(6) Å, N–N = 1.373 (5) Å, and N–B = 1.545 (6) Å in accord with values reported previously.[1]

That the arenethiolato ligand is terminal rather than bridging is a consequence of steric crowding around molybdenum, there being no available space for another ligand. The Mo–S bond length (2.305 (1) Å) is much shorter than Mo–S single bond distances (~2.45 Å) reported for a number of molybdenum–sulfur complexes.[16] For *terminal* Mo=S bonds an average length of 2.10 (2) Å is well established.[16] From these data we would infer that the formal 16-electron character of the Mo atom in complex **1** is removed by appreciable S→Mo $p\pi d\pi$ bonding. Of some interest in relation to our results are the structural data reported[17] for the complexes $(\eta^5\text{-}C_5H_5)Mo(CO)(CF_3C_2CF_3)(SC_6H_5)$ (**2**) and $\eta^5\text{-}C_5H_5)MoO(CF_3C_2CF_3)(SC_6F_5)$ (**3**). Both complexes are formal 16-electron species if the ligands donate their "normal" quota of electrons to the Mo atom (six from $C_5H_5^-$, two from $CF_3C_2CF_3$, two from CO, four from O^{2-}, and two from $C_6F_5S^-$). Woodward and co-workers have suggested that the acetylene ligand in complex **2** is a four-electron donor, this giving Mo a closed shell of electrons. A closed shell of electrons in complex **3** is also postulated via a triply bonded, six-electron-donor terminal oxide. We note however that the Mo–S bond lengths in these complexes (2.366 (1) Å for complex **2**, 2.403 (2) Å for complex **3**, although longer than in complex **1**, are still significantly shorter than would be expected for an Mo–S single bond (see above). It is possible therefore that in addition to the formulation invoked[17] for **2** and **3**, S→Mo $p\pi \rightarrow d\pi$ bonding also plays a part in producing a closed shell of electrons in these complexes.

The Mo–C(carbonyl) distances (1.969 and 1.977 (3) Å) are slightly longer than the corresponding bond lengths in $PhB(pz)_3Mo(CO)_2C_7H_7$[15] (1.938 and 1.946 (5) Å). The dimensions of the *p*-chlorobenzenethiolato moiety (Table II) are unexceptional with S–C = 1.778 (3) Å, Cl–C = 1.746 (4) Å, and mean C–C = 1.373 (5) Å. The conformation of the *p*-chlorobenzenethiolato ligand is such that the Mo–S–C(41)–C(42) torsion angle is 10.4° and the aromatic ring lies between two of the pyrazolyl rings of the $HB(Me_2pz)_3$ ligand with N(21)–Mo–S–C(41) and N(31)–Mo–S–C(41) torsion angles of −44.5 and 42.9°, respectively. That this conformation is adopted in the crystal in preference to any other is presumably ascribable to crystal-packing effects.

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Supplementary Material Available: Listings of structure factors, thermal parameters, and hydrogen positional parameters (23 pages). Ordering information is given on any current masthead page.

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Singlet $\rightleftharpoons$ Quintet Spin Transitions of Iron(II) Complexes with a P_4Cl_2 Donor Set. X-ray Structures of the Compound $FeCl_2(Ph_2PCH{=}CHPPh_2)_2$ and of Its Acetone Solvate at 130 and 295 K

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While the pseudooctahedral compounds $FeX_2(dppen)_2$ with a P_4X_2 donor set (dppen = *cis*-1,2-bis(diphenylphosphino)ethylene; X = Cl, Br) maintain μ_{eff} values close to 5.0 μ_B over the range 90–300 K or exhibit smoothly decreasing μ_{eff} values with decreasing temperature, the corresponding solvates, with formula $FeX_2(dppen)_2\cdot n$S (X = Cl, S = $(CH_3)_2CO$, CH_2Cl_2, $CHCl_3$; X = Br, S = $(CH_3)_2CO$) exhibit abrupt temperature-induced spin transitions in the range 190–230 K between the singlet and quintet ground states. An X-ray structural investigation performed on the compound $FeCl_2(dppen)_2\cdot 2(CH_3)_2CO$ at 295 K (high-spin isomer, space group $P2_1/a$, a = 17.867 (4) Å, b = 13.089 (4) Å, c = 11.519 (3) Å, β = 93.30 (3)°, Z = 2) and at 130 K (low-spin isomer, poor quality data, a = 17.02 (2) Å, b = 13.02 (2) Å, c = 11.28 (2) Å, β = 94.3 (1)°) has shown that the Fe–P bond distances decrease dramatically (by ca. 0.28, Å in the mean) in the quintet-to-singlet transition. Comparison with the structure of a polymorph of $FeCl_2(dppen)_2$ (295 K, high spin, space group $P2_1/n$, a = 16.086 (6) Å, b = 13.189 (6) Å, c = 10.840 (5) Å, β = 90.42 (5)°, Z = 2) indicates that crystal packing and the presence of solvent molecules in the lattice are the factors determining the magnetic properties of these compounds.

Introduction

A previous investigation on pseudooctahedral iron(II) chloride complexes with polyphosphines has shown that they may be either in the singlet ground state if the Fe–P bond lengths are in the normal range or in the quintet ground state if such bonds are abnormally long.[1] The correlation between such bond distances and the nature of the ground state was considered worthy of further investigation. Suitable compounds to this investigation were the iron(II) complex $FeCl_2(dppen)_2$ (dppen = *cis*-1,2-bis(diphenylphosphino)ethylene, $Ph_2PCH{=}CHPPh_2$), which has been assigned a trans-octahedral coordination geometry,[2] and its solvates with formula $FeCl_2(dppen)_2\cdot n$S (S = $(CH_3)_2CO$, CH_2Cl_2, $CHCl_3$), which have been obtained and characterized in this laboratory. The magnetic moment of the unsolvated compound was reported to vary smoothly in the temperature interval 83–353 K.[2] On the contrary, the magnetic moments of the solvated compounds vary abruptly, within a few degrees, from the high-spin to the low-spin values, as the temperature is lowered. Therefore the latter compounds provide the opportunity to

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detect the structural changes associated with the spin transition by determining, at the appropriate temperatures, the structures of the two spin isomers of the same compound.

We have isolated two different polymorphs of the compound $FeCl_2(dppen)_2$ having slightly different magnetic properties, which moreover differ from those previously reported for the same compound.[2] X-ray structural investigations have been carried out on one of the polymorphic modifications of the compound $FeCl_2(dppen)_2$, at room temperature, as well as on the acetone solvate, at the temperatures of 295 and 130 K, at which the high-spin and, respectively, the low-spin state exist. Although the accuracy of the low-temperature structure determination was limited by disorder in the solid, the results may be considered significant to the principal purposes of the present investigation.

The compounds $FeBr_2(dppen)_2{\cdot}2(CH_3)_2CO$ and $[FeI(dppen)_2]BPh_4$ have also been syntheiszed and characterized. Preliminary results of the structural analysis on the high-spin isomer of the compound $FeCl_2$ $(dppen)_2{\cdot}2(CH_3)_2CO$ have already been reported.[3]

Experimental Section

All reactions and manipulations were carried out in a dry nitrogen atmosphere. All reagents were obtained from commerical sources and used without further purification.

Synthesis of the Compounds. $FeCl_2(dppen)_2$, Form I. A hot (75 °C) solution of anhydrous $FeCl_2$ (130 mg, 1 mmol) in absolute ethanol (15 mL) was added to a boiling solution of the ligand (792 mg, 2 mmol) in absolute ethanol (30 mL). Heating was continued until yellow crystals precipitated. The crystals were filtered off and washed with hot alcohol and then petroleum ether before being dried in a current of nitrogen. Anal. Calcd for $C_{52}H_{44}Cl_2FeP_4$: C, 67.92; H, 4.82; Fe, 6.07; P, 13.47. Found: C, 67.83; H, 4.79; Fe, 5.76; P, 14.28.

$FeCl_2(dppen)_2$, Form II. Warm (60 °C) solutions of the reagents (see form I) were mixed. Heating was then discontinued. Pale yellow crystals precipitated almost immediately. The crystals were collected by the method described above. Anal. Calcd for $C_{52}H_{44}Cl_2FeP_4$: C, 67.92; H, 4.82; Fe, 6.07; Cl, 7.71. Found: C, 66.86; H, 4.83; Fe, 5.50; Cl, 7.43.

