values. We refer to case i as spin equilibrium, while we believe that case ii has to be named more properly spin crossover. This distinction does not mean that the whole phenomenon must originate from different mechanisms, but it is made for descriptive purposes. Actually, models have been proposed[20,21] that account simultaneously for the two kinds of behavior, assuming potential wells (one for each spin state) separated by an energy barrier: the transition occurs gradually when the thermal activation mechanism is prevalent in the whole range of temperatures, whereas sharp transitions are observed when thermal activation is being superimposed on nuclear tunneling, which prevails at low temperature.[21] Moreover, this latter intramolecular mechanism can trigger a cooperative effect, which leads to a first-order phase transition.[22,23]

The compound $[Fe(P_4)Br]BPh_4{\cdot}CH_2Cl_2$, where P_4 is the tetradentate linear ligand hexaphenyl-1,4,7,10-tetraphosphadecane, shows a smooth variation of magnetic moment between 86 K ($\mu_{eff} = 0.89\ \mu_B$) and 376 K ($\mu_{eff} = 2.26\ \mu_B$) and is a rare example of singlet–triplet equilibrium in iron(II) complexes,[24] as supported by Mössbauer spectroscopy.[25] At room temperature this compound has a magnetic moment ($\mu_{eff} = 1.60\ \mu_B$) that is intermediate between the values expected for singlet and triplet ground states.

An X-ray structural determination[26] has shown for the $[Fe(P_4)Br]^+$ chromophore a stereochemistry that can be described as a distorted trigonal bipyramid.

Table I. Crystal Data and Data Collection Details

mol formula	$C_{67}H_{64}BBrCl_2FeP_4$
mol wt	1210.62
a, Å	13.549 (9)
b, Å	19.058 (12)
c, Å	12.475 (8)
α, deg	72.0 (1)
β, deg	82.4 (1)
γ, deg	81.2 (1)
d_{calcd}, g cm^{-3}	1.333
V, $Å^3$	3015.4
Z	2
space group	$P\bar{1}$
abs coeff, μ(Mo Kα), cm^{-1}	11.4
color	green
habit	irregular prism
dimens, mm	0.17 × 0.10 × 0.06
diffractometer	Philips PW 1100
λ(Mo Kα), Å	0.7107
monochromator	graphite crystal
method	ω–2θ scan technique
scan speed, deg/s	0.10
scan width, deg	0.70
bkgd time	half the scan time
stds	3 every 100 readings
max dev std, %	±6
2θ limits, deg	$5 \leqslant 2\theta \leqslant 40$
octants collected	$\pm h, \pm k, +l$
no. of total data	5595
no. of data used ($I \geqslant 3\sigma(I)$)	3500
final no. of variables	250

Further interest in this compound has arisen since a singlet–triplet equilibrium was found in oxygenated hemoglobin, which indeed is characterized by temperature-dependent Mössbauer and susceptibility data very similar to those for the present compound.[19]

It is noteworthy that in the case of spin crossover a likely cracking of the crystal during the spin transition can prevent the collection of diffraction data, whereas the smooth variation of physical properties in spin equilibrium systems should ensure good-quality crystals even at temperatures at which low-spin species are stabilized.

On this basis we have undertaken the crystal structure determination of $[Fe(P_4)Br]BPh_4{\cdot}CH_2Cl_2$ at 150 K, where the complex is predominantly in the singlet ground state ($\mu_{eff} = 0.98\ \mu_B$).

Experimental Section

Crystals of the compound were prepared as described elsewhere.[24]

Collection and Reduction of X-ray Data. Diffraction data at 150 K were collected on a four-circle automatic Philips PW 1100 diffractometer, equipped by a Leybold-Heraeus cryostat, the cooling being effected by blowing a cold nitrogen gas stream onto the sample. The crystal chosen for data collection was mounted along the longest dimension with the *a* axis parallel to the φ axis of the diffractometer. The cell constants were obtained from a least-square refinement of the setting angles of 20 carefully centered reflections. The crystals are triclinic; the space group was assumed to be $P\bar{1}$, and the successful refinement of the structure confirmed this assumption. The space group does not change on cooling, and the cell volume goes from 3150.3 $Å^3$ at room temperature to 3015.4 $Å^3$ at 150 K. Crystal data and data collection details are reported in Table I. After correction for background, the standard deviations of the intensities, σ (*I*), were derived as elsewhere described[27] by using the value of 0.03 for the instability factor *p*. The intensities were corrected for Lorentz–polarization effects and for absorption, the transmission factors ranging from 0.875 to 0.788.

