Electron Spin Resonance Studies of Axial Ligation to Cobalt(II) Complexes. Part 2.[1] Interaction with Phosphorus Ligands. Analysis of the Cobalt Bonding Parameters and the Phosphorus Hyperfine Coupling

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Electron spin resonance spectra have been recorded for frozen solutions of six different low-spin cobalt(II) complexes with a range of up to seven phosphines or phosphites as ligands co-ordinated in the axial position. A detailed analysis of the various assumptions used in the theory of the low-spin d^7 ion (d_{z^2}) is given together with, for the first time, a full analysis of the phosphorus hyperfine tensor. A tentative correlation is made relating the polarisation contribution to the ^{31}P hyperfine tensor with the energy separation of the d_{xz} and d_{yz} orbitals.

In a previous paper[1] we presented e.s.r. results for a series of phosphine and phosphite adducts with cobalt(II) Schiff-base complexes having oxygen, sulphur, or selenium acting as two of the ligating atoms, the others being nitrogen. In this paper, we extend the series of Schiff bases and also include [Co(sacsac)$_2$] (sacsac = dithioacetylacetonate), [Co(dbms)$_2$] (dbms = thiodibenzoylmethanate), [Co(mosalen)] {mosalen = *NN'*-ethylenebis[(2-methoxy)salicylideneiminate]}, [Co(salphen)] [salphen = *o*-phenylenebis(salicylideneiminate)], [Co(pts)]$^{4-}$ (H$_2$pts^{4-} = phthalocyaninetetrasulphonate), [Co(Hdmg)$_2$] (Hdmg$^-$ = dimethylglyoximate), and [Co(amben)] [amben = *NN'*-ethylenebis(2-aminobenzylideneiminate)].

EXPERIMENTAL

[Co(mosalen)], [Co(salphen)], and [Co(sacsac)$_2$] were prepared by standard methods.[2] The complex [Co(dbms)$_2$] had not been reported previously, but was prepared by using the method described for the nickel analogue by Chaston *et al.*[3] Adducts were prepared by adding a small excess of the appropriate phosphine or phosphite to a solution of the complex in CH$_2$Cl$_2$ as described in Part 1. All materials and manipulations were handled or carried out under vacuum or dry nitrogen. E.s.r. spectra were recorded on a Varian E3 spectrometer at 77 K and at about 200 K, for fluid solution measurements.

RESULTS AND DISCUSSION

Low Symmetry Complexes.—Frozen solution spectra were recorded at 77 K and were usually well resolved. They were interpreted in terms of three well spaced g features, the two at higher fields (g_y and g_z) exhibiting cobalt hyperfine coupling (^{59}Co, $I = \frac{7}{2}$) and further splitting of each line into two by phosphorus (^{31}P, $I = \frac{1}{2}$). The g feature at low field (g_x) was broad and usually not resolved. At *ca.* 200 K, the fluid solution spectrum was at its optimum resolution, but even this usually only showed two lines due to interaction with phosphorus, whilst at higher temperatures, the spectra broadened considerably. Good values of g_y and g_z were obtained directly from the spectrum, and since $g_{iso.}$ was known from the fluid solution spectrum, it was possible to calculate g_x with confidence. Hyperfine coupling to cobalt on g_y and g_z could be accurately measured. The assignment of a value for A_x(Co) was more difficult, but from the line width and computer simulation, an estimate could be made. However, the accuracy of this value is not very important in the calculation of bonding parameters. In all cases, there was splitting of each cobalt hyperfine line into two, rather than three, components showing that only one phosphorus ligand was present, not two as has been observed in several cases with pyridine adducts.[4,5] The assignment of labels x, y, and z to the g values is arbitrary, but for consistency with our previous work,[1] g_z is assigned to the lowest g value since there is good reason to believe this is associated with the z axis of the molecule which we define as along the cobalt–phosphorus bond.