$FeBr_2(dppen)_2$. This compound was prepared by the procedure described for $FeCl_2(dppen)_2$, form II. Anal. Calcd for $C_{52}H_{44}Br_2FeP_4$: C, 61.93; H, 4.40; Fe, 5.54. Found: C, 61.38; H, 4.69; Fe, 5.26.

$FeX_2(dppen)_2{\cdot}nS$ ($X = Cl$, $nS = 2(CH_3)_2CO$, $2CH_2Cl_2$, $CHCl_3$; $X = Br$, $nS = 2(CH_3)_2CO$). A solution of anhydrous $FeCl_2$ (130 mg, 1 mmol), or $FeBr_2$(310 mg, 1 mmol), in absolute ehtanol (15 mL) was added to a solution of the ligand (792 mg, 2 mmol) in 30 mL of the appropriate solvent (S). The resulting solution was concentrated by distillation until crystallization was initiated. The yellow crystals which precipitated were filtered off and washed with alcohol and then petroleum ether before being dried in a current of nitrogen. Anal. Calcd for $C_{52}H_{44}Cl_2FeP_4{\cdot}C_6H_{12}O_2$: C, 67.26; H, 5.45; Fe, 5.39; P, 11.96; Cl, 6.84. Found: C, 67.52; H, 5.67; Fe, 5.04; P, 12.62; Cl, 6.48, Calcd for $C_{52}H_{44}Cl_2FeP_4{\cdot}C_2H_4Cl_4$: C, 59.53; H, 4.44; Fe, 5.13. Found: C, 60.18; H, 4.62; Fe, 4.95. Calcd for $C_{52}H_{44}Cl_2FeP_4{\cdot}CHCl_3$: C, 61.27; H, 4.37; Fe, 5.37. Found: C, 60.24; H, 4.44; Fe, 5.54. Calcd for $C_{52}H_{44}Br_2FeP_4{\cdot}C_6H_{12}O_2$: C, 61.94; H, 5.02; Fe, 4.97. Found: C, 62.37; H, 4.77; Fe, 4.95.

$[FeI(dppen)_2]BPh_4$. A solution of anhydrous FeI_2 (310 mg, 1 mmol) in ethanol (15 mL) was added to a solution of the ligand (792 mg, 2 mmol) in acetone (20 mL). Ater 1 mmol of $NaBPh_4$ dissolved in 10 mL of ethanol had been added to this solution, the solvent was removed by distillation until crystallization was initiated. The orange crystals were filtered off, washed with ethanol and petroleum ether, and dried in a current of nitrogen. Anal. Calcd for $C_{76}H_{64}BFeIP_4$: C, 70.50; H, 4.98; Fe, 4.31. Found: C, 68.82; H, 4.76; Fe, 4.55.

Physical Measurements. Magnetic susceptibilities were measured with use of the Gouy method, the apparatus and experimental technique being those previously described.[4] The other physical measurements were executed by the procedures described elsewhere.[5]

Table I. Electronic Spectra

compd		abs max,[a,b] cm^{-1} (ϵ_M for soln)
$FeCl_2(dppen)_2$ (form I)	a	9750, 13 900, 23 800 sh
$FeCl_2(dppen)_2$ (form II)	a	9250, 13 000
$FeBr_2(dppen)_2$	a	9200, 11 600
$FeCl_2(dppen)_2{\cdot}2(CH_3)_2CO$	a	10 100, 13 250
	b	14 400, 21 700 sh
$FeCl_2(dppen)_2{\cdot}2CH_2Cl_2$	a	10 000, 13 250
	b	14 300, 21 700 sh
$FeCl_2(dppen)_2{\cdot}CHCl_3$	a	10 000, 13 250
	b	14 400, 21 700 sh
$FeBr_2(dppen)_2{\cdot}2(CH_3)_2CO$	a	9700, 11 600
	b	13 900, 21 100
$[FeI(dppen)_2]BPh_4$[c]	a	6700, 10 300, 19 000
	c	7000 (70), 10 100 (40), 15 200 sh, 20 000 sh

[a] Key: a, solid (295 K); b, solid (100 K); c, 1,2-dichloroethane solution. [b] The 100 K reflectance spectra of $FeCl_2(dppen)_2$ and $FeBr_2(dppen)_2$ are identical, except for a blue shift of bands, to those recorded at 295 K; see ref 2 for the absorption spectra of these compounds. [c] The compound undergoes decomposition in solution.

Table II. Summary of Crystal Data, Intensity Collection, and Structure Refinement for $FeCl_2(dppen)_2$[a] (**1**) and $FeCl_2(dppen)_2{\cdot}2(CH_3)_2CO$[b] (**2**)

	1	2
formula	$C_{52}H_{44}Cl_2Fe_1P_4$	$C_{58}H_{56}Cl_2Fe_1O_2P_4$
fw	919.58	1035.74
space group	$P2_1/n$	$P2_1/a$
a, Å	16.086 (6)	17.867 (4)
b, Å	13.189 (6)	13.089 (4)
c, Å	10.840 (5)	11.519 (3)
β, deg	90.42 (5)	93.30 (3)
V, Å	2299.7	2689.4
Z	2	2
density, g cm^{-3}	1.328 (calcd), 1.31 (obsd)	1.279 (calcd), 1.25 (obsd)
temp, °C	22	22
cryst size, mm	0.3 × 0.3 × 0.1	0.4 × 0.4 × 0.5
μ(Mo Kα), cm^{-1}	6.15	5.36
transmission factors	0.86–0.94	0.77–0.97
scan speed, deg/min	4.8	5.0
scan range	$(1.1 + 0.3 \tan \theta)°$	$(1.1 + 0.3 \tan \theta)°$
bkgd[c]	$t_{b_1} = t_{b_2} = {}^1/_2 t_s$	$t_{b_1} = t_{b_2} = {}^1/_2 t_s$
2θ limits, deg	4–50	4–50
no. of unique data ($F_o^2 > 3\sigma(F_o^2)$)	2503	2346
no. of variables	269	276
R	0.037	0.057
R_w	0.037	0.054

[a] Form I of compound **1**. Form II crystallizes in space group $P\bar{1}$ with $a = 11.98$ Å, $b = 11.52$ Å, $c = 10.34$ Å, $\alpha = 119.2°$, $\beta = 98.3°$, $\gamma = 106.9°$, and $Z = 1$. The compound $FeBr_2(dppen)_2$ is isomorphous to form II of the chloride (see footnote 25 in ref 1). All solvated compounds are isomorphous to **2**. [b] 295 K structure; high-spin isomorph of compound **2**. [c] t_{b_1} and t_{b_2} are background count times; t_s is the total scan time.

The electronic spectral data are reported in Table I.

Collection and Reduction of X-ray Data. Diffraction data were collected for one of the polymorphic modifications (form I) of the compound $FeCl_2(dppen)_2$ (**1**) at 295 K and for the compound $FeCl_2(dppen)_2{\cdot}2(CH_3)_2CO$ (**2**) at 295 and 130 K on a Philips PW 1100 automated diffractomer using graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). At the temperatures of 295 and 130 K compound **2** may be considered to be completely in the high-spin and, respectively, in the low-spin state. Details on crystal data (including data for isomorphs), on the intensity collections performed at room temperature, and on the refinements of the room-temperature structures of compounds **1** and **2** are reported in Table II. Lattice constants were determined by least-squares refinement of the angular positions of 24 reflections for both compounds. The intensities of three standard reflections measured every 100 min showed no systematic

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Table III. Atomic Parameters for the Structure of $FeCl_2(dppen)_2$[a]

