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Correlation between Spin State and Nature of Donor Atoms for Five-Coordinate Iron(II) Complexes. X-Ray Structure Determination of Two Iron(II) Complexes with Tris(2-diphenylphosphinoethyl)amine and Tris(2-diphenylphosphinoethyl)phosphine

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The spin state of five-coordinate iron(II) complexes decreases from quintuplet to singlet with increasing overall nucleophilicity and with decreasing overall electronegativity of the donor atoms. Two inconsistencies in the correlation for the NP$_3$X and P$_4$X (X = halogen) donor sets have been elucidated through the x-ray structure determinations of the complexes (**1**) [FeBr(np$_3$)]PF$_6$, np$_3$ = tris(2-diphenylphosphinoethyl)amine, and (**2**) [FeBr(pp$_3$)]BPh$_4$, pp$_3$ = tris(2-diphenylphosphinoethyl)phosphine. The geometry of coordination in complex **1** (triclinic, $P\bar{1}$, a = 16.584 (10) Å, b = 13.345 (8) Å, c = 10.365 (6) Å, α = 85.02 (5)°, β = 77.72 (4)°, γ = 76.75 (4)°) is intermediate between trigonal bipyramidal and tetrahedral. The coordination in complex **2** (triclinic $P\bar{1}$, a = 18.910 (9) Å, b = 16.508 (8) Å, c = 10.157 (5) Å, α = 94.01 (5)°, β = 95.47 (5)°, γ = 97.37 (5)°) is trigonal bipyramidal.

Introduction

In recent years many five-coordinate complexes of 3d metals, particularly cobalt and nickel, have been prepared. Complexes of this type with a large variety of donor sets have been prepared in this laboratory. The aim has been to correlate both the nature of the donor atoms and the coordination geometry with the spin state of the metal and to determine the magnetic crossover point.[1] This has been accomplished for the cobalt(II) and nickel(II) complexes.[2] However, until recently, there was little information available for iron(II) complexes, so that only tentative correlations were possible.[3] Several five-coordinate iron(II) complexes with a variety of donor sets are now known.[4,5] These span a sufficiently wide range of $\sum\chi$ and $\sum n^\circ$ values (the overall electronegativity and overall nucleophilicity of the donor set,[2] respectively) to enable all accessible spin states from the singlet to the quintuplet to be attained.

The direct application of these results to the correlation between the nature of the donor set and the magnetic properties of the compounds was not possible in view of two inconsistencies. First, the complexes with the NP$_3$X donor set (the classification of complexes according to their donor set and the type of ligand is given below) have quintuplet ground states, even though they possess higher $\sum n^\circ$ values and lower $\sum\chi$ values than those of the complexes which exhibit quintuplet $\rightleftharpoons$ triplet equilibria. Second, among the complexes having the P$_4$X donor set, those formed by tripod ligands have triplet ground states, whereas those formed by a linear ligand exhibit singlet $\rightleftharpoons$ triplet equilibria.

To elucidate the above facts, detailed structural data were required. Indeed the structures of as many as possible of the complexes considered for the correlation are required since the coordination geometry is an important factor in determining the spin state of five-coordinate complexes.[2] Consequently an x-ray structural investigation has been carried out on the two "key" complexes [FeBr(np$_3$)]PF$_6$, np$_3$ = tris(2-diphenylphosphinoethyl)amine, which has the NP$_3$X donor set, and [FeBr(pp$_3$)]BPh$_4$, pp$_3$ = tris(2-diphenylphosphinoethyl)phosphine, which has the P$_4$X donor set and is formed by a tripod ligand (the structure of a P$_4$X complex formed by a linear ligand had been reported previously[6]). This study has resolved the apparent inconsistencies in the above-mentioned correlation for these five-coordinate iron(II) complexes.

Experimental Section

Physical Measurements. The methods used for the magnetic measurements and the recording of the UV-visible spectra have been described previously.[7]

Collection and Reduction of the X-Ray Intensity Data. To determine the coordination geometry of the iron(II) complexes with the NP$_3$X donor set, the structure of the compound [FeBr(np$_3$)]PF$_6$ was investigated, since that of the corresponding cobalt compound had been reported previously.[8] It was expected that the results obtained for the coordination geometry in the PF$_6$ derivative could be extended to analogous compounds as the spectral and magnetic properties of these iron(II) complexes are virtually independent of the nature of the counterion. The compound was prepared by the procedure previously described for the BPh$_4$ derivative,[5] and it was recrystallized from a petroleum ether-dichloromethane mixture. The elemental analysis data indicated that molecules from the solvent were probably present in the lattice. Anal. Calcd for $C_{42}H_{42}Br_1F_6Fe_1N_1P_4$: C, 53.98; H, 4.53; N, 1.50. Found: C, 54.14; H, 4.61; N, 1.52. In spite of this, crystals obtained by the above procedure were used for collection of intensities, as they provided a better material for diffraction studies than crystals obtained from other solvents.

Crystals of [FeBr(pp$_3$)]BPh$_4$ were obtained as described previously[9] and were recrystallized from a dichloromethane-ethanol mixture. Anal. Calcd for $C_{66}H_{62}B_1Br_1Fe_1P_4$: C, 70.42; H, 5.55. Found: C, 69.83; H, 5.5. The crystals were very fragile and decomposed slowly in air under exposure to the x rays. The crystal used for data collection was coated with a thin film of collodion: this was sufficient to prevent both decomposition and cracking of the crystal in the course of data collection.

Data were collected following essentially the same procedure for the two compounds. Details of the crystal data and the intensity collection method are reported in Table I. Both compounds belong to the triclinic system. The centric space group $P\bar{1}$ was assumed initially in each case and the choices were confirmed by the subsequent structure determinations. Lattice constants of [FeBr(np$_3$)]PF$_6$·0.5C$_5$H$_{12}$ and of [FeBr(pp$_3$)]BPh$_4$ (Table I) were determined by least-squares refinement of the angular positions of 22 and of 24 reflections, respectively, collected on a Philips PW 1100 automated diffractometer that was used for all operations.

