Magnetic Cross-over in Six-co-ordinate Iron(II) Complexes of *cis*-1,2-Bis(diphenylphosphino)ethylene

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Reaction of iron(II) halides and pseudohalides with *cis*-1,2-bis(diphenylphosphino)ethylene (dppen) yields the complexes [Fe(dppen)$_2$X$_2$] (X = Cl, Br, NCS, or N$_3$) and [Fe(dppen)Br$_2$]. Physical properties indicate that the [Fe(dppen)$_2$X$_2$] complexes have six-co-ordinate, probably *trans*, structures. Magnetic susceptibilities and Mössbauer spectra classify the complexes as having $S = 0$ (X = NCS or N$_3$) or $S = 2$ (X = Br) ground states, or as existing in a temperature-dependent high-spin $\rightleftharpoons$ low-spin equilibrium (X = Cl). The Mössbauer parameters of the complexes are discussed in terms of the bonding properties of dppen. The properties of [Fe(dppen)Br$_2$], and of the dominant species occurring in solutions of [Fe(dppen)$_2$X$_2$] (X = Cl or Br), are consistent with tetrahedral structures. The product of reaction of iron(III) chloride with dppen is the complex salt [Fe(dppen)$_2$Cl$_2$][FeCl$_4$] in which the cation contains the metal in the $S = \frac{1}{2}$ state.

THE transition-metal chemistry of phosphines and arsines is very extensive.[1] However, relatively little has been published on the adducts formed by iron(II) salts with ligands of this class. Iron(II)-phosphine complexes, particularly if high spin, appear appreciably less stable with respect to dissociation than complexes of, for example, cobalt(II), nickel(II), and the heavier transition-metal ions. This is not unexpected in view of the predominantly 'hard' (class a) character of the spin-free d^6 ion. Among the iron(II)-phosphine complexes described in the literature are the tetrahedral complexes [2] [FeL$_2$X$_2$] and [Fe(L–L)X$_2$] (L = monophosphine, L–L = bidentate diphosphine, X = halide), and five-co-ordinate complexes [3] of multidentate phosphines. In the latter the metal ion may be high or low spin. Of the few known six-co-ordinate iron(II)-phosphine complexes the best characterized are those of the type [Fe(L–L)$_2$X$_2$] [L–L = 1,2-bis(dialkylphosphino)ethane or *o*-phenylene-bis(diethylphosphine)].[4,5] Some analogous complexes of related diarsines have also been reported.[6] All these are diamagnetic.

In this paper we describe a series of Fe^{II} complexes [Fe(dppen)$_2$X$_2$] [dppen = *cis*-1,2-bis(diphenylphosphino)-ethylene and X = a unidentate anionic ligand]. From magnetic and Mössbauer-effect measurements these complexes are shown to exhibit a magnetic cross-over as the nature of X is altered.

RESULTS AND DISCUSSION

Table 1 lists the complexes investigated together with analytical data and certain physical properties. The complexes were prepared by addition of the appropriate Fe^{II} salt to (usually) an excess of dppen in ethanol or ethanol–acetone solution under oxygen-free conditions. The molar ratio of Fe^{II} : dppen was varied between 1 : 1

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[1] 'Transition Metal Complexes of Phosphorus, Arsenic, and Antimony Ligands,' ed. C. A. McAuliffe, Macmillan, London, 1973.

[2] L. Naldini, *Gazzetta*, 1960, **90**, 391; K. Issleib and G. Doll, *Z. anorg. Chem.*, 1960, **305**, 1; K. Issleib and G. Hohlfeld, *ibid.*, 1961, **312**, 169.

[3] M. T. Halfpenny, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1967, 627; R. B. King, R. N. Kapoor, M. S. Saran, and P. N. Kapoor, *Inorg. Chem.*, 1971, **10**, 1851, 1861; W. S. J. Kelly, G. H. Ford, and S. M. Nelson, *J. Chem. Soc.* (*A*), 1971, 388; W. V. Dahlhoff and S. M. Nelson, *ibid.*, p. 2184.

[4] J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1961, 2605.

[5] G. M. Bancroft, M. J. Mays, and B. E. Prater, *J. Chem. Soc.* (*A*), 1970, 956.

[6] R. D. Feltham and W. Silverthorn, *Inorg. Chem.*, 1968, **7**, 1154; R. D. Feltham, H. G. Metzzer, and W. Silverthorn, *ibid.*, p. 2003.

and 1 : 3 in different experiments. In no instance was a tris(dppen) complex isolated and only for [Fe(dppen)Br_2] was an analytically pure mono complex obtained. Attempts to prepare a pure iodo-derivative were unsuccessful. A useful criterion of purity in all cases was the absence of unwanted absorption in the Mössbauer spectra. In certain preparations of [Fe(dppen)$_2Cl_2$] a green by-product was observed. This was shown to be a Fe^{III} complex by comparison with the green complex of empirical formula Fe(dppen)Cl_3 obtained by reaction of $FeCl_3$ with dppen (see later). With the exception of [Fe(dppen)$_2(N_3)_2$] and [Fe(dppen)Br_2] which darkened slowly on storage, the complexes are stable in the solid state in a dry atmosphere for periods of up to 4 months.