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe	0	0	0	0.0348 (4)	0.0389 (4)	0.0337 (4)	−0.0024 (4)	0.0028 (3)	−0.0019 (3)
Cl	−0.0783 (1)	−0.0086 (1)	0.1815 (1)	0.0401 (4)	0.0625 (6)	0.0364 (4)	−0.0019 (5)	0.0055 (4)	0.0002 (5)
P1	0.1486 (1)	0.0034 (1)	0.1124 (1)	0.0309 (4)	0.0423 (5)	0.0380 (5)	−0.0004 (5)	−0.0003 (4)	−0.0009 (5)
P2	0.0264 (1)	0.1884 (1)	0.0223 (1)	0.0390 (5)	0.0378 (5)	0.0367 (5)	−0.0017 (4)	−0.0032 (4)	−0.0002 (4)
C1	0.1875 (2)	0.1307 (3)	0.0787 (3)	0.035 (2)	0.047 (2)	0.048 (2)	−0.002 (2)	−0.001 (2)	−0.004 (2)
C2	0.1380 (2)	0.2058 (3)	0.0442 (3)	0.042 (2)	0.039 (2)	0.049 (2)	−0.001 (2)	−0.003 (2)	−0.005 (2)
C11	0.2269 (2)	−0.0800 (3)	0.0454 (3)	0.031 (2)	0.048 (2)	0.039 (2)	−0.003 (2)	−0.004 (2)	0.000 (2)
C12	0.2633 (2)	−0.0556 (3)	−0.0671 (3)	0.035 (2)	0.063 (3)	0.051 (2)	0.004 (2)	0.005 (2)	0.000 (2)
C13	0.3151 (2)	−0.1262 (4)	−0.1252 (4)	0.044 (2)	0.093 (4)	0.059 (3)	−0.003 (3)	0.014 (2)	0.002 (2)
C14	0.3301 (2)	−0.2197 (4)	−0.0726 (5)	0.044 (3)	0.080 (3)	0.078 (3)	−0.026 (3)	−0.001 (2)	0.019 (2)
C15	0.2950 (2)	−0.2433 (3)	0.0386 (4)	0.045 (2)	0.055 (3)	0.072 (3)	−0.009 (2)	−0.014 (2)	0.011 (2)
C16	0.2433 (2)	−0.1746 (3)	0.0977 (3)	0.039 (2)	0.051 (2)	0.049 (2)	0.001 (2)	−0.005 (2)	0.004 (2)
C21	0.1730 (2)	−0.0052 (3)	0.2779 (3)	0.039 (2)	0.041 (2)	0.040 (2)	−0.004 (2)	−0.004 (2)	0.001 (2)
C22	0.2547 (2)	−0.0049 (3)	0.3222 (3)	0.044 (2)	0.072 (3)	0.054 (2)	−0.006 (3)	−0.008 (2)	0.007 (2)
C23	0.2704 (3)	−0.0113 (4)	0.4482 (4)	0.059 (3)	0.085 (3)	0.061 (3)	−0.009 (3)	−0.025 (2)	0.018 (3)
C24	0.2067 (3)	−0.0193 (3)	0.5306 (4)	0.086 (3)	0.082 (3)	0.042 (2)	−0.004 (2)	−0.015 (2)	0.009 (3)
C25	0.1264 (3)	−0.0181 (4)	0.4876 (4)	0.070 (3)	0.106 (4)	0.039 (2)	−0.005 (3)	0.002 (2)	−0.013 (3)
C26	0.1091 (2)	−0.0100 (3)	0.3626 (3)	0.047 (2)	0.079 (3)	0.043 (2)	−0.010 (2)	0.002 (2)	−0.009 (2)
C31	0.0020 (2)	0.2766 (3)	−0.1029 (3)	0.035 (2)	0.042 (2)	0.039 (2)	0.001 (2)	0.003 (2)	0.003 (2)
C32	0.0164 (2)	0.3812 (3)	−0.0940 (3)	0.057 (2)	0.047 (2)	0.044 (2)	0.001 (2)	0.000 (2)	−0.001 (2)
C33	−0.0051 (3)	0.4450 (3)	−0.1909 (4)	0.072 (3)	0.041 (2)	0.059 (3)	0.005 (2)	0.011 (2)	0.003 (2)
C34	−0.0412 (3)	0.4062 (3)	−0.2963 (4)	0.064 (3)	0.062 (3)	0.046 (2)	0.015 (2)	0.008 (2)	0.012 (2)
C35	−0.0560 (3)	0.3040 (3)	−0.3065 (3)	0.069 (3)	0.066 (3)	0.040 (2)	0.005 (2)	−0.003 (3)	−0.003 (2)
C36	−0.0338 (2)	0.2398 (3)	−0.2106 (3)	0.054 (2)	0.049 (2)	0.042 (2)	0.001 (2)	−0.001 (2)	−0.008 (2)
C41	−0.0182 (2)	0.2533 (2)	0.1552 (3)	0.043 (2)	0.032 (2)	0.036 (2)	−0.003 (2)	−0.002 (2)	0.001 (2)
C42	0.0269 (2)	0.2719 (3)	0.2619 (3)	0.056 (2)	0.063 (3)	0.042 (2)	−0.004 (2)	−0.009 (2)	0.020 (2)
C43	−0.0118 (3)	0.3154 (4)	0.3628 (3)	0.082 (3)	0.084 (3)	0.037 (2)	−0.005 (2)	−0.013 (2)	0.024 (3)
C44	−0.0949 (3)	0.3392 (3)	0.3583 (3)	0.074 (3)	0.078 (3)	0.039 (2)	−0.004 (2)	0.008 (2)	0.027 (2)
C45	−0.1401 (2)	0.3208 (3)	0.2533 (4)	0.053 (2)	0.075 (3)	0.062 (3)	−0.016 (2)	0.002 (2)	0.013 (2)
C46	−0.1018 (2)	0.2772 (3)	0.1517 (4)	0.047 (2)	0.069 (3)	0.055 (2)	−0.019 (2)	−0.005 (2)	0.002 (2)

[a] Standard deviations on the last significant digits are in parentheses. Anisotropic temperature factors of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + ... + 2U_{12}hka^*b^* + ...)]$.

trend for **1** and an overall linear decrease of ca. 6% for **2**; there were small oscillations (≤2%) superimposed on such trends. Data sets were rescaled and processed with use of values of 0.03 (**1**) and 0.05 (**2**) for p in the calculation of the $\sigma(I)$'s.[6] Corrections for absorption were applied, with use of the SHELX 76 system of computer programs. The principal computer programs used in the crystallographic calculations are listed in ref 7.

Data sets for the low-spin isomer of compound **2** were collected with the apparatus and following procedures previously described.[8] Crystals of the compound were coated with paraffin in order to prevent them from cracking under the cold gas flow. The dimensions of the unit cell undergo large and anisotropic variations in the course of the spin transition. The cell volume changes by ca. 8% between 295 and 130 K. The intensities of many reflections vary dramatically in such a temperature interval. Although data sets collected at 130 K with different crystals were essentially consistent with each other,significant differences in the intensites of some reflections were observed. The diffraction pattern of the material at 130 K was not rigorously consistent with either the symmetry requirements of the Laue group $P2/m$ or the systematic absences of the space group $P2_1/a$. The starting crystalline material could not be reversibly obtained by slowly warming to room temperature the crystals which had been cooled for long periods at 130 K. In spite of the poor quality of the low-temperature data, these were processed in an attempt to obtain from them all possible informations about the structure, in view of the fact that very few structural investigations have been reported until now on systems undergoing singlet $\rightleftharpoons$ quintet spin transitions.[9-11] Moreover, previous studies have generally been performed on iron(II) complexes having six nitrogen donor atoms. The lattice constants, determined from the angular settings of 22 reflections measured at 130 K on the crystal used for data collection, were a = 17.02 (2) Å b = 13.02 (2) Å, c = 11.28 (2) Å, β = 94.3 (1)° ($\alpha = \gamma = 90°$ within experimental error, V = 2492 Å^3). Monochromatized Mo Kα radiation was used throughout (λ = 0.7107 Å). The crystal used for data collection had approximate dimensions of 0.40 × 0.30 × 0.20 mm. No correction for absorption was applied in view of the poor quality of the data. Intensities for reflections $\pm h,\pm k,+l$ were measured in the range $4° \leq 2\theta \leq 32°$ by the θ–2θ scan technique with a fixed scan range of 0.90° and a scan speed of 9.0°/min in 2θ. Background measurements were performed as in the room-temperature data collections. The intensities of three standard reflections, monitored every 60 min, showed some oscillations about their average values in the course of data collection. Of the 3575 reflections measured in a hemisphere, 1922 having $I \geq 3\sigma(I)$ were considered observed. After the intensities of equivalent reflections were averaged with assumption that the correct space group was the $P2_1/a$, the number of independent observed reflections reduced to 1182.