The intensities of three standard reflections measured every 100 min, for both compounds, showed no systematic trend and no deviations >5% from their average values. Data sets were processed in the usual way, a value of 0.04 for p being used in the calculation of the $\sigma(I)$'s.[10] Corrections for absorption were applied.[11]

Solution and Refinement of the Structures. The structure of [FeBr(np$_3$)]PF$_6$·0.5C$_5$H$_{12}$ was solved by conventional Patterson and Fourier syntheses, which provided the positions of all nonhydrogen atoms. Full-matrix least-squares refinement minimized the function $\sum w(|F_o| - |F_c|)^2$, with weights $w = 1/\sigma^2(F_o)$. Anisotropic thermal parameters were used for all atoms heavier than carbon in the solution of structure. Hydrogen atoms were introduced in calculated positions (C-H = 1.00 Å, positions being recalculated every few refinement cycles) as fixed contributions, each with a temperature factor ca. 15% larger than that of the carbon atom to which it was attached.[11] Atomic scattering factors were taken from ref 12 and anomalous dispersion terms for the bromine, iron, and phosphorus atoms were included in F_c.[13]

A ΔF Fourier synthesis calculated at the conventional R value of 0.095 showed a set of four, or possibly five, diffuse and incompletely

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Table I. Summary of Crystal Data, Intensity Collection Method, and Refinement

	$[FeBr(np_3)]PF_6\cdot0.5C_5H_{12}$	$[FeBr(pp_3)]BPh_4$
Formula	$C_{44.5}H_{48}BrF_6FeNP_4$	$C_{66}H_{62}BBrFeP_4$
Mol wt	970.52	1125.69
a, A	16.584 (10)	18.910 (9)
b, A	13.345 (8)	16.508 (8)
c, A	10.365 (6)	10.157 (5)
α, deg	85.02 (5)	94.01 (5)
β, deg	77.72 (4)	95.47 (5)
γ, deg	76.75 (4)	97.37 (5)
V, A^3	2174.9	3119.3
Z	2	2
Density, g cm^{-3}	1.478 (calcd), 1.48 (exptl, by flotation in K_2HgI_4 water soln)	1.198 (calcd), 1.21 (exptl, by flotation in K_2HgI_4 water soln)
Space group	$P\bar{1}$	$P\bar{1}$
Crystal dimensions, mm	0.10 × 0.03 × 0.80	0.10 × 0.14 × 0.70
Crystal shape	Plates, [001] elongated	Needles, [001] elongated
Radiation	Mo K_α (λ 0.7107 A), graphite monochromated	Mo K_α (λ 0.7107 A), graphite monochromated
Temp, °C	24	24
μ, cm^{-1}	14.5	10.1
Transmission factors	0.85–0.96	0.85–0.91
Takeoff angle, deg	3	3.5
Scan speed, 2θ °/min	3	4
Scan range, deg	1.10, symmetric	1.10, symmetric
Background counting	$t_{b1} = t_{b2} = {}^1/_2 t_s$ (t_s = total scan time)	$t_{b1} = t_{b2} = {}^1/_2 t_s$ (t_s = total scan time)
2θ limits, deg	4.0–40.0	4.0–40.0
Final no. of variables	303	377
Unique data used ($I > 2.5\sigma(I)$)	1811	3608
Error in observation of unit wt, electrons	1.7	1.6
R	7.8	6.2
R_w	8.7	7.2

resolved peaks, with heights of ca. 1 e $Å^{-3}$. These symmetry-independent peaks lay in a region of positive residual density, close to an inversion center. They formed a nonlinear chain, with mean values of distances and angles of ca. 1.0 Å and 150° along the chain. There were no close contacts between the positions of these peaks and those of nonhydrogen atoms in the structure. Such features of the ΔF map were attributed to the presence of alkane molecules from the solvent, arranged in a very disordered fashion. In the absence of detailed information about the identity of such molecules, it was assumed that the site was occupied, on the average, by one molecule of *n*-pentane. This is one of the principal components of the solvent mixture used, and its molecule has a suitable size to fit into the cavity in the structure. The occupancy factor cannot exceed 0.5, due to the proximity to the position of an inversion center. Therefore, the (approximate) formula $[FeBr(np_3)]PF_6\cdot0.5C_5H_{12}$ was assigned to the material investigated, as it also accounts for the experimental value of the density (Table I).[14] Least-squares refinement of the model for the solvent was undertaken, assigning the carbon form factor and 0.5 occupancy factor to the five highest peaks in the difference map. After a few cycles of individual refinement (there were no definite indications about the model to be considered for rigid-group refinement), the temperature factor of an "atom", placed at one end of the chain, in the position of the lowest peak of the set in the ΔF Fourier synthesis, became extremely high. That atom was then excluded from the model, although it was apparent from inspection of the ΔF Fourier data that a four-atom model was incomplete (this was also suggested by the fact that assigning values <0.5 to the occupancy factors caused significant increases of *R* as well as increases of the ΔF values of several low-order reflections). Refinement of the four-atom model yielded positions essentially consistent (within the large esd's) with those of the highest peaks in the difference map, and it yielded values of the thermal parameters grouped about their average value ($U = 0.18$ $Å^2$). This overall temperature factor and values of the positional parameters from refinement of the solvent were introduced without further change in the final set of cycles. The improvement in *R* due to inclusion of the solvent in the model of the structure was about 0.01 unit. Full-matrix least-squares refinement on the rest of the structure converged to the *R* and R_w values of 0.078 and 0.087, respectively; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. A final ΔF Fourier synthesis showed four peaks with heights of ca. 0.6 e $Å^{-3}$ close to the heavy-atom positions and one peak with a height of 0.4 e $Å^{-3}$ in the region occupied by the solvent.