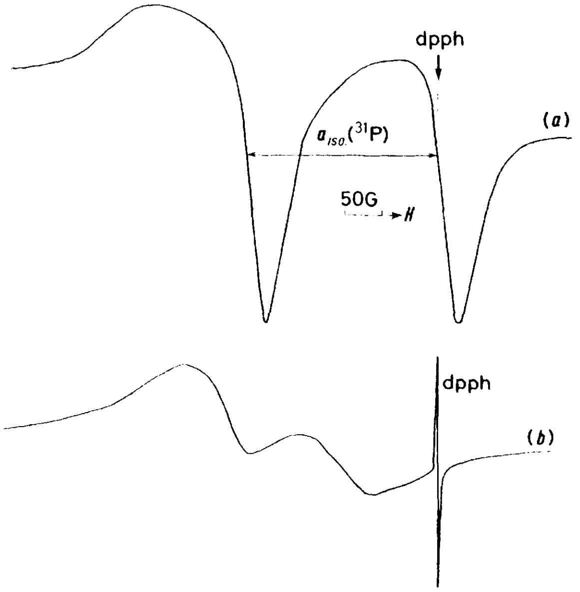

FIGURE 1 Fluid solution e.s.r. spectra at 200 K of (*a*) [Co(sacsac)$_2${P(OPh)$_3$}] and (*b*) [Co(sacsac)$_2$(PPh$_3$)]

Typical spectra are shown in Figures 1—3 and the experimental g and hyperfine tensors are given in Tables 1 and 2. The spectra were all interpreted in terms of an $^2A_1$ ($ad_{z^2} + bd_{x^2-y^2}$) ground state comprising a mixture of d_{z^2} and $d_{x^2-y^2}$ metal orbitals with coefficients such that $a^2 + b^2 = 1$. We use the group theory notation for C_{2v} symmetry which is used by most workers, recognising that the point group symmetry in reality is C_s at best.

The Cobalt Hyperfine Tensor.—For analysis of the g tensor and cobalt hyperfine tensor, we make use of the theory of low-spin d^7 ions which McGarvey[6] has developed and which is described in Part 1.[1] No assumptions were made about the sign of the cobalt hyperfine coupling constants, but the only reasonable fit of the experimental data to the theoretical expressions was obtained when A_z was positive and A_x and A_y negative. This is in accord with the conclusions of others who have made this analysis for ligands co-ordinating *via* phosphorus.[7-10] Earlier we said that A_x could not be measured and that the value of A_x selected had little effect upon the bonding parameters. The value selected was estimated from line widths, but a change of 25% in A_x only has <1% effect upon C_1 and C_2, 0.2% effect on C_3, 0.2% effect upon a and b, 1.7% effect on P, and 5% effect on κ.