Solution and Refinement of the Structures. The positions of nonhydrogen atoms in the room-temperature structures of compounds **1** and **2** were determined by Patterson and Fourier syntheses. The iron atom lies on an inversion center in both structures, so that the $FeCl_2(dppen)_2$ molecule has C_i crystallographic symmetry in both solids. In the full-matrix least-squares refinement anisotropic temperature factors were used for all nonhydrogen atoms. The hydrogen atoms of the ligand molecule were introduced in calculated positions (C–H = 1.00 Å), each one being applied a temperature factor close to that of the respective carbon atom, and their fixed contribution was added to the F_c. The acetone molecule, which occupies a general position in the structure of **2**, was refined as a rigid group with idealized geometry (C–C = 1.55 Å, C–O = 1.24 Å, C–C–C = C–C–O = 120°), and an overall temperature factor was applied. 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 atomic scattering factors were taken from ref 12, and anomalous dispersion terms for the metal atoms were included

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Table IV. Atomic Parameters for the Structure of $FeCl_2(dppen)_2 \cdot 2(CH_3)_2CO$[a,b] (295 K)

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe	0	0	0	0.037 (1)	0.058 (1)	0.039 (1)	0.005 (1)	0.010 (1)	0.000 (1)
Cl	−0.0546 (1)	−0.0658 (1)	0.1664 (1)	0.046 (1)	0.075 (1)	0.043 (1)	0.010 (1)	0.014 (1)	−0.002 (1)
P1	0.1206 (1)	−0.1104 (1)	0.0154 (2)	0.043 (1)	0.062 (1)	0.048 (1)	0.006 (1)	0.011 (1)	0.008 (1)
P2	0.0916 (1)	0.1136 (1)	0.1232 (2)	0.043 (1)	0.058 (1)	0.046 (1)	0.006 (1)	0.007 (1)	−0.003 (1)
C1	0.1957 (3)	−0.0167 (6)	0.0365 (6)	0.039 (3)	0.068 (5)	0.062 (5)	0.007 (4)	0.011 (3)	0.009 (3)
C2	0.1846 (3)	0.0723 (6)	0.0822 (6)	0.041 (4)	0.072 (5)	0.057 (5)	0.015 (4)	0.003 (3)	−0.004 (3)
C11	0.1411 (4)	−0.1802 (6)	−0.1167 (6)	0.054 (4)	0.074 (5)	0.047 (4)	0.007 (4)	0.013 (4)	0.024 (4)
C12	0.1822 (4)	−0.1374 (7)	−0.2020 (8)	0.090 (6)	0.102 (7)	0.075 (6)	−0.002 (5)	0.034 (5)	0.004 (5)
C13	0.1899 (6)	−0.1954 (10)	−0.3049 (9)	0.122 (8)	0.151 (10)	0.071 (7)	0.015 (7)	0.046 (6)	0.043 (8)
C14	0.1576 (6)	−0.2912 (9)	−0.3174 (9)	0.126 (9)	0.122 (9)	0.075 (7)	−0.031 (7)	−0.014 (6)	0.049 (7)
C15	0.1180 (6)	−0.3296 (7)	−0.2355 (8)	0.129 (8)	0.087 (7)	0.062 (6)	−0.014 (6)	0.009 (6)	0.018 (6)
C16	0.1088 (4)	−0.2760 (6)	−0.1348 (7)	0.080 (5)	0.068 (6)	0.076 (6)	−0.003 (5)	0.003 (4)	0.008 (4)
C21	0.1514 (4)	−0.2020 (5)	0.1291 (6)	0.052 (4)	0.066 (5)	0.051 (4)	0.007 (4)	0.003 (3)	0.004 (4)
C22	0.1108 (4)	−0.2131 (7)	0.2269 (7)	0.062 (5)	0.120 (7)	0.062 (5)	0.034 (5)	0.008 (4)	0.018 (5)
C23	0.1358 (5)	−0.2801 (8)	0.3129 (8)	0.088 (6)	0.142 (9)	0.089 (7)	0.057 (7)	0.010 (5)	0.012 (6)
C24	0.2000 (5)	−0.3363 (7)	0.3018 (9)	0.089 (6)	0.095 (7)	0.107 (8)	0.032 (6)	−0.008 (6)	0.020 (5)
C25	0.2396 (5)	−0.3255 (7)	0.2065 (9)	0.081 (6)	0.079 (6)	0.101 (7)	−0.002 (6)	−0.007 (6)	0.029 (5)
C26	0.2163 (4)	−0.2597 (6)	0.1214 (7)	0.070 (5)	0.077 (5)	0.065 (5)	−0.001 (4)	0.005 (4)	0.026 (4)
C31	0.0960 (4)	0.2532 (5)	0.1062 (7)	0.052 (4)	0.056 (4)	0.071 (5)	0.014 (4)	0.009 (4)	0.002 (4)
C32	0.1108 (5)	0.3183 (7)	0.1982 (8)	0.146 (8)	0.067 (6)	0.088 (7)	0.012 (6)	−0.023 (6)	−0.026 (6)
C33	0.1117 (6)	0.4225 (7)	0.1808 (11)	0.151 (10)	0.059 (6)	0.135 (10)	0.003 (6)	−0.007 (8)	−0.031 (6)
C34	0.0987 (5)	0.4637 (7)	0.0755 (12)	0.093 (6)	0.063 (6)	0.146 (10)	0.038 (7)	0.025 (7)	−0.004 (5)
C35	0.0833 (6)	0.4004 (8)	−0.0134 (9)	0.142 (9)	0.077 (7)	0.088 (7)	0.029 (6)	0.024 (7)	0.014 (6)
C36	0.0825 (4)	0.2956 (7)	0.0000 (7)	0.105 (6)	0.069 (6)	0.072 (6)	0.016 (5)	0.009 (5)	0.010 (5)
C41	0.0974 (4)	0.0967 (5)	0.2806 (6)	0.065 (4)	0.051 (4)	0.046 (4)	0.001 (3)	−0.001 (4)	−0.009 (3)
C42	0.1594 (4)	0.0565 (6)	0.3421 (7)	0.073 (5)	0.080 (5)	0.056 (5)	0.012 (4)	−0.009 (4)	−0.017 (4)
C43	0.1613 (6)	0.0444 (8)	0.4603 (8)	0.110 (7)	0.135 (8)	0.052 (6)	0.017 (6)	−0.017 (5)	−0.016 (6)
C44	0.1002 (7)	0.0730 (8)	0.5190 (7)	0.138 (9)	0.124 (8)	0.047 (5)	0.003 (5)	0.001 (6)	−0.050 (7)
C45	0.0369 (5)	0.1109 (7)	0.4612 (8)	0.109 (7)	0.103 (7)	0.068 (6)	−0.013 (6)	0.032 (6)	−0.034 (6)
C46	0.0341 (4)	0.1234 (6)	0.3415 (7)	0.075 (5)	0.084 (5)	0.061 (5)	−0.002 (4)	0.018 (4)	−0.007 (4)
C4	0.1186 (5)	0.4055 (8)	0.5719 (8)	0.295 (4)					
C5	0.1808 (5)	0.3430 (8)	0.6389 (8)	0.295 (4)					
C6	0.0358 (5)	0.3705 (8)	0.5724 (8)	0.295 (4)					
O	0.1351 (5)	0.4835 (8)	0.5179 (8)	0.295 (4)					

[a] Standard deviations on the last significant digits are 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 $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$. [b] Atoms C4–O belong to the acetone molecule.