Table 1

Analytical data and physical properties for the iron–diphosphine complexes

			Λ [b]/S cm^2 mol^{-1}		Analyses/%							
					Found				Calc.			
Complex	Colour	$\mu_{eff.}$ [a]/ B.M.	$C_2H_4Cl_2$	MeO_2	C	H	N	Halogen	C	H	N	Halogen
[Fe(dppen)$_2Cl_2$]	Lemon yellow	4.69	0.5	27.8	68.0	4.8		7.7	67.9	4.8		7.7
[Fe(dppen)$_2Br_2$]	Yellow	5.09	10.5	43.8	61.7	4.4		16.1	61.9	4.4		15.8
[Fe(dppen)$_2$(NCS)$_2$]	Violet	0.88	0.09		66.9	4.6	2.6		67.2	4.6	2.9	
[Fe(dppen)$_2(N_3)_2$]	Brown	1.30	0.98	7.1	66.7	4.9	8.9		67.0	4.8	9.0	
[Fe(dppen)Br_2]	Tan	5.15	12.3	48.1	51.4	3.7		16.1	51.0	3.6		15.8
[Fe(dppen)$_2Cl_2$]-[$FeCl_4$]	Green	4.45 [c]		87.7	56.2	3.9		18.8	55.9	4.0		19.0

[a] At 293 K; corrected for diamagnetism of ligands. [b] 10^{-3}M Solutions at 25 °C. [c] Based on the formula Fe(dppen)Cl_3.

The [Fe(dppen)$_2X_2$] complexes are assigned six-co-ordinate structures on the basis of electronic spectra, magnetic moments, and electrical-conductance behaviour discussed below. The question of whether the complexes have *cis* or *trans* geometry is more difficult to answer. Molecular models do not rule out either structure but suggest that interligand crowding is less in the *trans* form. A *trans* arrangement of two dppen ligands is, of course, known for square-planar [7] and square-pyramidal [8] Ni^{III} complexes, and in certain [FeL_2X_2] complexes where L is diphosphine or diarsine *trans* structures have also been established.[5,6] It therefore seems probable that the same applies to the present complexes. In principle it is possible to resolve the problem from a knowledge of the number of active metal–ligand vibrations in the far-i.r. region.[9] This was found to be a rather rich part of the spectrum and few assignments could be made with confidence. However, well defined single bands at 285 and 227 cm^{-1} are tentatively assigned to the Fe–Cl and Fe–Br stretching modes, respectively [ν(Fe–Br)/ν(Fe–Cl) = 0.79]. The occurrence of these absorptions as single bands is consistent with the assumption of *trans* geometry. It is also consistent with the assignment of the bands at 289 and 252 cm^{-1} in [Fe(dppen)Br_2] to the two Fe–Br vibrations expected for tetrahedral symmetry;[10] metal–halide vibrations are known to occur at higher energies in tetrahedral than in six-co-ordinate complexes.

The occurrence of the NCS asymmetric and symmetric stretching vibrations at 2 103 and 822 cm^{-1}, respectively, indicates [11] that the NCS groups are *N*-bonded. In the azido-complex ν_{asym} occurred as a split band centred at 2 060 cm^{-1} and ν_{sym} at 1 330 cm^{-1}, confirming the terminal co-ordination of this ion.[12] In none of the complexes was there evidence for any C=C stretching vibration in the 1 500—1 700 cm^{-1} region.

The room-temperature magnetic moments classify the [Fe(dppen)$_2X_2$] complexes as high (X = Cl or Br) or low spin (X = NCS or N_3) at this temperature (see Table 1 and discussion below).[13] Electrical-conductance measurements in 1,2-dichloroethane, chloroform, and nitromethane indicate that the two low-spin complexes are non-electrolytes. The data for the high-spin complexes similarly suggest that they are correctly formulated as neutral and six-co-ordinate but that there is appreciable decomposition into ionic species in 1,2-dichloroethane (bromide) and nitromethane (both chloride and bromide).