Refinement of the structure of $[FeBr(pp_3)]BPh_4$ was performed assuming as initial values of the atomic coordinates those from the structure of the compound $[Fe(SH)(pp_3)]BPh_4$,[15] allowing for the replacement of S by Br. Indeed, the similarity of the lattice constants and that of the intensities of reflections for the two compounds suggested that they were probably isostructural. Refinement proceeded as for the np_3 derivative. A ΔF Fourier synthesis calculated at $R = 0.064$ showed a few dispersed peaks with heights <0.5 e $Å^{-3}$, which could not be assigned any meaning. Convergence was attained at $R = 0.062$ and $R_w = 0.072$. In the last refinement cycle on both structures no shift was larger than 0.2 times the corresponding esd. calculated from the least-squares matrix, while the average values of the shift per error ratios were <0.05. The final positional and thermal parameters for the two compounds appear in Tables II and III. A listing of the observed and calculated structure amplitudes is available.[16]

Ligand Field Calculations. Assignment of bands in the spectrum of the d^6 high-spin chromophore $Fe(NP_3)Br$ has been made on the basis of angular overlap calculations in the additivity scheme.[17] States of the unique quintuplet term of iron(II) have been considered, taking advantage of the d^n–d^{5+n} similarity. Published values of the angular overlap parameters for the related d^7 chromophore $Co(NP_3)Br$[18] have been used. Parameter values have been adjusted systematically to take account of the small changes in geometry between the two chromophores. Consistent with the usual angular overlap procedures,[19] the $e'\sigma_L$ and $e'\pi_L$ values from ref 18 have been multiplied by the factor $S^2(Fe\text{–}L)/S^2(Co\text{–}L)$, where $S(M\text{–}L)$ is the overlap integral between the metal d_{z^2} and the ligand valence-shell p orbital calculated at the experimental bond distance. The atomic functions of ref 20 were used, and C_{3v} symmetry was assumed. Transferability of parameters between chromophores formed by two different metal atoms has been discussed previously.[19b]

Results and Discussion

To correlate the spin state of iron(II) in five-coordinate complexes with the nature of the donor atoms, complexes with donor sets formed predominantly of nitrogen and phosphorus atoms with halogen atoms or pseudohalogens have been investigated. The structures of most of the complexes considered have been determined by x-ray procedures. Such compounds are listed in Table IV according to increasing values of the parameter $\sum n°$, the overall nucleophilicity of the donor set,[2] which in turn generally corresponds to the order of decreasing values for the parameter $\sum \chi$, the overall electronegativity of the donor set.[2] On going from the lowest to the highest $\sum n°$ values in the table, the spin multiplicity of the ground state decreases from that of a quintuplet to that of a singlet state in thermal equilibrium with an excited triplet. For intermediate $\sum n°$ values, intermediate values of the spin multiplicity are found. Inspection of the table reveals two significant features which prompted the present investigation, namely, (a) that the complexes with the NP_3X donor set have a quintuplet ground state, in spite of the fact that their $\sum n°$ values are higher than those of the complexes exhibiting a quintuplet $\rightleftharpoons$ triplet equilibrium and (b) that among the complexes with P_4X donor sets, those formed by the pp_3 and qp tripod ligands have a triplet ground state, whereas those formed by the pppp linear ligand exhibit a singlet $\rightleftharpoons$ triplet equilibrium. The results of the present investigation, reported in more detail below, permit a rationalization of the above points. The complexes with NP_3X donor sets are not truly five-coordinated but have a coordination number intermediate between four and five, due to a "tetrahedral distortion" in the coordination, which determines the high values of their

Table II. Atomic Parameters for $[FeBr(np_3)]PF_6 \cdot 0.5C_5H_{12}$[a]

	x	*y*	*z*	*U*, A^2		*x*	*y*	*z*	*U*, A^2
Br	0.0576 (2)	0.2463 (2)	0.1451 (2)		C18	0.120 (1)	0.047 (2)	0.446 (2)	0.061 (7)
Fe	0.2013 (2)	0.1972 (3)	0.1754 (3)		C19	0.120 (1)	0.310 (2)	0.497 (2)	0.057 (7)
P1	0.2250 (4)	0.0106 (5)	0.2058 (5)		C20	0.133 (1)	0.275 (2)	0.630 (2)	0.082 (8)
P2	0.2091 (4)	0.2914 (5)	0.3628 (5)		C21	0.059 (2)	0.288 (2)	0.729 (3)	0.100 (9)
P3	0.2887 (4)	0.2439 (5)	−0.0299 (5)		C22	−0.017 (2)	0.327 (2)	0.708 (3)	0.110 (10)
P4	0.5472 (6)	0.2709 (7)	0.5214 (8)		C23	−0.029 (2)	0.363 (2)	0.582 (3)	0.115 (11)
F1	0.549 (1)	0.381 (1)	0.521 (2)		C24	0.042 (2)	0.352 (2)	0.480 (3)	0.093 (9)
F2	0.533 (1)	0.271 (2)	0.675 (2)		C25	0.231 (1)	0.412 (2)	0.322 (2)	0.060 (7)
F3	0.451 (1)	0.298 (1)	0.540 (2)		C26	0.214 (1)	0.463 (2)	0.201 (2)	0.068 (7)
F4	0.545 (1)	0.156 (1)	0.533 (1)		C27	0.234 (2)	0.555 (2)	0.164 (2)	0.090 (9)
F5	0.559 (1)	0.265 (2)	0.372 (1)		C28	0.268 (2)	0.607 (2)	0.240 (3)	0.122 (11)
F6	0.644 (1)	0.243 (2)	0.500 (2)		C29	0.284 (2)	0.562 (2)	0.357 (3)	0.112 (10)
N	0.358 (1)	0.132 (1)	0.215 (2)		C30	0.264 (2)	0.468 (2)	0.401 (3)	0.094 (9)
C1	0.373 (1)	0.029 (2)	0.261 (2)	0.056 (7)	C31	0.260 (1)	0.368 (2)	−0.118 (2)	0.050 (6)
C2	0.335 (1)	−0.041 (2)	0.194 (2)	0.057 (7)	C32	0.178 (2)	0.413 (2)	−0.113 (2)	0.071 (7)
C3	0.375 (1)	0.200 (2)	0.313 (2)	0.065 (7)	C33	0.154 (2)	0.508 (2)	−0.178 (3)	0.099 (9)
C4	0.299 (1)	0.221 (2)	0.425 (2)	0.057 (7)	C34	0.221 (2)	0.548 (2)	−0.247 (2)	0.085 (8)
C5	0.419 (1)	0.142 (2)	0.085 (2)	0.074 (8)	C35	0.300 (2)	0.507 (2)	−0.256 (3)	0.090 (9)
C6	0.392 (1)	0.238 (2)	0.005 (2)	0.055 (7)	C36	0.324 (1)	0.413 (2)	−0.194 (2)	0.080 (8)
C7	0.191 (1)	−0.073 (1)	0.103 (2)	0.043 (6)	C37	0.301 (1)	0.145 (1)	−0.150 (2)	0.046 (6)
C8	0.109 (1)	−0.058 (2)	0.106 (2)	0.064 (7)	C38	0.235 (1)	0.104 (2)	−0.145 (2)	0.058 (7)
C9	0.080 (2)	−0.123 (2)	0.029 (2)	0.082 (8)	C39	0.240 (2)	0.024 (2)	−0.235 (2)	0.080 (8)
C10	0.138 (2)	−0.194 (2)	−0.046 (2)	0.067 (7)	C40	0.314 (1)	−0.006 (2)	−0.317 (2)	0.067 (7)
C11	0.220 (1)	−0.207 (2)	−0.053 (2)	0.075 (8)	C41	0.382 (1)	0.035 (2)	−0.327 (2)	0.072 (8)
C12	0.253 (1)	−0.147 (2)	0.024 (2)	0.072 (8)	C42	0.377 (1)	0.113 (2)	−0.239 (2)	0.069 (7)
C13	0.175 (1)	−0.029 (2)	0.375 (2)	0.046 (6)	C43[b]	0.535	0.407	0.077	0.18
C14	0.189 (2)	−0.130 (2)	0.411 (3)	0.093 (8)	C44[b]	0.499	0.464	0.132	0.18
C15	0.147 (2)	−0.158 (2)	0.543 (3)	0.107 (10)	C45[b]	0.484	0.532	0.112	0.18
C16	0.094 (2)	−0.080 (2)	0.615 (2)	0.086 (9)	C46[b]	0.459	0.609	0.044	0.18
C17	0.079 (1)	0.019 (2)	0.576 (2)	0.073 (8)					