in F_c.[13] The final values of the discrepancy indices, defined by $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$ are shown in Table II. The final ΔF Fourier of compound **1** was essentially featureless. A late ΔF Fourier calculated for compound **2** showed one peak with height 0.8 e Å^{-3} and few lower peaks (<0.4 e Å^{-3}), all in the region occupied by the solvent molecule. The final positional and thermal parameters of the nonhydrogen atoms in the room-temperature structures of **1** and **2** are listed in Tables III and IV, respectively. Refinement of the structure of the low-spin isomer of compound **2** was undertaken both in the space group $P2_1/a$, which is that of the solid at room temperature, and in the lower symmetry space group $P\bar{1}$. The latter refinement, however, was not completed due to difficulties caused by correlations between parameters. Owing to the small number of data, a simpler model than that used for the high-spin isomer had to be adopted for the low-spin one. Phenyl groups were refined as rigid bodies with idealized geometry, their carbon atoms being applied independent isotropic temperature factors Hydrogen atom contributions were calculated as described above for the high-spin isomer. Since inspection of ΔF maps clearly showed that in the solid at 130 K the acetone molecule was almost equally distributed between two different orientations, two rigid groups were considered for the model of the solvent. Both had the idealized geometry used for the acetone model in the room-temperature structure, and their central carbon atoms were constrained to occupy the same position. An overall temperature factor was applied, and the population parameters of the two orientations were refined. In the final refinement the following sets of thermal parameters were tested for the metal and ligand atoms: (a) individual isotropic (final R value ca. 0.20); (b) individual anisotropic ($R = 0.140$; the temperature factors of two ligand atoms tended to become negative); (c) overall anisotropic (i.e., identical anisotropic factors for all atoms in the coordination polyhedron; $R = 0.144$). Model c was considered because the thermal ellipsoids from refinement b were found to be all extremely elongated and essentially parallel to each other (their shape was evidently due to effects of stored strain in the lattice rather than to effects of thermal motion). Since model c led to an R value comparable to that of model b with less parameters, it was considered to be better than the latter, so the results from refinement c are reported here (Table V). However it has to be stressed that the positional parameters from the three refinements (a–c) agree with each other within 3σ. The results of this structural investigation are admittedly inaccurate according to the usual standards and the esd's on the parameters are probably underestimated due to systematic errors in the data. However, there are indications (successful refinement of the disordered solvent molecule; reasonable values of nongroup bond distances and angles in the ligand molecule) that the low-temperature data do provide meaningful informations about the structure. We are confident that the positions of the heaviest atoms, which are the results of importance to the present study, should have been derived with sufficient accuracy to the purpose of the analysis performed in this paper and in the accompanying one.[1] Listings of the structure factor amplitudes for the room-temperature and low-temperature structure determinations are available.[14]

Results and Discussion

The stabilities as well as the solubilities of the compounds with formula $FeX_2(dppen)_2 \cdot nS$ (X = Cl, S = $(CH_3)_2CO$, CH_2Cl_2, $CHCl_3$; X = Br, S = $(CH_3)_2CO$) are essentially similar to those of the unsolvated compounds previously reported.[2] The chloro derivatives containing solvent molecules in the lattice are paramagnetic at room temperature, with μ_{eff} values corresponding to the quintet ground state. On lowering the temperature, their magnetic moments decrease abruptly within few degrees, in the 230–190 K range (see Figure 1), reaching values typical of the iron(II) complexes in the singlet ground state. The molar susceptibility values measured for

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(13) Reference 12, p 148 ff.

(14) Supplementary material.

Table V. Atomic Parameters for the Structure of $FeCl_2(dppen)_2 \cdot 2(CH_3)_2CO$[a,b] (130 K)

atom	*x/a*	*y/b*	*z/c*	*U*, Å^2
Fe	0.0	0.0	0.0	*c*
Cl	−0.0569 (4)	−0.0595 (7)	0.1684 (6)	*c*
P1	0.1075 (4)	−0.1088 (8)	0.0064 (7)	*c*
P2	0.0872 (4)	0.1017 (9)	0.1112 (7)	*c*
C1	0.193 (2)	−0.028 (2)	0.032 (2)	0.011 (7)
C2	0.187 (2)	0.075 (2)	0.078 (2)	0.029 (8)
C11	0.127 (1)	−0.188 (1)	−0.128 (2)	0.031 (9)
C12	0.168 (1)	−0.144 (1)	−0.218 (2)	0.034 (9)
C13	0.183 (1)	−0.202 (1)	−0.319 (2)	0.036 (9)
C14	0.157 (1)	−0.303 (1)	−0.329 (2)	0.041 (9)
C15	0.116 (1)	−0.347 (1)	−0.239 (2)	0.038 (9)
C16	0.101 (1)	−0.289 (1)	−0.139 (2)	0.036 (9)
C21	0.140 (1)	−0.202 (2)	0.125 (2)	0.034 (9)
C22	0.103 (1)	−0.206 (2)	0.232 (2)	0.070 (12)
C23	0.132 (1)	−0.272 (2)	0.322 (2)	0.085 (14)
C24	0.197 (1)	−0.333 (2)	0.306 (2)	0.061 (11)
C25	0.234 (1)	−0.329 (2)	0.200 (2)	0.041 (10)
C26	0.205 (1)	−0.263 (2)	0.109 (2)	0.053 (11)
C31	0.091 (1)	0.239 (2)	0.092 (1)	0.022 (8)
C32	0.114 (1)	0.303 (2)	0.188 (1)	0.043 (10)
C33	0.118 (1)	0.409 (2)	0.172 (1)	0.058 (11)
C34	0.098 (1)	0.451 (2)	0.060 (1)	0.056 (11)
C35	0.075 (1)	0.387 (2)	−0.036 (1)	0.037 (9)
C36	0.071 (1)	0.281 (2)	−0.019 (1)	0.030 (9)
C41	0.095 (1)	0.088 (1)	0.275 (1)	0.027 (8)
C42	0.161 (1)	0.043 (1)	0.334 (1)	0.032 (9)
C43	0.165 (1)	0.033 (1)	0.458 (1)	0.031 (9)
C44	0.103 (1)	0.068 (1)	0.522 (1)	0.029 (8)
C45	0.037 (1)	0.113 (1)	0.462 (1)	0.023 (8)
C46	0.033 (1)	0.123 (1)	0.339 (1)	0.034 (9)
C4	0.393 (2)	0.902 (2)	0.447 (2)	0.099 (9)
C51	0.369 (3)	0.833 (4)	0.338 (4)	0.099 (9)
C52	0.346 (3)	0.804 (3)	0.407 (8)	0.099 (9)
C61	0.456 (3)	0.864 (4)	0.543 (4)	0.099 (9)
C62	0.484 (2)	0.901 (4)	0.450 (8)	0.099 (9)
O1	0.357 (2)	0.984 (3)	0.461 (4)	0.099 (9)
O2	0.360 (4)	0.961 (5)	0.514 (6)	0.099 (9)

[a] Standard deviations on the last significant digits are 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 $\exp[-2\pi^2 (U_{11}h^2a^{*2} + ... + 2U_{12}hka^*b^* + ...)]$. [b] Atoms C4–O2 belong to the acetone molecule: the population parameters are 1.00 for C4, 0.58 for C51, C61, and O1, and 0.42 for C52, C62, and O2. [c] The anisotropic temperature factor components (Å^2), which are identical for all heavy atoms (see text), are $U_{11} = 0.010$ (4), $U_{22} = 0.110$ (4), $U_{33} = 0.017$ (2), $U_{23} = 0.025$ (3), $U_{13} = 0.010$ (1), and $U_{12} = 0.012$ (3).

all of the compounds over the temperature range investigated are listed in Table VI. The reflectance spectra of the solvated compounds vary gradually in the course of the spin transition: the intensities of the bands at ca. 10 000 and 13 000 cm^{-1}, which are typical of the d^6 high-spin chromophores with tetragonal symmetry,[15] decrease with decreasing temperature, whereas the intensites of the bands at higher frequencies (ca. 14 000 and 22 000 cm^{-1}), characteristic of the low-spin species,[15] gradually increase (Figure 2 and Table I). At sufficiently high (low) temperatures only the spectral features of the high (low) spin species are evident.