Electronic spectra of solids and solutions ($C_2H_4Cl_2$ or $CHCl_3$) were measured in the range 5 000—30 000 cm^{-1}. Only in the case of [Fe(dppen)$_2$(NCS)$_2$] was there good agreement between solid and solution spectra. This complex exhibited two well resolved bands at 21 200 and 17 000 cm^{-1} which are assigned to the two spin-allowed transitions $^1A_{1g}\rightarrow{}^1T_{2g}$ and $^1A_{1g}\rightarrow{}^1T_{1g}$, respectively, in O_h symmetry. Since phosphine and isothiocyanate occur close together in the spectrochemical series the absence of any splitting in these bands is not surprising. No absorption at lower energies attributed to the spin-forbidden transition was detected and thus the Racah parameter *C* could not be evaluated. However, it has been suggested [14] that *C* maintains a fairly constant value at *ca.* 3 300 cm^{-1} in different complexes. On

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[7] H. N. Ramaswamy, H. B. Jonassen, and A. M. Aguiar, *Inorg. Chim. Acta*, 1967, **1**, 141.

[8] C. A. McAuliffe and D. W. Meek, *Inorg. Chem.*, 1969, **8**, 904.

[9] D. M. Adams, 'Metal–Ligand and Related Vibrations,' Edward Arnold, 1967.

[10] C. D. Burbridge and D. M. L. Goodgame, *J. Chem. Soc.* (*A*), 1968, 1074.

[11] P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1960, 1912.

[12] S. M. Nelson and J. Nelson, *J. Chem. Soc.* (*A*), 1969, 1557.

[13] B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 1964, **6**, 37.

[14] J. C. Dabrowiak, P. H. Merrell, and D. H. Busch, *Inorg. Chem.*, 1972, **11**, 1979.

substitution of this value in the expression[15] $E(^1A_{1g} \rightarrow {}^1T_{1g}) = 10\,Dq - C$ an estimate of 20 300 cm^{-1} is obtained for 10 Dq.

The solid-state spectrum of $[\mathrm{Fe(dppen)_2(N_3)_2}]$ showed two bands at 19 800 and 14 500 cm^{-1}. The lower-energy band was broad and probably composite. Since the azide ion falls below phosphine in the spectrochemical series the effective site symmetry for the metal will be D_{4h}, on the assumption of *trans* geometry. In this symmetry the $^1T_{1g}$ level splits into ^1E_g and $^1A_{2g}$.[16] We tentatively assign the 19 800 cm^{-1} band to $^1A_{1g} \rightarrow {}^1T_{2g}$ and the broad unresolved absorption at 14 500 cm^{-1} to the two transitions to the split $^1T_{1g}$ level.

TABLE 2

Electronic spectra[a] of the iron–diphosphine complexes

Complex	State	
$[\mathrm{Fe(dppen)_2Cl_2}]$	Mull	28.5, 15.4, 13.0—9.0 (br)
	$C_2H_4Cl_2$	29.7 (950), 15.4 (25), 11.0 (3), 7.2 (65)
	$C_2H_4Cl_2$ + dppen[b]	15.8 (25), *ca.* 11.0 (85), 7.2 (45)
$[\mathrm{Fe(dppen)_2Br_2}]$	Mull	28.4, 10.9, 8.5
	$C_2H_4Cl_2$	29.8 (1 450), 25.6 (sh), 23.4 (sh), 21.0 (sh), 11.0—8.0 (br) (4), 7.0 (80)
	$C_2H_4Cl_2$ + dppen[b]	11.0—8.0 (br) (7), 7.0 (55)
$[\mathrm{Fe(dppen)_2(NCS)_2}]$	Mull	28.7, 21.3, 17.0
	$CHCl_3$	28.7 (2 030), 21.3 (150), 17.0 (9.5)
$[\mathrm{Fe(dppen)_2(N_3)_2}]$	Mull	29.2, 19.8 (sh), 14.5 (br)
	$C_2H_4Cl_2$	29.6 (2 300), 28.0 (sh), *ca.* 22.0 (sh), *ca.* 16.0 (sh)
$[\mathrm{Fe(dppen)Br_2}]$	Mull	30.6, *ca.* 21.0 (sh), *ca.* 16.0 (sh), 7.0
	$C_2H_4Cl_2$	29.9 (1 650), *ca.* 21.0 (sh), 7.0 (95)

[a] Absorption maximum in 10^3 cm^{-1}; absorption coefficients (ε/l mol^{-1} cm^{-1}) are given in parentheses. [b] 10^{-2}M in complex, 5×10^{-2}M in dppen.