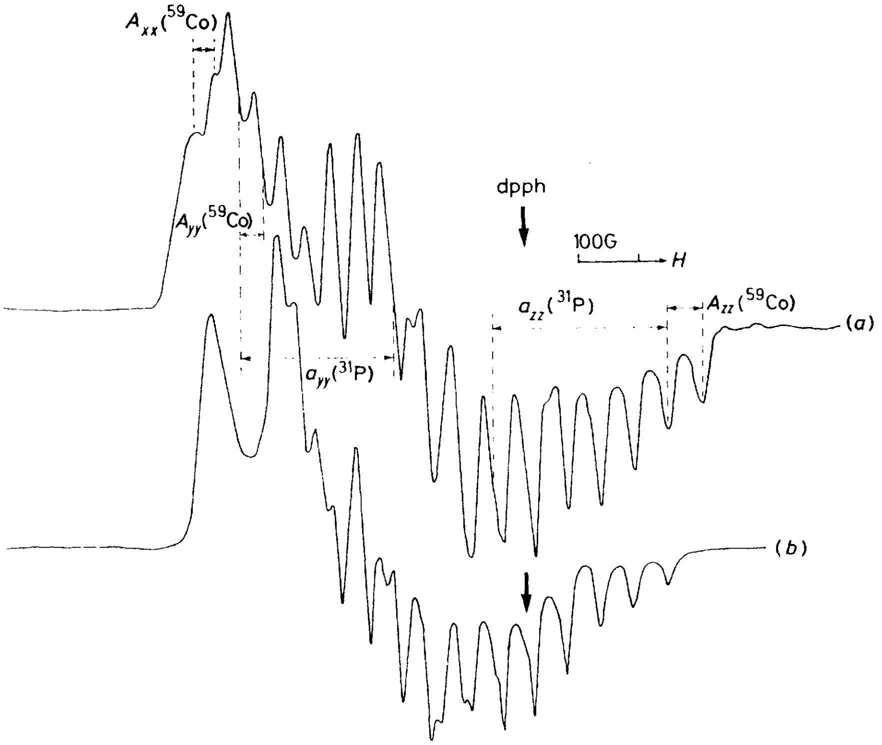

FIGURE 2 Frozen solution e.s.r. spectra at 77 K of (a) [Co(dbms)$_2${P(OPh)$_3$}] and (b) [Co(dbms)$_2$(PPh$_3$)]

Cobalt Spin Densities.—From the deduced values of a^2, we find that as before the contribution of the d_{z^2} orbital to the ground state of the cobalt is about 99%. The spin density in this cobalt orbital (C_{3d}^2) is given by the ratio of P/P^{2+} where $P = g_e g_N \beta_e \beta_N \langle r^{-3} \rangle$ (from our calculations) and P^{2+} is the value calculated for the free Co^{2+} ion.[11] Values of C_{3d}^2 vary considerably with different phosphines and with the equatorial ligating atom. Thus for any one phosphine, C_{3d}^2 for [Co(salphen)] and [Co(mosalen)] are much larger than for [Co(sacsac)$_2$], and intermediate for [Co(dbms)$_2$]. The absence of nitrogen hyperfine coupling to the equatorial nitrogen atoms shows that there is very little spin delocalisation *via* σ bonding from the x and y components of the d_{z^2} orbital to the equatorial ligating atoms. Since the total spin density in the cobalt $d_{z^2} + d_{x^2-y^2}$ orbital and in the P→Co σ bond (sp^n hybrid) for the thio-complexes is so much less than unity, and there is not likely to be much spin density straying beyond the phosphorus atom, then the balance of spin density must be delocalised into the Schiff base *via* π bonding. This is in accord with the expected increase in the π bonding to S and was found also for [Co(sacen)], [Co(seacen)], and [Co(sbzacen)].[1] In the previous paper we suggested that the cobalt must be significantly out of plane and the molecule is saddle-shaped to accommodate this π bonding. As the strength of the bonds between cobalt and the ligating atoms increases in association with axial co-ordination, so will the cobalt move further out of the plane. This postulate is supported by the absence of any 2 : 1 adducts formed even in neat phosphines. Only in the case of cobalt complexes with strictly planar equatorial ligands are 2 : 1 adducts formed.[10,12] Our spin-density calculations can account for all of the unpaired electron in [Co(salphen)] and [Co(mosalen)] complexes, thus suggesting that little if any is delocalised onto the Schiff base, whereas with [Co(sacsac)$_2$], as much as 25% of the unpaired electron is delocalised onto the equatorial ligands. Actually, our spin-density calculations over-