The first polymorph, form I, of the unsolvated $FeCl_2(dppen)_2$ complex is in the quintet state even at temperatures lower than 190 K; only at ca. 120 K does its magnetic moment begin to decrease (Figure 1). The second polymorph, form II, maintains the quintet ground state throughout the temperature range investigated. Neither of the above magnetic behaviors agrees with that reported for the same compound by the previous authors,[2] who found that the magnetic moment varied smoothly with temperature and lay slightly below the high-spin values even at room temperature. Such differences in the magnetic properties between different crystalline forms or even different samples of a compound which is at the verge of a magnetic crossover are not unusual. No bands of the low-spin species could be observed in the spectra recorded at 100 K on our samples of this compound. On the other hand, the magnetic behavior of the unsolvated bromide $FeBr_2(dppen)_2$, which is high spin from room temperature down to 90 K, matches that previously reported.[2] The magnetic moment of the solvated bromide $FeBr_2(dppen)_2 \cdot 2(CH_3)_2CO$ varies with the temperature essentially as does that of the corresponding chloride, but in the low-temperature range it plateaus at relatively high values (Figure 1). This may be rationalized with assumption that a fraction of the high-spin isomer is frozen in the lattice.[16]

The iodo derivative $[FeI(dppen)_2]BPh_4$ decomposes rapidly at the air. It is soluble in polar organic solvents like acetone and 1,2-dichloroethane, in which it behaves as a 1:1 electrolyte. The value of its magnetic moment, 3.30 μ_B, corresponds to the triplet ground state, and it does not change significantly on lowering the temperature down to 90 K. It is reasonable to

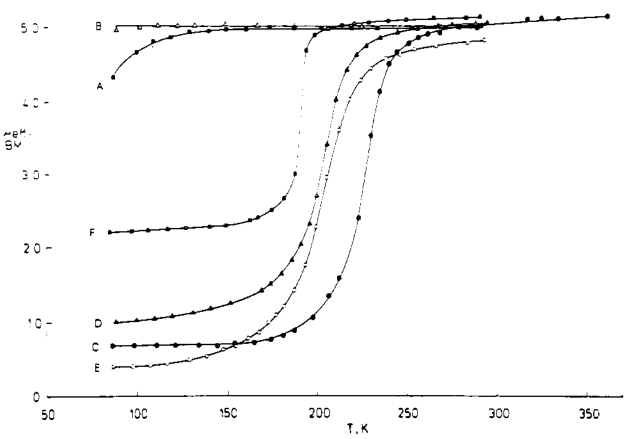

Figure 1. Temperature dependence of the effective magnetic moment, μ_{eff}: A, $FeCl_2(dppen)_2$ (form I); B, $FeCl_2(dppen)_2$ (form II); C, $FeCl_2(dppen)_2 \cdot 2(CH_3)_2CO$; D, $FeCl_2(dppen)_2 \cdot 2CH_2Cl_2$; E, $FeCl_2(dppen)_2 \cdot CHCl_3$; F, $FeBr_2(dppen)_2 \cdot 2(CH_3)_2CO$.

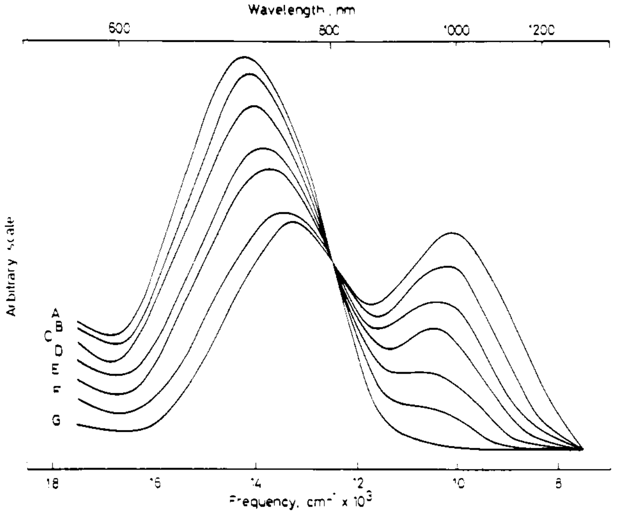

Figure 2. Reflectance spectrum of $FeCl_2(dppen)_2 \cdot 2(CH_3)_2CO$ in the 8000–18 000-cm^{-1} region, at different temperatures; A, 200 K; B, 215 K; C, 221 K; D, 226 K; E, 231 K; F, 250 K; G, 290 K.

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Table VI. Magnetic Susceptibility Data[a] and Effective Magnetic Moment Values[b] for the Compounds

T, K	$10^6\chi_M^{cor}$, cgs/mol	μ_{eff}, μ_B	T, K	$10^6\chi_M^{cor}$, cgs/mol	μ_{eff}, μ_B
(a) $FeCl_2(dppen)_2$ (form I)					
87	27 036	4.34	174	17 765	4.97
100	27 239	4.67	188	16 495	4.98
109	26 338	4.79	203	15 200	4.97
119	24 783	4.86	219	14 128	4.97
130	23 281	4.92	233	13 291	4.98
140	21 897	4.95	253	12 178	4.96
150	20 557	4.96	289	10 644	4.96
161	19 139	4.96			
(b) $FeCl_2(dppen)_2$ (form II)					
89	34 201	4.93	167	18 896	5.02
102	30 665	5.00	188	16 624	5.00
112	28 348	5.04	225	13 878	5.00
123	25 812	5.04	268	11 549	4.97
132	24 101	5.04	291	10 539	4.96
149	21 266	5.03			
(c) $FeCl_2(dppen)_2 \cdot 2(CH_3)_2CO$					
86	685	0.69	230	6 823	3.54
98	644	0.71	235	9 131	4.14
111	540	0.69	240	10 580	4.51
121	499	0.69	244.5	11 056	4.65
134	439	0.69	251	11 408	4.78
144	405	0.68	256	11 501	4.85
154	416	0.71	261.5	11 491	4.90
165	417	0.74	268.5	11 377	4.94
174	431	0.77	278	11 201	4.99
181	483	0.84	286	10 952	5.00
187	541	0.90	293	10 870	5.05
198.5	652	1.02	317	10 207	5.09
206.5	1 120	1.36	324.5	9 959	5.08
211.5	1 493	1.59	335	9 700	5.10
217	2 051	1.89	347	9 379	5.10
223	3 252	2.41	362	9 007	5.11
(d) $FeCl_2(dppen)_2 \cdot 2CH_2Cl_2$					
88	1 400	0.99	200	4 514	2.69
99	1 356	1.04	206	6 986	3.39
109	1 291	1.06	210	9 578	4.01
119	1 193	1.07	216.5	11 364	4.44
130	1 258	1.14	221.5	12 061	4.62
140	1 247	1.18	227	12 431	4.75
151	1 280	1.24	235	12 584	4.86
161	1 356	1.32	245	12 410	4.93
169	1 526	1.44	257	12 083	4.98
174	1 628	1.50	267	11 745	5.01
180	1 876	1.64	275	11 440	5.02
186	2 227	1.82	288	10 928	5.02
191	2 685	2.02	294	10 765	5.03
195.5	3 360	2.29			
(e) $FeCl_2(dppen)_2 \cdot CHCl_3$					
86	284	0.44	193	1 993	1.75
97	215	0.41	199	3 219	2.26
107	191	0.40	205	5 328	2.95
116	238	0.47	212	7 676	3.61
128	238	0.49	218	9 303	4.03
138	253	0.53	224	10 238	4.28
147	342	0.63	230	10 727	4.44
154	371	0.68	238	10 971	4.57
161	488	0.79	246	10 970	4.64
168	552	0.86	254	10 866	4.70
173	732	1.01	266	10 535	4.73
177	842	1.09	284	10 048	4.78
182	1 007	1.21	293	9 860	4.81
187	1 354	1.42			
(f) $FeBr_2(dppen)_2 \cdot 2(CH_3)_2CO$					
85	7 127	2.20	194	14 264	4.70
97	6 565	2.26	198.5	15 006	4.88
106	5 935	2.24	206	14 950	4.96
117	5 374	2.24	214	14 703	5.02
127	5 059	2.27	221	14 433	5.05
140	4 677	2.29	229	13 983	5.06
149	4 407	2.29	240	13 432	5.08
163	4 272	2.36	250	12 938	5.09
167	4 250	2.38	265	12 253	5.10
175	4 486	2.51	283	11 612	5.12
182	4 890	2.67	291	11 196	5.10
188	5 947	2.99			

[a] Molecular weights and (diamagnetic corrections ($\times 10^{-6}$ cgs/mol)): (a) 919.58 (−599); (b) 919.58 (−599); (c) 1035.74 (−644); (d) 1089.45 (−703); (e) 1038.96 (−668); (f) 1124.65 (−698). [b] $\mu_{eff} = 2.828(\chi_M^{cor}T)^{1/2}$.