The complex $[\mathrm{Fe(dppen)_2Cl_2}]$, which at room temperature is predominantly in the high-spin state, had a weak broad absorption centred at *ca.* 11 000 cm^{-1}, while in $[\mathrm{Fe(dppen)_2Br_2}]$ two overlapping weak bands at 10 900 and 8 500 cm^{-1} could be distinguihsed. High-spin octahedral Fe$^{\mathrm{II}}$ complexes show a single spin-allowed transition $^5T_{2g} \rightarrow {}^5E_g$ in the 8 000—11 000 cm^{-1} range. In D_{4h} symmetry both levels split and two transitions (from the ground state to $^5A_{1g}$ and $^5B_{1g}$) are expected.[16] On the basis of this assignment the splitting of the ^5E_g level is *ca.* 2 400 cm^{-1} in the case of $[\mathrm{Fe(dppen)_2Br_2}]$. The splitting in the chloride is expected to be less, consistent with the unresolved nature of the broad band centred at *ca.* 11 00 cm^{-1}. The origin of the weak absorption at 15 400 cm^{-1} in the spectrum of $[\mathrm{Fe(dppen)_2Cl_2}]$ is uncertain. Possibly it is due to a spin-forbidden transition to a triplet state. Alternatively, it may be a property of the low-spin complex known from Mössbauer spectra to be present in small amounts at room temperature.

In the solution spectra of both $[\mathrm{Fe(dppen)_2Cl_2}]$ and $[\mathrm{Fe(dppen)_2Br_2}]$ the quintet→quintet bands at 8 000—11 000 cm^{-1} were barely detectable and were replaced by much more intense bands at 7 200 (chloride) and 7 000 cm^{-1} (bromide). The solution spectrum of the latter complex is virtually identical to that of solid $[\mathrm{Fe(dppen)Br_2}]$, for which a pseudotetrahedral stereochemistry is assumed. In known tetrahedral Fe$^{\mathrm{II}}$ complexes the single spin-allowed transition $^5E \rightarrow {}^5T_2$ has been observed in the range 3 000—6 000 cm^{-1}.[10] In C_{2v} symmetry the degeneracy of both ground and excited states is lifted and a total of three transitions is predicted in this frequency region though only two appear to have been distinguished.[10] In the dppen complexes no second or third bands were detected though this region of the spectrum was complicated by the presence of a number of narrow vibrational bands. It would seem either that the C_{2v} splitting is small or that one or more of the component bands occur below the resolution wavelength (5 000 cm^{-1}) of the spectrophotometer. The energies of the bands at 7 000 and 7 200 cm^{-1} are the highest yet reported for tetrahedral Fe$^{\mathrm{II}}$ complexes. Addition of excess of dppen to these solutions diminished the intensities of these bands and slightly restored those at 8 000—11 000 cm^{-1}. Thus, the equilibrium (1) is indicated.

$$\underset{\text{six-co-ordinate}}{[\mathrm{Fe(dppen)_2X_2}]} \rightleftharpoons \underset{\text{tetrahedral}}{[\mathrm{Fe(dppen)X_2}]} + \text{dppen} \qquad (1)$$

Magnetic Properties.—Both $[\mathrm{Fe(dppen)_2Br_2}]$ and $[\mathrm{Fe(dppen)Br_2}]$ are high spin over the complete temperature range (90—360 K) studied (see Table 3). The moments of 4.9—5.2 B.M. are consistent with the spin-free tetragonal and tetrahedral structures assigned, respectively, to them.[13,*]

TABLE 3

Magnetic data for the iron–diphosphine complexes

$[\mathrm{Fe(dppen)_2Cl_2}]$		$[\mathrm{Fe(dppen)_2(NCS)_2}]$		$[\mathrm{Fe(dppen)_2(N_3)_2}]$	
$\mu_{\mathrm{eff.}}$[a]/B.M.	T/K	$\mu_{\mathrm{eff.}}$[a]/B.M.	T/K	$\mu_{\mathrm{eff.}}$[a]/B.M.	T/K
4.84	353	0.94	373	1.65	343
4.75	313	0.90	333	1.41	323
4.69	293	0.88	293	1.30	293
4.53	263	0.80	253	1.27	263
4.40	233	0.75	213	1.18	233
4.23	193	0.71	173	1.14	203
4.07	153	0.69	133	1.09	173
3.91	123	0.61	92	1.07	153
3.70	93			1.03	133
3.41	83			1.00	113
				0.98	103
				0.98	93
$[\mathrm{Fe(dppen)_2Br_2}]$		$[\mathrm{Fe(dppen)Br_2}]$		$[\mathrm{Fe(dppen)_2Cl_2}]$-$[\mathrm{FeCl_4}]$[b]	
5.09	333	5.20	363	4.46	353
5.11	314	5.17	323	4.47	333
5.08	293	5.15	293	4.45	313
4.97	233	5.11	253	4.45	293
4.96	193	5.13	213	4.44	233
4.93	93	5.09	173	4.46	193
		5.05	133	4.46	153
		5.01	93	4.43	93

[a] Corrected for diamagnetism of ligands. [b] Based on formula $\mathrm{Fe(dppen)Cl_3}$.