TABLE 1

g and ^{59}Co hyperfine tensors and deduced parameters *

Complex	Axial ligand (L)	g_x	g_y	g_z	$g_{av.}$	Hyperfine coupling $-A_x$	$-A_y$	A_z	P	κ	a^2	b^2	Coefficients C_1	C_2	C_3	Spin densities C_{3d}^2	C_{4s}^2	C_L^2	Orbital energies/cm^{-1} ΔB_1	ΔB_2	ΔQ
[Co(sacsac)$_2$]	P(OMe)$_3$	2.138	2.118	2.023	2.093	47	48	48	148	0.168	1.000	0.000	0.016	0.019	0.104	0.58	0.020	0.125	19 230	16 230	2 980
	P(OEt)$_3$	2.133	2.116	2.027	2.092	47	47	48	147	0.160	1.000	0.000	0.015	0.018	0.113	0.58	0.020	0.124	20 340	17 550	2 730
	P(OPh)$_3$	2.175	2.107	2.018	2.100	48	48	50	156	0.174	0.999	0.001	0.016	0.025	0.093	0.61	0.020	0.115	20 700	12 980	3 530
	P(OEt)$_2$Ph	2.129	2.118	2.023	2.090	45	48	51	151	0.154	1.000	0.000	0.016	0.018	0.104	0.59	0.022	0.118	20 040	17 600	3 050
	PBu$_3$	2.200	2.106	2.021	2.109	41	46	43	143	0.180	0.999	0.001	0.015	0.029	0.102	0.56	0.017	0.110	19 920	10 400	2 950
	PPh$_3$	2.360	2.098	2.016	2.158	45	43	48	187	0.203	0.984	0.016	0.018	0.049	0.101	0.74	0.019	0.082	22 060	7 940	3 900
	dppe	2.289	2.105	2.020	2.138	45	45	48	171	0.189	0.993	0.007	0.017	0.040	0.104	0.67	0.020	0.101	21 270	8 890	3 440
[Co(dbms)$_2$]	PPh$_3$	2.422	2.157	2.027	2.202	5	30	57	171	0.117	0.998	0.002	0.025	0.062	0.130	0.67	0.030	0.108	14 540	5 830	2 760
	P(OPh)$_3$	2.406	2.150	2.032	2.196	15	43	57	193	0.151	0.998	0.002	0.022	0.059	0.138	0.76	0.028	0.147	18 250	6 910	2 940
[Co(mosalen)]	P(OMe)$_3$	2.418	2.179	2.025	2.207	12	28	76	228	0.117	0.994	0.006	0.030	0.060	0.125	0.90	0.040	0.186	15 760	8 000	3 820
	P(OEt)$_3$	2.384	2.184	2.029	2.199	12	28	73	210	0.104	0.997	0.003	0.029	0.055	0.130	0.83	0.039	0.190	15 000	7 960	3 380
	P(OPh)$_3$	2 426	2 173	2 019	2 206	12	29	82	246	0.119	0.993	0.017	0.031	0.062	0.114	0.97	0.042	0.150	16 830	8 390	4 530
	P(OEt)$_2$Ph	2.353	2.175	2.030	2.186	12	26	75	202	0.083	0.998	0.002	0.027	0.051	0.130	0.80	0.041	0.186	15 710	8 330	3 260
	PBu$_3$	2 433	2.169	2 025	2.209	12	29	69	215	0.127	0.993	0.007	0.029	0.061	0.127	0.85	0.036	0.135	15 620	7 340	3 570
	PPh$_3$	2.449	2.168	2.106	2.211	12	26	84	254	0.124	0.990	0.010	0.031	0.064	0.110	1.00	0.043	0.120	16 960	9 320	4 860
	dppe	2.435	2.167	2.022	2.208	12	28	78	236	0.120	0.992	0.008	0.029	0.062	0.121	0.93	0.040	0.121	16 830	8 020	4 100
[Co(salphen)]	P(OMe)$_3$	2 408	2.184	2.029	2.207	12	31	76	229	0.116	0.996	0.004	0.030	0.058	0.132	0.90	0.040	0.195	16 090	8 220	3 640
	P(OEt)$_3$	2.407	2.174	2.028	2.203	12	34	76	229	0.117	0.997	0.003	0.028	0.059	0.130	0.90	0.040	0.195	17 130	8 200	3 690
	P(OPh)$_3$	2 422	2 181	2.024	2.209	12	29	82	248	0.116	0.994	0.006	0.031	0.060	0.124	0.98	0.043	0.159	16 770	8 610	4 210
	P(OEt)$_2$Ph	2.382	2.165	2.026	2.191	12	35	74	213	0.110	0.998	0.002	0.026	0.056	0.125	0.84	0.038	0.158	17 170	8 000	3 580
	PBu$_3$	2.409	2.172	2.025	2.202	12	30	68	206	0.122	0.996	0.004	0.029	0.059	0.125	0.81	0.035	0.127	15 160	7 330	3 470
	PPh$_3$	2.447	2.176	2.025	2.216	12	26	82	253	0.119	0.990	0.010	0.031	0.063	0.127	1.00	0.043	0.124	17 040	8 490	4 170
	dppe	2.447	2.163	2.020	2.210	12	32	76	238	0.133	0.992	0.008	0.029	0.064	0.118	0.94	0.038	0.132	17 210	7 820	4 230

* A_x, A_y, A_z, and P are in cm^{-1} × 10^{-4}.

estimate the spin density on the cobalt, and this will be discussed later.