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br	0.071 (2)	0.097 (2)	0.045 (2)	−0.019 (2)	−0.022 (1)	−0.002 (2)
Fe	0.068 (2)	0.065 (3)	0.021 (2)	−0.021 (2)	−0.013 (2)	−0.007 (2)
P1	0.061 (5)	0.066 (5)	0.025 (4)	−0.016 (4)	−0.013 (3)	−0.007 (3)
P2	0.068 (5)	0.064 (5)	0.021 (3)	−0.018 (4)	−0.014 (3)	−0.005 (3)
P3	0.063 (5)	0.062 (5)	0.032 (4)	−0.013 (4)	−0.008 (3)	−0.009 (4)
P4	0.100 (8)	0.068 (7)	0.069 (7)	−0.019 (6)	−0.021 (5)	−0.006 (5)
F1	0.26 (3)	0.06 (1)	0.21 (2)	−0.04 (1)	−0.05 (2)	−0.01 (1)
F2	0.26 (2)	0.21 (2)	0.06 (1)	−0.03 (2)	−0.05 (1)	−0.03 (1)
F3	0.08 (1)	0.20 (2)	0.16 (2)	−0.01 (1)	−0.04 (1)	−0.04 (1)
F4	0.24 (2)	0.08 (1)	0.09 (1)	−0.03 (1)	0.02 (1)	−0.02 (1)
F5	0.31 (3)	0.31 (3)	0.04 (1)	−0.11 (2)	−0.04 (1)	0.01 (1)
F6	0.08 (1)	0.30 (3)	0.24 (3)	−0.02 (2)	−0.04 (1)	−0.08 (2)
N	0.07 (1)	0.04 (1)	0.05 (1)	−0.02 (1)	−0.02 (1)	0.00 (1)

[a] In the tables of atomic parameters standard deviations on the last significant digits are given in parentheses. Isotropic temperature factors are of the form $\exp[-8\pi^2 U(\sin^2 \theta)/\lambda^2]$ and anisotropic temperature factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)$; these forms are used throughout. [b] Atoms of the solvent molecule, not refined during the last set of cycles (see text); the esd's on positional parameters of these atoms are <0.01.

magnetic moments. The parametrization discussed here is not applicable to such complexes. Their structures are grossly different from the majority of the series; consequently, no meaningful correlation is possible with the other complexes in Table IV. Also, among the complexes with P_4X donor sets, those formed by the tripod-like pp$_3$ or qp ligands have a coordination geometry different from that of the derivatives of the linear pppp ligand. This difference and the different values of the metal–ligand bond lengths (see below) for the two classes of compounds reasonably account for their different magnetic moments. Indeed, it has been found previously that even small changes in the geometry of the coordination may affect substantially the spin state of complexes located in the proximity of a crossover point.[2,21]

Therefore, by analogy with the results obtained for the cobalt(II) and nickel(II) five-coordinate complexes,[2] the values of the $\sum n°$ and of the $\sum \chi$ parameters, calculated for each donor set, do correlate with the spin state of iron(II) in five-coordinate complexes, provided the gross features of the coordination geometry are taken into account. The crossover point between the quintuplet and the triplet states is located at a value of ca. 29 on the $\sum n°$ scale. A discussion of the results of the structure determinations follows.