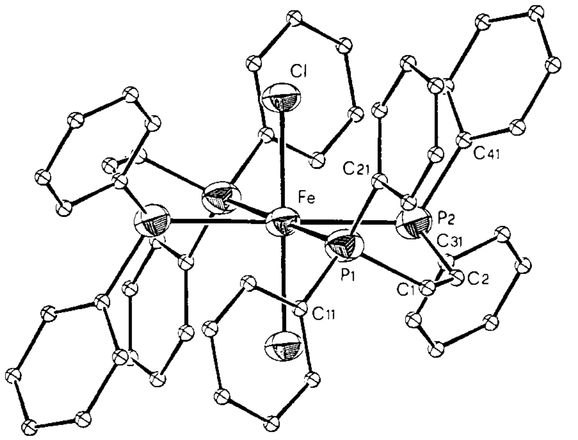

Figure 3. Perspective view of the $FeCl_2(dppen)_2$ molecule.

assume that this compound, whose structure could not be investigated as no suitable crystals were obtained, has the same five-coordinate geometry with the P_4I donor set that has been previously assigned to its nickel analogue.[17]

The structure of the compound $FeCl_2(dppen)_2$ consists of isolated molecules of the above formula. That of the compound $FeCl_2(dppen)_2 \cdot 2(CH_3)_2CO$, which has a different packing, contains in addition acetone molecules of crystallization. The metal atom in the $FeCl_2(dppen)_2$ molecule is coordinated by two chlorine atoms and by the four phosphorus atoms of the two dppen ligands, with trans-octahedral geometry, as had been anticipated.[2] The molecule of the complex has crystallographic C_i symmetry in both structures, so that the metal atom lies rigorously in the plane of the four phosphorus atoms. The Fe–Cl bond forms an angle of ca. 7° with the normal to the above plane. Figure 3 shows a perspective

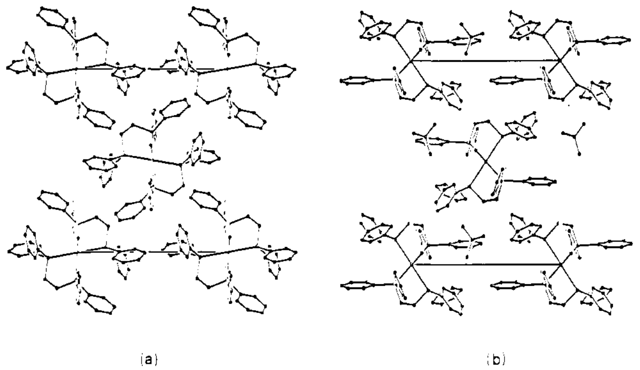

Figure 4. Unit cell of (a) $FeCl_2(dppen)_2$ and (b) $FeCl_2(dppen)_2 \cdot 2(CH_3)_2CO_2$ viewed along the *c* axis.

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(17) McAuliffe, C. A.; Meek, D. W. *Inorg. Chem.* **1969**, *8*, 904.

Table VII. Selected Bond Lengths (Å) and Angles (Deg) for the Structures of $FeCl_2(dppen)_2$ (**1**) and $FeCl_2(dppen)_2 \cdot 2(CH_3)_2CO$ (**2**)

atoms	**1**	**2** (295 K)	**2** (130 K)
Fe–Cl	2.347 (1)	2.363 (2)	2.329 (6)
Fe–P1	2.675 (1)	2.592 (2)	2.312 (8)
Fe–P2	2.532 (1)	2.576 (2)	2.289 (9)
P1–C1	1.830 (4)	1.823 (7)	1.80 (3)
P1–C11	1.828 (3)	1.831 (7)	1.88 (2)
P1–C21	1.837 (3)	1.836 (7)	1.86 (2)
P2–C2	1.824 (4)	1.834 (7)	1.79 (3)
P2–C31	1.828 (4)	1.840 (7)	1.80 (2)
P2–C41	1.827 (3)	1.823 (7)	1.85 (2)
C1–C2	1.324 (5)	1.299 (10)	1.45 (4)
Cl–Fe–P1	95.9 (1)	97.0 (1)	98.4 (3)
Cl–Fe–P2	93.3 (1)	92.4 (1)	92.1 (3)
P1–Fe–P2	78.0 (1)	77.6 (1)	81.8 (3)
Fe–P1–C1	103.3 (1)	103.7 (2)	106.0 (10)
Fe–P1–C11	115.2 (1)	115.3 (2)	119.8 (10)
Fe–P1–C21	128.9 (1)	128.8 (2)	127.7 (11)
C1–P1–C11	103.6 (2)	105.4 (3)	104.7 (10)
C1–P1–C21	100.4 (2)	99.0 (3)	94.4 (11)
C11–P1–C21	102.0 (2)	101.6 (3)	99.5 (9)
Fe–P2–C2	107.5 (1)	104.1 (2)	110.9 (10)
Fe–P2–C31	121.3 (1)	122.9 (2)	122.2 (6)
Fe–P2–C41	117.9 (1)	118.4 (2)	119.0 (7)
C2–P2–C31	102.8 (2)	102.7 (3)	97.2 (12)
C2–P2–C41	103.3 (2)	102.7 (3)	101.1 (10)
C31–P2–C41	101.8 (2)	103.1 (3)	102.4 (9)
P1–C1–C2	122.5 (3)	121.9 (5)	121.2 (20)
P2–C2–C1	122.1 (3)	122.0 (5)	110.5 (21)

view of the $FeCl_2(dppen)_2$ molecule, the overall molecular conformation being strictly similar for both the solvated and the unsolvated compounds, in spite of the different crystal packing. Packing diagrams of $FeCl_2(dppen)_2$ and $FeCl_2(dppen)_2 \cdot 2(CH_3)_2CO$ are shown in Figure 4. Selected values of bond distances and angles for the structure of $FeCl_2(dppen)_2$ and for the structures of $FeCl_2(dppen)_2 \cdot (CH_3)_2CO$ at 295 and 130 K are listed in Table VII. The two symmetry-independent Fe–P distances in the unsolvated compound (2.675 (1) and 2.532 (1) Å) as well as those in the high-spin isomer of the acetone solvate (2.592 (2) and 2.576 (2) Å) are very large, due to the effect of ligand rigidity and nonbonded interactions which are discussed below. Although such distances are shorter than those existing in the high-spin compound $FeCl_2(ppp)_2 \cdot 2(CH_3)_2CO$ described in the previous paper[1] (2.713 (3) and 2.665 (3) Å), they are much longer than those, ranging from 2.23 and 2.27 Å, that exist in the low-spin complexes with the same P_4Cl_2 donor set.[1] It is remarkable that the two symmetry-independent Fe–P distances in the unsolvated compound $FeCl_2(dppen)_2$, whose values have been quoted above, are so different from each other, whereas the corresponding distances in the room-temperature structure of the acetone solvate are close to each other. This may be attributed to the different packing of the two compounds, which causes the molecular environment to be less symmetrical in the structure of the unsolvated compound than in the other one. In particular, the shorter of the two Fe–P bonds in the structure of $FeCl_2(dppen)_2$ is parallel to the direction (of the crystallographic *b* axis) along which the shortest intermolecular contacts are established.

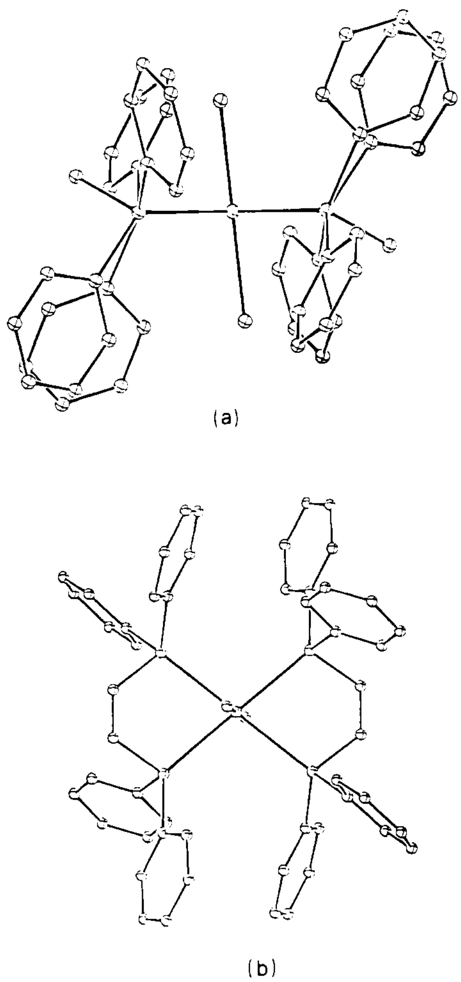

Figure 5. Two views of the $FeCl_2(dppen)_2$ molecule, along directions respectively (a) parallel and (b) perpendicular to the plane of the metal and phosphorus atoms.