The cobalt spin density for any one Schiff-base complex varies in a consistent way. Thus, for the phosphite, P decreases in the order P(OPh)$_3$ > P(OMe)$_3$ ≈ P(OEt)$_3$ > P(OEt)$_2$Ph and for the phosphines, PPh$_3$ > dppe > PBu$_3$ [dppe = 1,2-bis(diphenylphosphino)ethane]. The explanation for this will be given after consideration of the phosphorus hyperfine tensor see below.

Since in C_{2v} or lower symmetries, the d_{z^2} orbital can mix with s orbitals, then the value of $A_{iso.}$ (^{59}Co) arises from a combination of real spin density in the 4s orbital together with a contribution from spin polarisation of

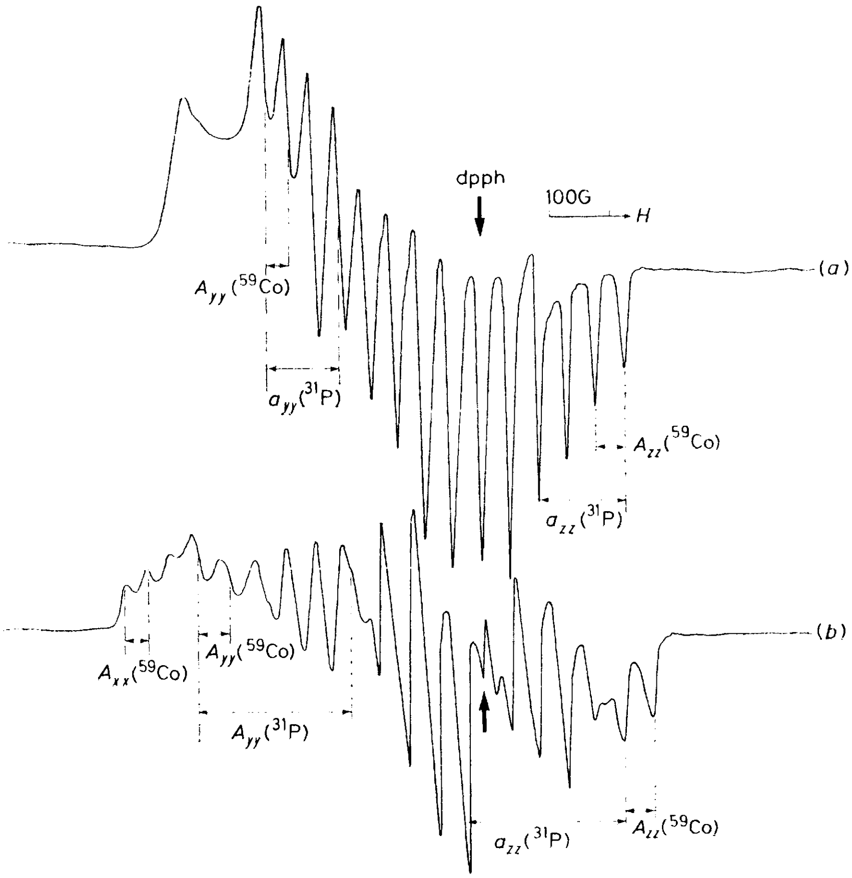

FIGURE 3 Frozen solution e.s.r. spectra at 77 K of (a) [Co(sacsac)$_2$(PPh$_3$)] and (b) [Co(sacsac)$_2${P(OPh)$_3$}]

filled *s* orbitals by the unpaired electron. This contribution is of opposite sign to that of real spin density. Symons and Wilkinson[13] have formulated a semi-quantitative relationship whereby the contact term $-\kappa P$ is defined as in equation (1). In this equation,

$$-\kappa P = C_{4s}^2 A_{\text{iso.}}(4s) + C_{3d}^2 A(3d \text{ polarisation}) \quad (1)$$