The structure of the compound $[FeBr(np_3)]PF_6{\cdot}0.5C_5H_{12}$ consists of $[FeBr(np_3)]^+$ cations and of PF_6^- anions. There are in addition hydrocarbon molecules from the solvent occupying cavities in the structure. The coordination geometry is similar to that previously found for the high-spin $[CoX(np_3)]^+$ cations.[8,22] There are a set of four donor atoms, one bromine and three phosphorus atoms, which surround the metal at "normal" bond distances (Fe–Br 2.403 (4) Å; Fe–P 2.435 (10) Å, mean) in a distorted tetrahedral arrangement, and an additional "donor", the nitrogen atom of the ligand molecule, which lies at a very long distance from the metal (Fe–N 2.65 (2) Å), outside the tetrahedron formed by the four closest ligand atoms. The same type of coordination may be assigned to the other iron(II) complexes formed by the np$_3$ ligand,[5] in view of the similarity of their spectral and magnetic properties. The distortion toward tetrahedral coordination in $[FeBr(np_3)]PF_6$ is slightly smaller than that found in the compound $[CoBr(np_3)]PF_6$.[8] Figure 1 shows a perspective view of the complex cation. Distances and angles about the metal atom are reported in Table V. Values of bond distances and angles in the ligand molecule are normal; selected values

Table III. Atomic Parameters for $[FeBr(pp_3)]BF_4$

	x	*y*	*z*	*U*, Å^2		*x*	*y*	*z*	*U*, Å^2
Br	0.1036 (1)	0.1784 (1)	0.2316 (1)		C32	0.284 (1)	0.400 (1)	0.603 (1)	0.086 (4)
Fe	0.2200 (1)	0.1620 (1)	0.3249 (1)		C33	0.302 (1)	0.485 (1)	0.589 (2)	0.121 (5)
P1	0.2090 (1)	0.0178 (2)	0.3155 (2)		C34	0.275 (1)	0.515 (1)	0.473 (1)	0.101 (5)
P2	0.2868 (1)	0.2224 (2)	0.1664 (3)		C35	0.235 (1)	0.469 (1)	0.375 (1)	0.085 (4)
P3	0.2161 (1)	0.2425 (2)	0.5214 (2)		C36	0.217 (1)	0.384 (1)	0.390 (1)	0.070 (4)
P4	0.3282 (1)	0.1510 (2)	0.4203 (3)		C37	0.134 (1)	0.240 (1)	0.601 (1)	0.049 (3)
C1	0.339 (1)	0.046 (1)	0.457 (1)	0.051 (3)	C38	0.123 (1)	0.188 (1)	0.700 (1)	0.075 (3)
C2	0.299 (1)	−0.012 (1)	0.342 (1)	0.051 (3)	C39	0.056 (1)	0.185 (1)	0.759 (1)	0.099 (5)
C3	0.401 (1)	0.181 (1)	0.317 (1)	0.053 (3)	C40	0.007 (1)	0.229 (1)	0.719 (1)	0.093 (4)
C4	0.379 (1)	0.252 (1)	0.240 (1)	0.054 (3)	C41	0.019 (1)	0.281 (1)	0.623 (1)	0.099 (5)
C5	0.351 (1)	0.212 (1)	0.581 (1)	0.058 (3)	C42	0.083 (1)	0.287 (1)	0.564 (1)	0.080 (4)
C6	0.284 (1)	0.216 (1)	0.645 (1)	0.056 (3)	C43	0.551 (1)	0.319 (1)	0.740 (1)	0.052 (3)
C7	0.162 (1)	−0.027 (1)	0.447 (1)	0.052 (3)	C44	0.493 (1)	0.295 (1)	0.808 (1)	0.057 (3)
C8	0.113 (1)	0.013 (1)	0.504 (1)	0.070 (4)	C45	0.451 (1)	0.349 (1)	0.863 (1)	0.070 (3)
C9	0.070 (1)	−0.023 (1)	0.600 (1)	0.095 (4)	C46	0.464 (1)	0.430 (1)	0.847 (1)	0.080 (4)
C10	0.082 (1)	−0.097 (1)	0.632 (1)	0.093 (4)	C47	0.521 (1)	0.459 (1)	0.783 (1)	0.086 (4)
C11	0.132 (1)	−0.136 (1)	0.585 (1)	0.107 (5)	C48	0.565 (1)	0.405 (1)	0.729 (1)	0.070 (4)
C12	0.174 (1)	−0.102 (1)	0.487 (1)	0.088 (4)	C49	0.686 (1)	0.291 (1)	0.722 (1)	0.056 (3)
C13	0.165 (1)	−0.050 (1)	0.171 (1)	0.049 (3)	C50	0.707 (1)	0.327 (1)	0.849 (1)	0.074 (4)
C14	0.095 (1)	−0.039 (1)	0.124 (1)	0.054 (3)	C51	0.780 (1)	0.355 (1)	0.896 (1)	0.094 (4)
C15	0.060 (1)	−0.094 (1)	0.019 (1)	0.068 (4)	C52	0.828 (1)	0.347 (1)	0.812 (1)	0.093 (4)
C16	0.092 (1)	−0.155 (1)	−0.030 (1)	0.075 (4)	C53	0.814 (1)	0.312 (1)	0.687 (1)	0.093 (4)
C17	0.159 (1)	−0.166 (1)	0.011 (1)	0.084 (4)	C54	0.741 (1)	0.283 (1)	0.644 (1)	0.071 (4)
C18	0.198 (1)	−0.112 (1)	0.116 (1)	0.072 (4)	C55	0.579 (1)	0.166 (1)	0.724 (1)	0.044 (3)
C19	0.292 (1)	0.145 (1)	0.031 (1)	0.048 (3)	C56	0.603 (1)	0.148 (1)	0.850 (1)	0.058 (3)
C20	0.230 (1)	0.094 (1)	−0.018 (1)	0.055 (3)	C57	0.582 (1)	0.073 (1)	0.901 (1)	0.061 (3)
C21	0.232 (1)	0.033 (1)	−0.120 (1)	0.070 (4)	C58	0.535 (1)	0.015 (1)	0.824 (1)	0.056 (3)
C22	0.295 (1)	0.026 (1)	−0.172 (1)	0.069 (4)	C59	0.508 (1)	0.029 (1)	0.700 (1)	0.050 (3)
C23	0.354 (1)	0.074 (1)	−0.131 (1)	0.071 (4)	C60	0.529 (1)	0.104 (1)	0.652 (1)	0.044 (3)
C24	0.357 (1)	0.137 (1)	−0.027 (1)	0.064 (3)	C61	0.590 (1)	0.255 (1)	0.511 (1)	0.050 (3)
C25	0.265 (1)	0.310 (1)	0.081 (1)	0.053 (3)	C62	0.611 (1)	0.191 (1)	0.428 (1)	0.062 (3)
C26	0.309 (1)	0.383 (1)	0.095 (1)	0.069 (4)	C63	0.607 (1)	0.188 (1)	0.289 (1)	0.080 (4)
C27	0.291 (1)	0.449 (1)	0.023 (1)	0.084 (4)	C64	0.584 (1)	0.253 (1)	0.229 (1)	0.078 (4)
C28	0.229 (1)	0.439 (1)	−0.055 (1)	0.083 (4)	C65	0.563 (1)	0.316 (1)	0.302 (1)	0.068 (3)
C29	0.182 (1)	0.370 (1)	−0.069 (1)	0.092 (4)	C66	0.565 (1)	0.316 (1)	0.437 (1)	0.058 (3)
C30	0.201 (1)	0.303 (1)	0.001 (1)	0.075 (4)	**B**	0.600 (1)	0.258 (1)	0.671 (1)	0.043 (3)
C31	0.241 (1)	0.350 (1)	0.503 (1)	0.054 (3)					