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* 1 B.M. ≈ 9.27×10^{-24} A m^2.

[15] R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, 1965, **4**, 709.

[16] D. M. L. Goodgame, M. Goodgame, M. A. Hitchman, and M. J. Weeks, *Inorg. Chem.*, 1966, **5**, 635.

The complexes [Fe(dppen)$_2$(NCS)$_2$] and [Fe(dppen)$_2$(N$_3$)$_2$] must be considered as spin-paired $t_{2g}^6e_g^0$ systems. The small susceptibility of the thiocyanate, which at 293 K corresponds to a moment of 0.88 B.M., is presumably largely due to the temperature-independent paramagnetism (t.i.p.) usually found for low-spin d^6 complexes.[13] The origin of the rather higher paramagnetism of the azide is not clear. It could be due to paramagnetic impurity though none was evident in the Mössbauer spectra at any temperature. Alternatively, it is possible that this complex is on the verge of a magnetic cross-over to the high-spin state. It is to be noted that $\mu_{\text{eff.}}$ begins to rise fairly rapidly above room temperature. It rises more steeply with further increase in temperature above *ca.* 343 K but here hysteresis effects set in. Thus the observed moment of 2.4 B.M. at 393 K decreased only to 1.9 B.M. on cooling to 293 K. These observations are consistent with the occurrence of a singlet $\rightleftharpoons$ quintet equilibrium superimposed on an irreversible decomposition evident above *ca.* 343 K. However, no definite evidence for the presence of any high-spin isomer was found in the 293 K Mössbauer spectrum.

TABLE 4

Mössbauer parameters for the Fe^{II} complexes

		$S = 0$		$S = 1$	
		δ [a,b]	ΔE_Q [b]	δ [a,b]	ΔE_Q [b]
Complex	T/K	mm s^{-1}		mm s^{-1}	
[Fe(dppen)$_2$(NCS)$_2$]	293	0.26	0.30		
	77	0.29	0.39		
[Fe(dppen)$_2$(N$_3$)$_2$]	293	0.33	0.35		
	195	0.38	0.27		
[Fe(dppen)$_2$Cl$_2$]	293	0.38 ± 0.1	0.70 ± 0.1	0.78	2.47
	195	0.46 ± 0.02	0.69 ± 0.02	0.83	2.53
	77	0.51	0.67	0.89	2.59
[Fe(dppen)$_2$Br$_2$]	293			0.83 ± 0.02	2.66 ± 0.02
	77			0.93 ± 0.05	2.68 ± 0.05
[Fe(dppen)Br$_2$]	293			0.58 ± 0.1	2.76 ± 0.1
	77			0.63	

[a] Relative to natural ion. [b] Estimated error ±0.01 mm s^{-1} except where otherwise indicated.

The magnetic moment of [Fe(dppen)$_2$Cl$_2$] decreased from 4.84 B.M. at 353 K to 3.41 B.M. at 83 K (Table 3). The behaviour was reversible with respect to temperature and the measured susceptibilities were independent of the magnetic-field strength. We propose that in this complex there is a temperature-controlled equilibrium between the $S = 2$ and 0 spin states, the former lying above the latter by an energy interval of the order of kT. This appears to be the first example of a spin cross-over in Fe^{II} phosphine complexes. Assuming moments of 5.1 and 0.6 B.M. for the $S = 2$ and 0 states the proportions of the high-spin isomer present at 293, 195, and 83 K are *ca.* 90, 81, and 62%, respectively.

Mössbauer Spectra.—Spectra were recorded at absorber temperatures of 293, 195, and 77 K. Isomer shifts (quoted relative to natural iron) and quadrupole splittings are in Table 4 and representative spectra are shown in Figures 1 and 2. Conclusions based on the magnetic measurements and the Mössbauer spectra are in excellent accord. Thus, [Fe(dppen)$_2$(NCS)$_2$] and [Fe(dppen)$_2$(N$_3$)$_2$] which were shown to be (predominantly) low spin at all temperatures exhibited one quadrupole-split doublet. The isomer shifts, δ, of 0.2—0.4 mm s^{-1} and quadrupole splittings, ΔE_Q, of 0.2—0.4 mm s^{-1} are typical [17] of Fe^{II} in the $S = 0$ ground state (Figure 1). In sharp contrast the high-spin complex [Fe(dppen)$_2$Br$_2$] gave δ and ΔE_Q values of 0.9 and 2.7 mm s^{-1}, respectively, typical [17] of Fe^{II} in the $S = 2$ ground state (Figure 1).