C_{4s}^2 is the real spin density in the cobalt 4*s* orbital, $A_{\text{iso.}}(4s) = 1\,232 \times 10^{-4}$ cm^{-1}, C_{3d}^2 is the spin density in the 3*d* orbital ($P/0.0254$), and $A(3d$ polarisation) is the value estimated by McGarvey[14] for the polarisation contribution to $A_{\text{iso.}}$ (-84×10^{-4} cm^{-1}) from an electron entirely in a 3*d* orbital. Values of C_{4s}^2 range from *ca.* 1.7—4.5% and are typical of those found for other low-spin cobalt(II) complexes. However, closer analysis shows that the range of C_{4s}^2 found in all the complexes studied in this and in the previous paper is greater than that found by Symons and Wilkinson[13] for a range of four-, five-, and six-co-ordinate complexes having similar ligating atoms (C-bonded). Thus, whilst Symons and Wilkinson found that C_{4s}^2 was dependent upon co-ordination number (ranging from 3 to 6.5%, increasing with decrease in co-ordination number), there is a further effect that C_{4s}^2 is dependent upon the ligand atom electronegativity (increasing with increase in electronegativity). Thus, for PPh$_3$ adducts of Co^{II} with various equatorial ligands, C_{4s}^2 is 4.5 for bzacen (' N_2O_2 '), 4.3 for salphen (' N_2O_2 '), 3.95 for sacen (' N_2S_2 '), 3.0 for dbms (' O_2S_2 '), and 1.9 for sacsac (' S_4 '). The results for other phosphines and phosphites follow the same pattern with, in general, C_{4s}^2 varying as PPh$_3$ > P(OPh)$_3$, dppe > P(OMe)$_3$ ≈ P(OEt)$_3$ > P(OEt)$_2$Ph > PBu$_3$. The range in values of C_{4s}^2 is 1.7—4.5% and for any one phosphine or phosphite, there is a range of up to 2.6% units over the complexes studied. Thus the range in our values of C_{4s}^2 for different adducts is as great as that for different co-ordination complexes of the type [Co(CNR)$_n$] (n = 4—6). We suspect that the trend in the amount of the 4*s* orbital which can mix with the d_{z^2} orbital is primarily related to the electronegativity of the equatorial ligands. For the ligating atoms O, N, and S, the order of stability of the a_1 bonding molecular orbital (m.o.) (d_{z^2} + ligand) will be O > N > S, whilst that for the corresponding antibonding m.o. (a_1^*) will be S > N > O. Since symmetry allows some mixing of 4*s* with d_{z^2}, then the a_1^* energy level of the O complexes will be nearer the 4*s* energy level than in the N or S complexes. Hence, the amount of mixing of 4*s* with the d_{z^2} orbital containing the unpaired electron will decrease in the order O > N > S. No mixing of *s* with d_{z^2} can occur in strictly O_h or T_d molecules.

The g *Tensor*.—The large separation between g_x and g_y reflects the strong perturbing effect by the asymmetry of the equatorial ligating atoms of the Schiff base. This in turn will influence the π bonding to the phosphorus and unbalance the phosphorus hyperfine tensor. The effect of σ bonding between the phosphorus and the cobalt upon the cobalt energy levels is such as to destabilise the d_{z^2} orbital containing the unpaired electron, whilst π bonding will stabilise the d_{xz} and d_{yz} orbitals. Thus changes in g_x and g_y will reflect the net change in σ and π bonding in the Co–P bond. As a consequence, it is unfortunately not possible to make a useful correlation because the two effects cannot be separated.