The comparison between the structures of the two spin isomers of $FeCl_2(dppen)_2 \cdot 2(CH_3)_2CO$ shows that large differences exist between their iron–phosphorus distances (0.28 Å in the mean; see Table VII). Even allowing for the uncertainty on values of parameters derived from the low-temperature data, such variations in metal–ligand bond lengths with the change of spin multiplicity are definitely larger than any of those previously reported (0.20 Å, for Fe–N bonds) for iron(II) complexes exhibiting temperature-dependent singlet–quintet transitions.[9-11] On the other hand, the difference between the Fe–Cl bond lengths in the two spin isomers is small (0.03 Å) and may not be statistically significant. A rationalization for the scarce sensitivity of the iron–chlorine distance to the change in the ground-state spin multiplicity of these iron(II) complexes has been proposed.[1] In the course of the spin transition the interligand and the intraligand P···P distances decrease by 0.54 and 0.23 Å, respectively, on going from the high-spin to the low-spin isomer. The mean of the Cl···P distances decreases by 0.23 Å, whereas that of the shortest (≤4.0 Å) Cl···C(phenyl) contact distances decreases only by 0.11 Å. Thus on going from the high-spin to the low-spin state, the structural changes taking place in the inner part of the molecule, which is directly affected by the electronic rearrangement on the metal center, are larger than those occurring in the outer parts, which are opposed by intramolecular crowding. Crowding in the $FeCl_2(dppen)_2$ molecule is due to short contacts between the chlorine atoms and carbon atoms of the phenyl groups. Such interactions exist independently of the spin state and of the lattice type. They have important effects on the molecular conformation (see Figure 5), causing (a) the (chelate) plane of the PC=CP moiety to bend with respect to the equatorial plane (i.e., to the plane containing the metal and phosphorus atoms), in such a way that the metal atom lies very far from the plane of the chelate ring (0.8–1.0 Å, depending on the compound and spin state) and (b) the Fe–Cl bond to deviate from the normal to the equatorial plane, as has been pointed out in a previous part of a discussion. Moreover, the above steric interactions and the rigidity of the PC=CP chain favor the lengthening of the iron–phosphorus bonds, thus favoring the molecular conformation which is associated with the high-spin state. The low-spin geometry with "normal" iron–phosphorus bond lengths is favored, on the contrary, by electronic factors.[1] The existence of such opposing factors may account for the fact that the two molecular conformations associated with the different spin states have comparable energies, so that either spin state may become more stable than the other one in the appropriate temperature range.

The large differences in magnetic behavior between the solvated and the unsolvated compounds, however, are not rationalized by the above factors. In particular, the sharp change in μ_{eff} exhibited by the solvated compounds should be attributed to cooperative factors.[18] Since these are sensitive to lattice effects, the following features of the structures of these compounds probably play an important role in determining the magnetic properties: (a) the complex molecules are more regularly packed in the solvated than in the unsolvated compounds (Figure 4; see also footnote *a* to Table II and ref 25 in the companion paper[1]); (b) the shortest contacts in the lattice are established between the solvate molecules and those of the complex. Both factors should favor the propagation through the lattice of the local deformations associated with the change of spin state on a metal center, thus favoring the growth of domains of the alternative spin isomer.[19]

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Registry No. **1**, 58031-48-4; **2**, 74255-93-9; $\mathrm{FeBr_2(dppen)_2}$, 58031-47-3; $\mathrm{[FeI(dppen)_2]BPh_4}$, 78217-10-4.

Supplementary Material Available: Listings of structure factor amplitudes (31 pages). Ordering information is given on any current masthead page.

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[19] A reviewer has suggested that the transition to the low-spin state may occur through a mechanism of the following sort. A small twisting of the $\mathrm{FeP_2}$ planes, possibly induced by a phase change in the solid, would cause a new symmetry at the metal center, leading to a new electronic ground state which would in turn bring on the Fe–P bond distance changes. While we consider this to be a likely possibility (in particular, one of the low-lying triplet states, which are more sensitive to geometric distortions than the singlet or the quintet states as shown by calculations on model systems, may become the ground state), we also wish to stress that such an hypothesis is not in contrast with the conclusions draw at the end of this paper. It just goes in more depth into the mechanism of the spin transition. On the other hand, it finds no direct support by the material which is presented here.

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Low-Spin and High-Spin Six-Coordinate Iron(II) Complexes with a P_4Cl_2 Donor Set. X-ray Structures of $\mathrm{FeCl_2[(Ph_2PCH_2CH_2)_2PPh]_2{\cdot}2(CH_3)_2CO}$ and of $\mathrm{FeCl_2(Me_2PCH_2CH_2PMe_2)_2}$

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Structural investigations by X-ray diffraction methods have been carried out on two iron(II) chloride complexes formed with the poly(tertiary phosphines) bis[2-(diphenylphosphino)ethyl]phenylphosphine (ppp) and 1,2-bis(dimethylphosphino)ethane (dme). The complexes, with formulas $\mathrm{FeCl_2(ppp)_2{\cdot}2(CH_3)_2CO}$ (**1**) and $\mathrm{FeCl_2(dme)_2}$ (**2**), are, respectively, in the quintet and in the singlet ground state. Crystal data: (**1**) space group $P\bar{1}$, $a = 15.786$ (12) Å, $b = 13.717$ (10) Å, $c = 10.239$ (10) Å, $\alpha = 125.6$ (1)°, $\beta = 95.1$ (1)°, $\gamma = 103.2$ (1)°, $Z = 1$; (**2**) space group $P2_1/n$, $a = 9.554$ (3) Å, $b = 12.012$ (5) Å, $c = 9.123$ (3) Å, $\beta = 92.05$ (3)°, $Z = 2$. Both complexes have a distorted octahedral geometry with the $\mathrm{P_4Cl_2}$ donor set, the ppp ligand acting as bidentate in **1**. The symmetry-independent Fe–Cl distance is practically identical in the two compounds (2.354 (3) Å in **1** and 2.352 (1) Å in **2**), whereas the Fe–P distances differ dramatically, being in the range 2.66–2.71 Å for the high-spin complex **1** and in the range 2.23–2.24 Å for the low-spin complex **2**. Such large differences in the Fe–P bond lengths account for the different ground-state spin multiplicities of the compounds. Correlations between structural, spectral, and magnetic data for iron(II) complexes with the above donor set and geometry have been performed.

Introduction

It is well-known that the octahedral iron(II) complexes are either in a quintet or in a singlet ground state, depending on the nature of the donor set. Among the pseudooctahedral complexes, those with the $\mathrm{P_4Cl_2}$ donor set so far reported are low-spin[1] with the exception of the complex $\mathrm{FeCl_2(dppen)_2}$ (dppen = *cis*-1,2-bis(diphenylphosphino)ethylene), which exhibits a singlet ⇌ quintet temperature-dependent equilibrium.[2] To our knowledge no structure of iron(II) complexes with the $\mathrm{P_4Cl_2}$ donor set has been reported so far.

In the course of investigations on the coordinating behavior of poly(tertiary phosphine) ligands toward first-row transition-metal atoms, the ligand bis[2-(diphenylphosphino)ethyl]phenylphosphine, $\mathrm{(C_6H_5)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)_2}$, ppp, has generally been found to act as tridentate, yielding low-spin complexes.[3] However, a high-spin compound with formula $\mathrm{FeCl_2(ppp)_2{\cdot}2(CH_3)_2CO}$, whose magnetic and spectral properties could not be rationalized in terms of the possible donor sets and coordination geometries was isolated. Therefore, a structural investigation on this compound was undertaken by X-ray diffraction methods. This study revealed

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