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br	0.038 (1)	0.081 (1)	0.059 (1)	0.015 (1)	−0.007 (1)	0.007 (1)
Fe	0.033 (1)	0.048 (1)	0.034 (1)	0.005 (1)	0.001 (1)	0.008 (1)
P1	0.039 (2)	0.049 (2)	0.037 (2)	0.004 (1)	0.002 (1)	0.008 (1)
P2	0.042 (2)	0.051 (2)	0.043 (2)	0.005 (1)	0.003 (1)	0.013 (2)
P3	0.045 (2)	0.045 (2)	0.034 (2)	0.006 (1)	0.003 (1)	0.009 (1)
P4	0.032 (2)	0.051 (2)	0.043 (2)	0.005 (1)	−0.001 (1)	0.007 (2)

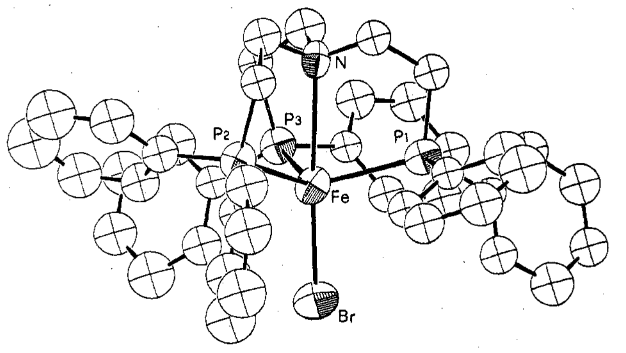

Figure 1. Perspective view of the cation in the structure of $[FeBr(np_3)]PF_6 \cdot 0.5C_2H_{12}$.

are reported in Table VI. The anion shows the usual effects of high thermal motion but is not affected by disorder. The mean of the P–F distances, uncorrected for thermal motion, is 1.53 (2) Å. There are no contact distances involving fluorine atoms below 3.30 Å and no contacts formed by the four atoms of the model of the solvent shorter than 3.37 Å.

The structure of $[FeBr(pp_3)]BPh_4$ consists of $[FeBr(pp_3)]^+$ cations and of BPh_4^- anions. The coordination geometry about the metal atom is essentially trigonal bipyramidal, with the three peripheral phosphorus atoms of the tripod ligand lying in the equatorial plane (Fe–P 2.343 (14) Å, mean) and with the bromine atom and the central phosphorus atom of the ligand in the axial positions (Fe–Br 2.369 (2) Å, Fe–P4 2.214 (3) Å). The other iron(II) complexes formed by the pp_3[9] and qp[23] ligands may be safely assigned the same type of coordination. This has been also found for the mercapto derivative $[Fe(SH)(pp_3)]BPh_4$.[15] On the other hand, a different coordination geometry, intermediate between square pyramidal and trigonal bipyramidal, has been found for the complex $[FeBr(pppp)]BPh_4$,[6] which has the same donor set as $[FeBr(pp_3)]BPh_4$. Such a difference in the geometry of coordination may be the cause of the different magnetic moments of the two compounds (Table IV). In particular, the metal–ligand distances in the complex $[FeBr(pppp)]BPh_4$ are shorter (by 0.06 Å, on the average, probably due to geometric requirements of the pppp ligand) than in the pp_3 derivative. This is consistent with the fact that the former compound exhibits a lower spin mutiplicity than the latter. A perspective view of the $[FeBr(pp_3)]^+$ complex cation is shown in Figure 2. Distances and angles about the metal atom are reported in Table VII and selected values for the rest of the structure in Table VIII. The dimensions of the anion match those previously reported.[24] There are no contact distances in the structure below 3.38 Å.