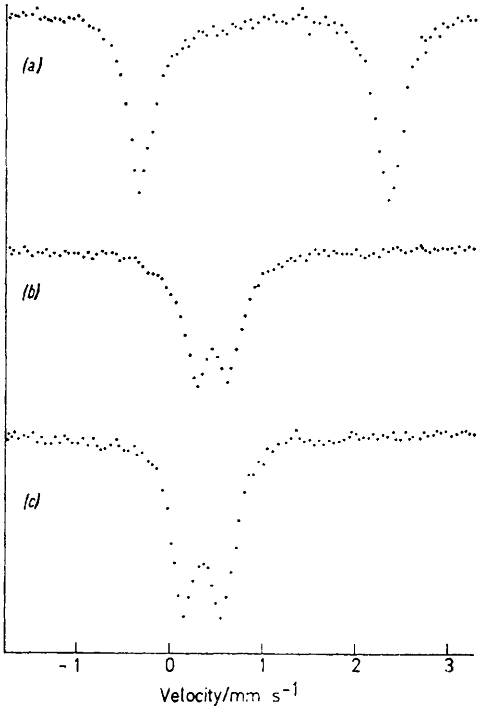

FIGURE 1 Mössbauer spectra for [Fe(dppen)$_2$Br$_2$] at 293 K (*a*), [Fe(dppen)$_2$(N$_3$)$_2$] at 298 K (*b*), and [Fe(dppen)$_2$(NCS)$_2$] at 77 K (*c*)

The spectra of [Fe(dppen)$_2$Cl$_2$] confirmed the occurrence of a temperature-controlled singlet $\rightleftharpoons$ quintet equilibrium. All the spectra, at the three temperatures studied, displayed two sets of quadrupole-split doublets

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[17] N. N. Greenwood and T. C. Gibb, ' Mössbauer Spectroscopy,' Chapman and Hall, London, 1971.

whose relative intensities varied with temperature in the expected sense. Thus the doublet composed of the two centre lines increased in intensity, as temperature was lowered, at the expense of the two outer lines (see Figure 2). Isomer shifts and quadrupole splittings for the inner and outer doublets are once again in good agreement with their assignment to low- and high-spin Fe^{II}, respectively.

It is of interest to compare the Mössbauer parameters with those found for other complexes of similar constitution. For the three low-spin species the isomer shifts increase in the order $NCS < N_3 < Cl$, *i.e.* the inverse relation between δ and the ligand-field strength noted previously[5,18] applies. On the basis of this relation Bancroft *et al.*[5] predicted that the critical isomer-shift value for magnetic cross-over should fall in the range 0.3—0.4 mm s^{-1} (with respect to natural iron). Table 4 shows that δ(293 K) of both $[Fe(dppen)_2Cl_2]$ and $[Fe(dppen)_2(N_3)_2]$ falls within this range.

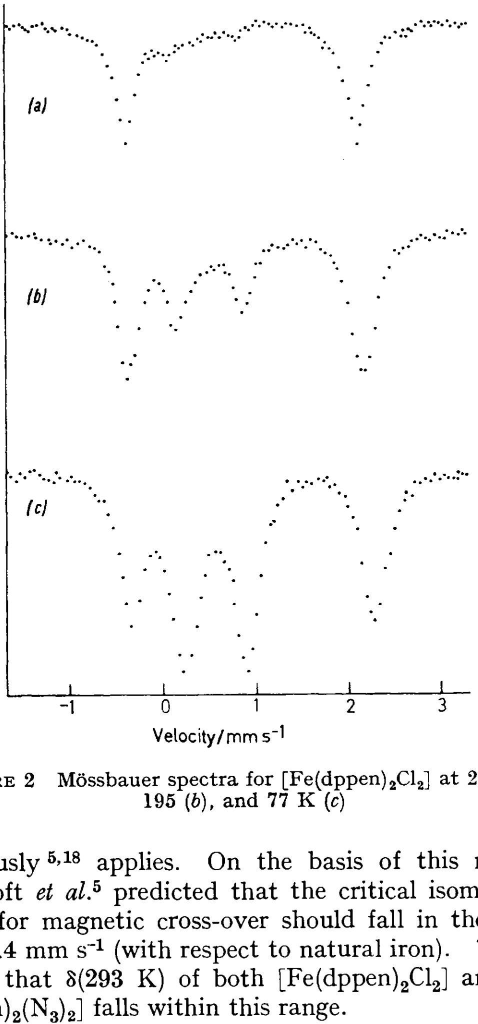

FIGURE 2 Mössbauer spectra for $[Fe(dppen)_2Cl_2]$ at 293 (*a*), 195 (*b*), and 77 K (*c*)