Solution and Refinement of the Structure. All the calculations were carried out by using the SHELX 76 crystallographic system of programs[28]

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Table II. Positional ($\times 10^4$) and Thermal ($\times 10^3$) Parameters

atom	x	y	z	U, Å^2
Br	2091 (1)	1234 (1)	−364 (2)	*a*
Fe	2448 (2)	2033 (1)	−2174 (2)	*a*
P1	3927 (3)	2279 (2)	−1834 (3)	*a*
P2	2235 (3)	3221 (2)	−2808 (3)	*a*
P3	931 (3)	2102 (2)	−2745 (3)	*a*
P4	2978 (3)	1749 (2)	−3738 (3)	*a*
Cl1^b	162 (6)	2123 (4)	2891 (5)	*a*
Cl2^b	−681 (9)	904 (5)	2591 (9)	*a*
Cl3^b	2095 (9)	721 (6)	3241 (8)	*a*
Cl4^b	1292 (8)	−714 (6)	4267 (10)	*a*
C1	4283 (10)	3092 (7)	−2975 (11)	23 (4)
C2	3388 (10)	3633 (7)	−3450 (12)	25 (4)
C3	1261 (10)	3563 (7)	−3781 (11)	24 (4)
C4	426 (11)	3077 (7)	−3243 (12)	32 (4)
C5	1012 (11)	1799 (9)	−4022 (12)	40 (4)
C6	2009 (11)	2009 (9)	−4711 (13)	38 (4)
C7	4978 (6)	1580 (5)	−1722 (9)	28 (4)
C8	4823 (6)	835 (5)	−1425 (9)	41 (4)
C9	5641 (6)	286 (5)	−1374 (9)	62 (5)
C10	6613 (6)	483 (5)	−1621 (9)	76 (6)
C11	6769 (6)	1229 (5)	−1918 (9)	75 (6)
C12	5951 (6)	1777 (5)	−1968 (9)	47 (5)
C13	3936 (7)	2534 (4)	−544 (6)	26 (4)
C14	3956 (7)	3269 (4)	−574 (6)	33 (4)
C15	3957 (7)	3447 (4)	430 (6)	42 (4)
C16	3938 (7)	2889 (4)	1464 (6)	46 (5)
C17	3918 (7)	2154 (4)	1493 (6)	46 (5)
C18	3917 (7)	1976 (4)	490 (6)	33 (4)
C19	1752 (7)	3657 (4)	−1693 (6)	27 (4)
C20	1713 (7)	4427 (4)	−1967 (6)	37 (4)
C21	1407 (7)	4782 (4)	−1133 (6)	45 (4)
C22	1139 (7)	4367 (4)	−26 (6)	42 (4)
C23	1178 (7)	3597 (4)	248 (6)	37 (4)
C24	1484 (7)	3242 (4)	−586 (6)	27 (4)
C25	−18 (8)	1617 (4)	−1810 (9)	28 (4)
C26	−634 (8)	1934 (4)	−1052 (9)	47 (5)
C27	−1301 (8)	1517 (4)	−246 (9)	58 (5)
C28	−1352 (8)	782 (4)	−198 (9)	63 (5)
C29	−736 (8)	465 (4)	−956 (9)	51 (5)
C30	−69 (8)	882 (4)	−1762 (9)	42 (4)
C31	3212 (8)	749 (6)	−3523 (7)	39 (4)
C32	3020 (8)	237 (6)	−2467 (7)	50 (5)
C33	3233 (8)	−523 (6)	−2337 (7)	72 (6)
C34	3637 (8)	−771 (6)	−3261 (7)	58 (5)
C35	3830 (8)	−260 (6)	−4317 (7)	54 (5)
C36	3617 (8)	500 (6)	−4447 (7)	44 (4)
C37	4062 (6)	2091 (4)	−4651 (7)	26 (4)
C38	5019 (6)	1727 (4)	−4418 (7)	32 (4)
C39	5863 (6)	2049 (4)	−5013 (7)	38 (4)
C40	5751 (6)	2734 (4)	−5842 (7)	33 (4)
C41	4794 (6)	3098 (4)	−6075 (7)	36 (4)
C42	3950 (6)	2777 (4)	−5480 (7)	35 (4)
C43	7576 (7)	3870 (4)	6525 (7)	27 (4)
C44	7656 (7)	4228 (4)	5364 (7)	31 (4)
C45	7922 (7)	3814 (4)	4602 (7)	33 (4)
C46	8107 (7)	3041 (4)	5000 (7)	35 (4)
C47	8027 (7)	2683 (4)	6161 (7)	31 (4)
C48	7761 (7)	3098 (4)	6923 (7)	33 (4)
C49	7491 (6)	3848 (5)	−1236 (7)	25 (4)
C50	6754 (6)	3409 (5)	−617 (7)	35 (4)
C51	6870 (6)	2990 (5)	503 (7)	44 (4)
C52	7722 (6)	3010 (5)	1005 (7)	50 (5)
C53	8459 (6)	3449 (5)	386 (7)	43 (4)
C54	8343 (6)	3868 (5)	−734 (7)	30 (4)
C55	6080 (6)	4748 (5)	7451 (6)	29 (4)
C56	5502 (6)	4827 (5)	6566 (6)	28 (4)
C57	4504 (6)	5142 (5)	6612 (6)	32 (4)
C58	4083 (6)	5378 (5)	7543 (6)	32 (4)
C59	4661 (6)	5299 (5)	8428 (6)	29 (4)
C60	5660 (6)	4984 (5)	8383 (6)	31 (4)
C61	8024 (5)	5072 (5)	7041 (7)	28 (4)
C62	7711 (5)	5739 (5)	7295 (7)	25 (4)
C63	8368 (5)	6274 (5)	7061 (7)	31 (4)
C64	9339 (5)	6142 (5)	6574 (7)	33 (4)
C65	9653 (5)	5475 (5)	6321 (7)	36 (4)
C66	8996 (5)	4939 (5)	6554 (7)	30 (4)
C67^b	77 (23)	1648 (16)	1939 (25)	37 (8)
C68^b	1492 (35)	126 (25)	4433 (39)	85 (14)
B	7312 (13)	4375 (10)	7445 (15)	30 (5)