The reflectance spectrum of $[FeBr(np_3)]PF_6$ is practically identical with those of the related halides.[5] It shows two bands

Table IV. Five-Coordinate Iron(II) Complexes, Donor Sets, Spin States, and Geometries[a]

Compd[b]	Donor set	Σn°	$\Sigma\chi$	Spin state	Coordination geometry
$[FeCl(nn_3)]Cl$[c]	N_4Cl	15.44	15.11	Quintuplet	
$[FeCl(nnnn)]I$[d]	N_4Cl	15.44	15.11	Quintuplet	Distorted TBP[d]
$[FeBr(nn_3)]Br$[c]	N_4Br	16.58	15.02	Quintuplet	TBP[e]
$[FeI(nn_3)]I$[c]	N_4I	17.82	14.49	Quintuplet	
$[FeCl_2(pnp)]$[f]	NP_2Cl_2	26.76	12.85	Quintuplet	
$[FeBr_2(pnp)]$[f]	NP_2Br_2	29.04	12.67	Quintuplet	
$[FeI(NCS)(pnp)]$[f]	N_2P_2I	29.20	12.47	Quintuplet ⇌ triplet	
$[FeI_2(pnp)]$[f]	NP_2I_2	31.52	11.61	Quintuplet ⇌ triplet	
$[FeCl(np_3)]PF_6$[g]	NP_3Cl	32.51	12.08	Quintuplet	
$[FeBr(np_3)]PF_6$[g]	NP_3Br	33.65	11.99	Quintuplet	Tetrahedrally distorted TBP[h]
$[FeI(np_3)]PF_6$[g]	NP_3I	34.89	11.46	Quintuplet	
$[FeCl(qp)]BPh_4$[i]	P_4Cl	38.20	11.07	Triplet	
$[FeBr(qp)]BPh_4$[i]	P_4Br	39.34	10.98	Triplet	
$[Fe(SH)(pp_3)]BPh_4$[j,k]	P_4S		10.68	Triplet	TBP[j]
$[FeI(qp)]BPh_4$[i]	P_4I	40.58	10.45	Triplet	
$[FeCl(pp_3)]BPh_4$[l]	P_4Cl	38.20	11.07	Triplet	
$[FeBr(pp_3)]BPh_4$[l]	P_4Br	39.34	10.98	Triplet	TBP[m]
$[FeI(pp_3)]BPh_4$[l]	P_4I	40.58	10.45	Triplet	
$[FeCl(pppp)]BPh_4$[n]	P_4Cl	38.20	11.07	Singlet ⇌ triplet	
$[FeBr(pppp)]BPh_4$[n]	P_4Br	39.34	10.98	Singlet ⇌ triplet	TBP distorted toward SP[o]
$[FeI(pppp)]BPh_4$[n]	P_4I	40.58	10.45	Singlet ⇌ triplet	

[a] The geometry of coordination is reported for the complexes whose structure has been determined by x-ray diffraction (TBP = trigonal bipyramidal, SP = square pyramidal). [b] nn_3 = tris(2-dimethylaminoethyl)amine; nnnn = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene; pnp = 2,6-bis(2-diphenylphosphinoethyl)pyridine; np_3 = tris(2-diphenylphosphinoethyl)amine; pp_3 = tris(2-diphenylphosphinoethyl)phosphine; qp = tris(*o*-diphenylphosphinophenyl)phosphine; pppp = hexaphenyl-1,4,7,10-tetraphosphadecane. [c] M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 1150 (1966). [d] V. L. Goedken, J. Molin-Case, and G. G. Christoph, *Inorg. Chem.*, **12**, 2894 (1973). [e] M. Di Vaira and P. L. Orioli, *Acta Crystallogr., Sect. B*, **24**, 1269 (1968). The same coordination geometry as that determined for the bromide may be assigned to the analogous chloride and iodide derivatives. [f] W. S. J. Kelly, G. H. Ford, and S. M. Nelson, *J. Chem. Soc. A*, 388 (1971). [g] Reference 5. [h] Present work. The coordination geometry determined for the bromide may be assigned also to the chloride and iodide. [i] Reference 23. [j] Reference 15. [k] The Σn° value is not reported for this compound, because the n° value for sulfur is uncertain. [l] Reference 9. [m] Present work. The same TBP geometry may be assigned to all the complexes listed in this table, formed by the pp_3 and qp ligands. [n] Reference 4. [o] Reference 6.

Table V. Bond Lengths (A) and Angles (deg) within the Coordination Polyhedron of $[FeBr(np_3)]PF_6 \cdot 0.5C_5H_{12}$[a]

	Distances		
Fe-Br	2.403 (4)	Fe-P3	2.427 (6)
Fe-P1	2.433 (7)	Fe-N	2.65 (2)
Fe-P2	2.445 (7)		
	Angles		
Br-Fe-P1	103.3 (2)	P1-Fe-P3	110.1 (2)
Br-Fe-P2	106.6 (2)	P2-Fe-P3	112.9 (3)
Br-Fe-P3	106.5 (2)	N-Fe-P1	73.4 (4)
Br-Fe-N	176.6 (4)	N-Fe-P2	74.3 (4)
P1-Fe-P2	116.4 (2)	N-Fe-P3	75.9 (4)

[a] Esd's in parentheses.

Table VI. Selected Interatomic Distances (A) and Angles (deg) in the $[FeBr(np_3)]^+$ Complex Cation[a]

	Distances		
P1-C2	1.78 (2)	P3-C37	1.84 (2)
P1-C7	1.87 (2)	N-C1	1.40 (3)
P1-C13	1.86 (2)	N-C3	1.53 (3)
P2-C4	1.79 (2)	N-C5	1.51 (3)
P2-C19	1.79 (2)	C1-C2	1.53 (4)
P2-C25	1.72 (3)	C3-C4	1.51 (3)
P3-C6	1.81 (2)	C5-C6	1.51 (3)
P3-C31	1.84 (2)		
	Angles		
Fe-P1-C2	109.1 (8)	C6-P3-C31	106.1 (1.1)
Fe-P1-C7	123.9 (7)	C6-P3-C37	107.3 (1.0)
Fe-P1-C13	111.6 (7)	C31-P3-C37	105.7 (1.0)
C2-P1-C7	104.6 (1.0)	Fe-N-C1	112 (1)
C2-P1-C13	104.6 (9)	Fe-N-C3	110 (1)
C7-P1-C13	101.2 (1.0)	Fe-N-C5	109 (1)
Fe-P2-C4	106.3 (8)	C1-N-C3	110 (2)
Fe-P2-C19	117.7 (9)	C1-N-C5	108 (1)
Fe-P2-C25	114.5 (8)	C3-N-C5	108 (2)
C4-P2-C19	108.1 (1.0)	N-C1-C2	115 (2)
C4-P2-C25	103.7 (1.1)	P1-C2-C1	110 (1)
C19-P2-C25	105.5 (1.1)	N-C3-C4	109 (2)
Fe-P3-C6	106.6 (7)	P2-C4-C3	110 (1)
Fe-P3-C31	121.9 (7)	N-C5-C6	113 (2)
Fe-P3-C37	108.5 (7)	P3-C6-C5	110 (2)

[a] Esd's in parentheses.