Following the procedure of Bancroft *et al.*[5] isomer shifts and quadrupole splittings may be resolved into component partial centre shifts * (p.c.s.) and partial quadrupole splittings (p.q.s.) for the individual ligands. The use of p.c.s. and p.q.s. values assumes the property of additivity, *i.e.* that the p.c.s. or p.q.s. value of a ligand in a complex will not alter significantly as associated ligands are varied. Assuming, as argued above, that the dppen complexes are *trans*, that the six donor atoms lie on mutually orthogonal axes, that the sign of ΔE_Q is positive, as found[19] for $[Fe(depe)_2Cl_2]$, and using the same p.c.s. and p.q.s. values derived by Bancroft *et al.*[5,19] for $[NCS]^-$, N_3^-, and Cl^-, the p.c.s. and p.q.s. values for dppen in the present complexes may be calculated. The p.c.s. for each donor atom in dppen (+0.07 mm s^{-1}) † is found to be the same within experimental uncertainty as that derived for $\frac{1}{2}$dmpe, $\frac{1}{2}$depe, and $\frac{1}{2}$depb (+0.06 mm s^{-1}). However, the average value of p.q.s. for $\frac{1}{2}$dppen (−0.50 mm s^{-1}) is significantly more positive (p.q.s. = −0.67, −0.62, and −0.56 mm s^{-1}, respectively, for $\frac{1}{2}$dmpe, $\frac{1}{2}$depe, and $\frac{1}{2}$depb). Since centre shift decreases with increase in σ-donor and in π-acceptor properties and since partial quadrupole splittings generally move to more positive values with increasing π-back donation and decreasing σ bonding,[5,19] it is concluded that dppen is a better π acceptor and poorer σ donor than dmpe, depe, and depb. It has previously been suggested, on the basis of the structures and electronic spectra of Ni^{II} complexes, that dppen is a better π acceptor than the corresponding saturated diphosphine, 1,2-bis(diphenylphosphino)ethane, an effect attributed to the presence of vacant antibonding *p*-orbitals in dppen.[8]

The positive values of δ for high-spin $[Fe(dppen)_2Cl_2]$ and $[Fe(dppen)_2Br_2]$ are typical of $^5T_{2g}$ ground states.[17] The magnitudes of ΔE_Q (2.4—2.7 mm s^{-1}) suggest that the sign of the quadrupole splitting is positive,[20] *i.e.* that the ground-state splitting is such that d_{xy} lies lower than d_{xz} or d_{yz}. The isomer shift of $[Fe(dppen)Br_2]$ is lower (by *ca.* 0.25 mm s^{-1}) than that for $[Fe(dppen)_2Br_2]$. This is a generally observed trend attributable to greater covalency in the tetrahedral case.[10] The value is also lower than those reported for mixed $[FeL_2X_2]$ complexes (L = an oxygen or nitrogen donor).[10] However, ΔE_Q (2.76 mm s^{-1} at 293 K) is similar to, for example, that of $[Fe(quinoline)Br_2]$ (2.71 mm s^{-1}) suggesting comparable measures of ground-state splitting ($E \rightarrow A_1 + A_2$ in C_{2v}).[10]

The Iron(III) *Complex*.—The complex of empirical formula $Fe(dppen)Cl_3$ is formulated as the complex salt $[Fe(dppen)_2Cl_2][FeCl_4]$ comprising a low-spin Fe^{III} cation and a high-spin tetrahedral $[FeCl_4]^-$ anion. The magnetic moment, which is almost temperature independent, is 4.45 B.M. (293 K) calculated on a formula of $Fe(dppen)Cl_3$. Assuming the above salt structure and using a value of 5.92 B.M. for the moment of $[FeCl_4]^-$, the moment of the $[Fe(dppen)_2Cl_2]^+$ cation is calculated to be 2.14 B.M. in good agreement with expectation for a

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* For this purpose the centre shift is taken to be the same as the isomer shift at 293 K, *i.e.* the second-order Doppler shift is assumed to be negligible.

† Quoted relative to stainless steel in order to permit direct comparisons with the p.c.s. values of Bancroft *et al.*[5] dmpe = 1,2-Bis(dimethylphosphino)ethane; depe = 1,2-bis(diethylphosphosphino)ethane; and depb = *o*-phenylenebis(diethylphosphine).

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[20] C. D. Burbridge, D. M. L. Goodgame, and M. Goodgame, *J. Chem. Soc.* (*A*), 1967, 349.

species having one unpaired electron.[13] The i.r. spectrum showed a strong absorption at 380 cm^{-1} characteristic of the Fe-Cl stretch in $[FeCl_4]^-$.[9] The complex is a 1 : 1 electrolyte in nitromethane. Attempts to replace the $[FeCl_4]^-$ anion by $[ClO_4]^-$ yielded products in which both anions were present. The i.r. and Mössbauer spectra and magnetic susceptibilities of these derivatives were all consistent with the coexistence of the two salts in varying proportions in different preparations. A complete replacement was not achieved.