^{a} Anisotropic. ^{b} Population parameter 0.5.

on a SEL 32/77 computer. The atomic scattering factors for nonhydrogen atoms were taken from ref 29, while those for hydrogen atoms were taken from ref 30. Anomalous dispersion terms, both real and imaginary parts, were introduced in F_c for all the non-hydrogen atoms.[31] The final parameters of the room-temperature structure[26] were used as starting parameters for the low-temperature structure determination. Full-matrix least-squares cycles, where isotropic temperature factors were assigned to all the non-hydrogen atoms, were followed by mixed cycles, where anisotropic temperature factors were attributed to bromine, iron, and phosphorus atoms. During the refinement the phenyl rings were treated as rigid bodies of D_{6h} symmetry. The hydrogen atoms were introduced in calculated positions (C–H = 0.95 Å), but not refined. In the least-squares refinement the function $\sum w(|F_o| - |F_c|)^2$ was minimized with weights $w = 1/\sigma^2(F_o)$.

The final values of the discrepancy indices R and R_w are both 0.079. A final difference Fourier map showed no particular features except some residual electron density in the solvent molecule region. The disorder detected can partially account for the rather high R value. Listings of final atomic parameters are given in Table II.

Results and Discussion

Table III shows bond distances and angles within the coordination polyhedron of $[Fe(P_4)Br]^+$ at 150 K ($\mu_{eff} = 0.98\ \mu_B$) and 298 K ($\mu_{eff} = 1.60\ \mu_B$). Perspective views of the cation at both temperatures are shown in Figures 1 and 2.

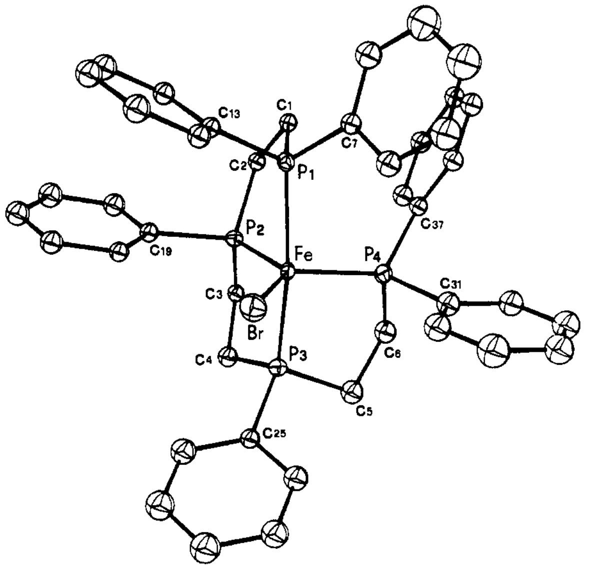

Figure 1. Perspective view of the complex cation $[Fe(P_4)Br]^+$ at 150 K (ORTEP drawing with 30% probability ellipsoids).