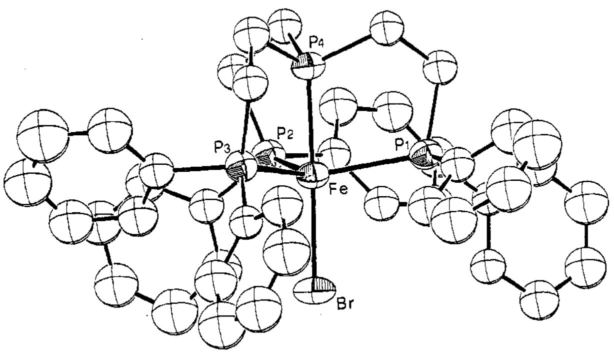

Figure 2. Perspective view of the cation in the structure of $[FeBr(pp_3)]BPh_4$.

at ca. 0.50 and 0.92 μm^{-1} that essentially do not shift in $(CH_2Cl)_2$ solution. The two transitions may be respectively assigned as $^5E(e_a{}^3e_b{}^2a_1) \rightarrow {}^5E(e_a{}^2e_b{}^3a_1)$ and $^5E(e_a{}^3e_b{}^2a_1) \rightarrow {}^5A_1(e_a{}^3e_ba_1{}^2)$ on the basis of the angular overlap calculations (calcd 0.54 and 1.0 μm^{-1}) described above. It is noteworthy that such an agreement has been obtained by making direct use of the values of the angular overlap parameters calculated for a related chromophore.

The spectrum of $[FeBr(pp_3)]BPh_4$ in $(CH_2Cl)_2$ solution shows two d–d transitions, at 0.83 and 1.90 μm^{-1}, respectively. The first band, having shoulders both on the high- and the low-energy sides, was not recorded previously.[9] A shoulder at ca. 2.7 μm^{-1} and additional features at higher frequencies,

Table VII. Bond Lengths (A) and Angles (deg) within the Coordination Polyhedron of $[FeBr(pp_3)]BPh_4$[a]

Distances			
Fe–Br	2.369 (2)	Fe–P3	2.332 (3)
Fe–P1	2.358 (3)	Fe–P4	2.214 (3)
Fe–P2	2.339 (3)		
Angles			
Br–Fe–P1	99.8 (1)	P1–Fe–P3	122.4 (1)
Br–Fe–P2	99.1 (1)	P2–Fe–P3	116.4 (1)
Br–Fe–P3	95.5 (1)	P4–Fe–P1	81.9 (1)
Br–Fe–P4	177.2 (1)	P4–Fe–P2	82.0 (1)
P1–Fe–P2	115.2 (1)	P4–Fe–P3	81.7 (1)

[a] Esd's in parentheses.

Table VIII. Selected Interatomic Distances (A) and Angles (deg) in the $[FeBr(pp_3)]^+$ Complex Cation[a]

Distances			
P1–C2	1.83 (1)	P3–C37	1.81 (1)
P1–C7	1.82 (1)	P4–C1	1.83 (1)
P1–C13	1.84 (1)	P4–C3	1.84 (1)
P2–C4	1.83 (1)	P4–C5	1.84 (1)
P2–C19	1.82 (1)	C1–C2	1.52 (1)
P2–C25	1.81 (1)	C3–C4	1.53 (1)
P3–C6	1.83 (1)	C5–C6	1.48 (1)
P3–C31	1.81 (1)		
Angles			
Fe–P1–C2	108.2 (3)	C6–P3–C31	105.0 (5)
Fe–P1–C7	114.2 (4)	C6–P3–C37	106.4 (5)
Fe–P1–C13	123.6 (3)	C31–P3–C37	103.7 (5)
C2–P1–C7	104.0 (5)	Fe–P4–C1	113.0 (3)
C2–P1–C13	104.5 (5)	Fe–P4–C3	113.6 (3)
C7–P1–C13	100.3 (5)	Fe–P4–C5	113.6 (4)
Fe–P2–C4	108.7 (3)	C1–P4–C3	104.5 (5)
Fe–P2–C19	109.2 (3)	C1–P4–C5	104.6 (5)
Fe–P2–C25	124.5 (4)	C3–P4–C5	106.8 (5)
C4–P2–C19	104.8 (5)	P4–C1–C2	107.8 (7)
C4–P2–C25	104.7 (5)	P1–C2–C1	106.6 (7)
C19–P2–C25	103.3 (5)	P4–C3–C4	107.5 (7)
Fe–P3–C6	107.9 (3)	P2–C4–C3	107.3 (7)
Fe–P3–C31	111.8 (4)	P4–C5–C6	108.4 (7)
Fe–P3–C37	120.9 (3)	P3–C6–C5	108.2 (7)

[a] Esd's in parentheses.

which probably have little d–d transition character, have been reported previously.[9] The ligand field spectrum is similar to those of the $[Fe(SR)(pp_3)]BPh_4$ compounds and may be assigned analogously.[15] However, in the case of the present compound there seem to be less components under the two main band envelopes than in the case of the –SR derivatives. This may be due to the intensities of some of the transitions being lower for the halides than for the –SR derivatives. Such an effect has been observed for the two corresponding classes of nickel(II) compounds,[15] and it has been attributed to the fact that the D_{3h} selection rules become less and less effective as the coordinated halogen atom is replaced by the –SR group.

Registry No. $[FeBr(np_3)]PF_6 \cdot 0.5C_5H_{12}$, 65120-31-2; $[FeBr(pp_3)]BPh_4$, 39708-53-7.

Supplementary Material Available: Listings of structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

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