The 293 K Mössbauer spectrum of $[Fe(dppen)_2Cl_2]$-$[FeCl_4]$ showed lines which could be assigned to the metal ion in two different environments. The two outer lines (δ 0.26 ± 0.01 mm s^{-1} and ΔE_Q 2.02 ± 0.02 mm s^{-1}) are assigned to the low-spin cation and the two inner lines (δ 0.22 ± 0.05 mm s^{-1} and ΔE_Q 0.27 ± 0.05 mm s^{-1}) to the $[FeCl_4]^-$ anion.[17] The parameters for the low-spin Fe^{II} complex compare well with those found previously for *trans*-$[Fe(pdma)_2X_2]^+$ [pdma = *o*-phenylenebis(dimethylarsine), X = Cl or Br].[21] The occurrence of a measurable quadrupole splitting for the $[FeCl_4]^-$ counter ion indicates that there must be some deviation from local T_d symmetry, presumably arising from distortion due to lattice effects.

EXPERIMENTAL

Preparations.— *cis*-1,2-Bis(diphenylphosphino)ethylene (dppen) was prepared from *cis*-1,2-dichloroethylene by the method of Aguiar and Daigle.[22] In the preparation of the complexes all operations were carried out in a nitrogen atmosphere and in deoxygenated solvents.

Bis[cis-1,2-*bis(diphenylphosphino)ethylene*]*dichloroiron*(II), $[Fe(dppen)_2Cl_2]$.—An ethanolic solution of $FeCl_2 \cdot 4OH_2$ (1 mmol) was heated under reflux over iron filings and filtered into an ethanolic solution of dppen (3 mmol) with stirring at 60—70 °C. The lemon-yellow *product* which separated on cooling was washed with ethanol and acetone and dried *in vacuo*.

Bis[cis-1,2-*bis(diphenylphosphino)ethylene*]*dibromoiron*(II), $[Fe(dppen)_2Br_2]$.—An ethanolic solution of $FeBr_2$ (1 mmol) was prepared by heating under reflux the appropriate quantity of iron powder with an excess of bromide. On addition to a solution of dppen (3 mmol) in ethanol a yellow *solid* separated on cooling. This was washed with ethanol and acetone and dried *in vacuo*. The complex $[Fe(dppen)_2Br_2]$ was prepared similarly except that the dppen solution (1 mmol) was added to the $FeBr_2$ solution (1.2 mmol).

Bis[cis-1,2-*bis(diphenylphosphino)ethylene*]*di-isothiocyanatoiron*(II), $[Fe(dppen)_2(NCS)_2]$.—A solution of $Fe[ClO_4]_2 \cdot 6OH_2$ (1 mmol) in ethanol was mixed with an ethanolic solution of dppen (2.5 mmol). To this stirred solution at *ca.* 70 °C was added an ethanolic solution of Na[NCS] (2 mmol). An immediate mauve *precipitate* separated. This was washed with ethanol and dried *in vacuo*. The complex $[Fe(dppen)_2(N_3)_2]$ was prepared in a similar manner using a warm aqueous solution of NaN_3. The buff-coloured *product* was washed with aqueous ethanol followed by ethanol.

Bis[cis-1,2-*bis(diphenylphosphino)ethylene*]*dichloroiron*(III) *Tetrachloroferrate*(III), $[Fe(dppen)_2Cl_2][FeCl_4]$.—A solution containing $FeCl_3$ (2 mmol) in methanol was added to dppen (2.5 mmol) in methanol–acetone at 70 °C. The brown solution turned green on cooling and deposited a deep green *solid*. This was washed with cold methanol–acetone.

Physical Measurements.—I.r. spectra in KBr pellets were recorded on a Perkin-Elmer model 457 spectrophotometer. Electronic spectra were obtained using a Unicam SP 700 instrument. Electrical conductivities were measured at 1 000 Hz using a resistance–capacitance bridge with magic-eye detector in a Pt-electrode cell of cell constant 0.038. Magnetic measurements were made by the Gouy method using a Newport Instruments variable-temperature magnetic balance.

Mössbauer spectra were recorded at 293 ± 2 and 77 K and sometimes 195 K, with a ^{57}Co in Pd source using a constant-acceleration Harwell spectrometer. The equipment was calibrated with an iron-foil standard at 295 K. Absorber thicknesses were not more than 50 mg cm^{-2}. Isomer shifts and quadrupole splittings were determined by visual inspection to ±0.01 mm s^{-1} in most cases; values were checked by repeating the measurements several times using different samples in most cases. Approximately equal line intensities were found in all spectra except those of the iron(III) complex; here, the more negative absorption line consistently showed the greater intensity.

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