The $[Fe(P_4)Br]^+$ chromophore does not possess any crystallographic symmetry at either 150 or 298 K. The title compound crystallizes in the $P\bar{1}$ space group at both temperatures. Although the complex cation retains a distorted trigonal-bipyramidal coordination geometry at low tempera-

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Table III. Selected Bond Distances (Å) and Angles (deg)

dist	150 K	298 K
Fe-Br	2.338 (3)	2.361 (4)
Fe-P1	2.247 (4)	2.299 (5)
Fe-P2	2.141 (4)	2.181 (5)
Fe-P3	2.235 (4)	2.248 (5)
Fe-P4	2.186 (4)	2.215 (6)
P1-C1	1.83 (1)	1.83 (2)
P1-C7	1.78 (1)	1.77 (2)
P1-C13	1.82 (1)	1.80 (2)
P2-C2	1.83 (1)	1.83 (2)
P2-C3	1.82 (1)	1.82 (2)
P2-C19	1.83 (1)	1.78 (2)
P3-C4	1.82 (1)	1.85 (2)
P3-C5	1.84 (1)	1.80 (2)
P3-C25	1.78 (1)	1.78 (2)
P4-C6	1.81 (1)	1.86 (2)
P4-C31	1.82 (1)	1.80 (2)
P4-C37	1.81 (1)	1.78 (2)
C1-C2	1.52 (2)	1.53 (2)
C3-C4	1.52 (2)	1.51 (2)
C5-C6	1.54 (2)	1.47 (3)

angle	150 K	298 K
P1-Fe-P3	165.2 (2)	164.1 (2)
P1-Fe-P2	80.7 (1)	80.7 (2)
P1-Fe-P4	96.9 (2)	97.2 (2)
P1-Fe-Br	95.8 (1)	96.7 (2)
P3-Fe-P2	84.6 (2)	83.7 (2)
P3-Fe-P4	83.7 (2)	84.1 (2)
P3-Fe-Br	95.3 (1)	95.6 (2)
P2-Fe-P4	100.5 (2)	105.0 (2)
Br-Fe-P2	130.9 (1)	130.5 (2)
Br-Fe-P4	128.4 (1)	124.2 (2)
Fe-P1-C1	107.6 (5)	106.8 (5)
Fe-P1-C7	119.0 (3)	119.3 (6)
Fe-P1-C13	116.3 (4)	116.1 (5)
C1-P1-C7	106.8 (5)	106.9 (7)
C1-P1-C13	104.6 (5)	105.2 (7)
C7-P1-C13	101.3 (5)	101.4 (7)
Fe-P2-C2	113.8 (5)	112.1 (5)
Fe-P2-C3	112.7 (5)	112.7 (5)
Fe-P2-C19	112.3 (3)	113.6 (6)
C2-P2-C3	110.1 (6)	110.6 (7)
C2-P2-C19	105.1 (5)	104.4 (7)
C3-P2-C19	101.8 (6)	102.8 (7)
Fe-P3-C4	108.5 (5)	109.6 (5)
Fe-P3-C5	111.4 (5)	110.8 (6)
Fe-P3-C25	120.4 (4)	120.5 (5)
C4-P3-C5	102.6 (7)	104.9 (7)
C4-P3-C25	107.7 (6)	106.9 (7)
C5-P3-C25	104.7 (6)	103.0 (8)
Fe-P4-C6	111.5 (5)	109.5 (6)
Fe-P4-C31	112.8 (3)	115.7 (7)
Fe-P4-C37	123.5 (4)	122.1 (6)
C6-P4-C31	100.9 (6)	101.9 (8)
C6-P4-C37	102.3 (6)	103.3 (8)
C31-P4-C37	103.2 (4)	101.9 (8)
P1-C1-C2	113.2 (9)	112.3 (10)
P2-C2-C1	108.9 (9)	111.4 (10)
P2-C3-C4	104.5 (9)	106.1 (10)
P3-C4-C3	110.9 (10)	109.8 (10)
P3-C5-C6	107.1 (10)	111.1 (12)
P4-C6-C5	107.9 (10)	108.5 (12)

ture, significant variations are observed on cooling. As already noticed for iron(II),[23,32] iron(III),[33-35] and cobalt(II),[36] the variation of the spin state is accompanied by variation in the metal–ligand distances; as a matter of fact in the title compound the Fe–L distances at 150 K are all shorter than those at 298 K with differences ranging from 0.013 to 0.052 Å.

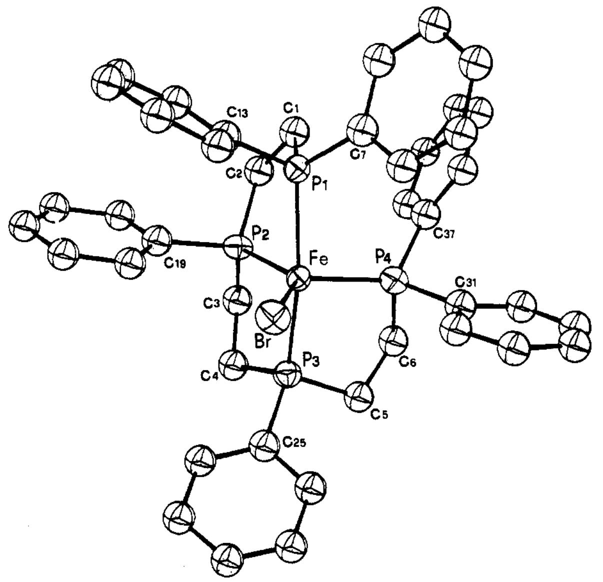

Figure 2. Perspective view of the complex cation $[Fe(P_4)Br]^+$ at 298 K (ORTEP drawing with 30% probability ellipsoids).

Table IV. Root-Mean-Square Displacements (Å) of Principal Axes of Thermal Ellipsoids

	axis 1		axis 2		axis 3	
	150 K	298 K	150 K	298 K	150 K	298 K
Fe	0.122	0.186	0.140	0.217	0.166	0.240
Br	0.192	0.212	0.222	0.278	0.246	0.303
P1	0.139	0.195	0.156	0.236	0.164	0.247
P2	0.138	0.190	0.157	0.219	0.169	0.279
P3	0.145	0.230	0.163	0.243	0.186	0.258
P4	0.134	0.235	0.157	0.259	0.213	0.309

We have previously[36] noticed that, unlike octahedral complexes, five-coordinated ones, owing to their larger fluxionality, show significant differences also in bond angles. In the present compound the Br–Fe–P4 angle changes from 124.2 (2) to 128.4 (1)° with the corresponding decrease of the P4–Fe–P2 angle from 105.0 (2) to 100.5 (2)° in such a way that the two equatorial Br–Fe–P angles approach 130°. Moreover the P1–Fe–P3 axial angle changes from 164.1 (1) to 165.2 (1)°. Thus on going toward a pure singlet ground state, the arrangement of the ligands around the metal approximates the C_{2v} symmetry more closely than in the mixed-spin state.

In our room-temperature study[26] we excluded the simultaneous existence, in the mixed-spin state, of two chromophores differing in bond distances and angles, corresponding to the singlet and triplet ground states. As a matter of fact, although the structural parameters of the molecule in the triplet ground state are unknown, we can assume that this form would show differences with respect to the pure singlet form even larger than those described above. For these reasons such differences should clearly appear as disorder or anomalous thermal motion if the "anomalous" magnetic moment would arise from the simultaneous presence in the lattice of two different chromophores. An examination of Table IV showing the root-mean-square displacements of the principal axes of the thermal ellipsoids at 150 and 298 K seems to support our earlier hypothesis of the existence of only one molecule with intermediate geometry and a mixed-spin state.[26] However it has to be stressed that this statement *does not* exclude the possibility of an *intramolecular* rearrangement between two limit species but simply that the present and other experiments[24-26] can "see" only an intermediate chromophore. In other words, the system can be visualized by an asymmetric double-well po-

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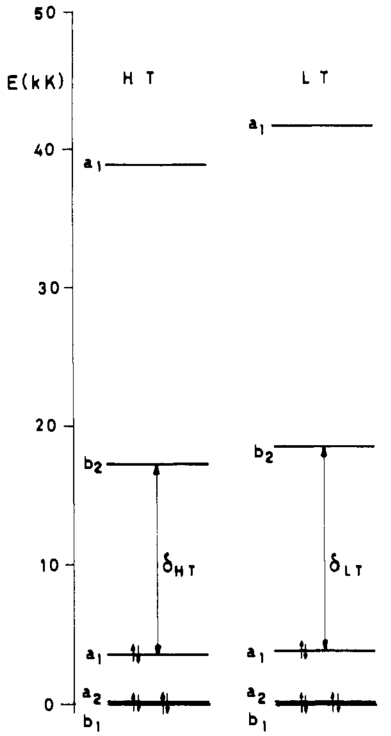

Figure 3. One-electron-level scheme for the chromophore $[Fe(P_4)Br]^+$ computed at 298 K (HT) and 150 K (LT). The point-group symmetry was assumed to be C_{2v} and π contributions have been neglected ($e_\sigma = 12 \times 10^3$ cm^{-1} at HT; 1 kK = 10^3 cm^{-1}).

tential, each well corresponding to the chromophore in a pure spin state,[21] so that, by a quantum-mechanical point of view, the stationary states describing the molecule are indeed a mixture of the starting singlet and triplet wave functions. Of course the admixture degree is a function of the shape of the potential hypersurface connecting the two minima, and therefore, for highly asymmetric potentials, the ground state is a nearly pure-spin state. On the other hand, when a statistical ensemble is taken into account, a temperature-dependent distribution over the different levels must be considered. As a consequence a temperature decrease will depopulate the excited levels, for which a larger contribution from the triplet wave function occurs, as is shown in the following, and a reduced mean value of the magnetic moment will be observed.

By the use of room-temperature crystal structure data, it was demonstrated[26] that nearly degenerate singlet and triplet ground states can occur for reasonable parameter values in both crystal field (CF) and angular overlap (AO) approaches, thus justifying the spin-equilibrium hypothesis. The AO model seems particularly suitable for a qualitative (or even semiquantitative) picture of the electronic structure of metal complexes at different temperatures, when crystal data are available. In fact the energy change e_λ of a given metal orbital, due to the interaction with a ligand orbital, is assumed in the AO approximation to be proportional to S_λ^2, where S_λ is the diatomic overlap integral and λ indicates the bonding symmetry with respect to the metal–ligand axis (σ, π, δ). The LF strength generally follows a R_{ML}^{-n} law, where R_{ML} is the internuclear metal–ligand distance and n can assume different values but commonly is very close to 5.[37-39] Here we do not enter into the dispute about the best value of the exponent n, which is beyond our purposes, but directly assume the energy e_σ to be proportional to R^{-5},[38] while π interactions are neglected owing to their smaller contribution.[26]

From the crystal data reported in Table III, the maxium and minimum contributions to the change of e_σ are given by the atoms P1 [$e_\sigma(150\text{ K}) = 1.121e_\sigma(298\text{ K})$] and P3 [$e_\sigma(150\text{ K}) = 1.029e_\sigma(298\text{ K})$], respectively. However, assuming a common mean value [$e_\sigma(150\text{ K}) = 1.072e_\sigma(298\text{ K})$] for all the coordinating atoms, a one-electron-level scheme, as displayed in Figure 3, is obtained, if the same geometry (C_{2v} point group) and $e_\sigma(298\text{ K})$ value as in ref 26 are considered.

The energy gap between the HOMO and LUMO levels increases by about 1000 cm^{-1} in passing from room temperature to 150 K, if only bond distance changes are considered. Another factor leading to the increase of δ_{LT} is the appreciable change of the angle Br–Fe–P4 from 124.2 (2)° (at 298 K) to 128.4 (1)° (at 150 K), which produces a further destabilization of the b_2 level (C_{2v} notation) besides a stabilization of the first excited a_1 level. Consequently, the singlet state will be stabilized at low temperature with respect to the triplet one.

In conclusion, the present crystal structure determination, together with the above qualitative considerations, seems to confirm, in the case of spin equilibria, the existence of a smooth temperature dependence of the LF strength. As for its origin, a continuous variation of the equilibrium coordinates in the whole configurational space, due to anharmonicity of the double-well potential hypersurface, seems the most likely hypothesis.

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Registry No. $[Fe(P_4)Br]BPh_4{\cdot}CH_2Cl_2$, 51922-37-3.

Supplementary Material Available: Tables of anisotropic thermal parameters, calculated hydrogen positions, and observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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