From the equations of McGarvey,[6] the energy separations $\Delta B_1(d_{z^2} - d_{xz})$, $\Delta B_2(d_{z^2} - d_{yz})$, and ΔQ (average energy of quartet states above ground state) can easily be calculated. The values of ΔB_1 and ΔB_2 are *ca.* 16 000 and 8 000 cm^{-1} respectively for [Co(mosalen)], and for [Co(salphen)] they are slightly larger. For [Co(sacsac)$_2$], the values are both much larger. The energy gap for all complexes, ΔQ, is much smaller, *ca.* 3 000—4 000 cm^{-1}, and shows how important these low-lying quartet states are. One problem which cannot be resolved unambiguously is whether the principal directions of the *g* and the *A* (^{59}Co) tensors are collinear or not. No e.s.r. single-crystal study has been carried out on any relevant adduct molecule nor does, at present, any adduct seem amenable for such a study since no corresponding isostructural diamagnetic nickel or zinc analogue is known. In this work, as in that of others, the axes are assumed collinear because of the strong axial domination by the phosphine or phosphite. In contrast, the low-spin parent complexes (d_{z^2} ground state) have non-collinear tensors; *e.g.* in Vitamin B_{12r}[15] and [Co(sacen)],[16] the directions of the in-plane *g* and *A*(^{59}Co) principal directions are separated by 50° and 37° respectively.

The Phosphorus Hyperfine Tensor.—Since the unpaired electron in an orbital of A_1 symmetry interacts directly with the phosphorus atom, the isotropic hyperfine coupling will be positive. The value of A_x could not be determined with accuracy and was calculated from A_y, A_z and $A_{\text{iso.}}$, assuming that A_y and A_z were both positive as would be expected. The anisotropic tensor was calculated after correction for indirect dipolar coupling. The correction used the dipolar approximation and assumed a value of 0.25 nm for the Co–P bond distance. The principal value of this tensor was 2 G * (to the nearest integer). Experimental hyperfine couplings on each *g* feature were not converted to cm^{-1}, there being no need to correct them for spin–orbit coupling (unlike those for Co) because both the value of the spin–orbit coupling constant for ^{31}P is lower and the spin density on P is very small.

The corrected anisotropic hyperfine tensor was strongly asymmetric and was decomposed into two tensors. The choice of which two, of the three possible tensors, was governed by the obvious need for the principal direction of one tensor to be along the Co–P bond (the *z* axis). The principal direction of the second tensor could be along either the *x* or the *y* axes. Each was considered in turn. When the second tensor was directed along the *y* axis, the principal value was large

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* Throughout this paper: 1 G = 10^{-4} T.

and positive (2—4 times that of the first tensor). This was rejected because there is no way in which positive spin density can get into a p (or d) orbital on phosphorus along the y axis. On the other hand, when the second tensor was along the x axis, the principal value was negative and could readily be explained by spin polarisation.

TABLE 2

^{31}P hyperfine tensors and deduced parameters. The units of hyperfine coupling are in Gauss

Complex	Axial ligand (L)	Experimental hyperfine coupling				Anisotropic hyperfine tensor			Principal values of decomposed tensors		Spin densities on ^{31}P				
		A_x	A_y	A_z	$A_{iso.}$	A_{xx}	A_{yy}	A_{zz}	A_{zz}	A_{xx}	C_{3s}^2	C_{3p}^2	Total	λ^2	θ
[Co(sacsac)$_2$]	P(OMe)$_3$	226	264	284	258	−31	7	24	11	−25	0.070	0.054	0.125	0.78	99° 48′
	P(OEt)$_3$	222	260	280	254	−31	7	24	11	−25	0.069	0.054	0.124	0.79	99° 54′
	P(OPh)$_3$	262	278	294	278	−15	1	14	8	−10	0.076	0.040	0.115	0.52	96° 25′
	P(OEt)$_2$Ph	207	236	256	233	−25	4	21	11	−19	0.063	0.054	0.118	0.86	99° 28′
	PBu$_3$	141	167	190	166	−24	2	22	13	−16	0.045	0.064	0.110	1.43	103° 5′
	PPh$_3$	110	170	185	155	−44	16	28	8	−39	0.042	0.040	0.082	0.94	100° 5′
	dppe	106	164	186	152	−45	13	32	12	−38	0.041	0.059	0.101	1.44	103° 8′
[Co(dbms)$_2$]	PPh$_3$	103	152	177	144	−40	9	31	14	−32	0.039	0.069	0.108	1.77	105° 41′
	P(OPh)$_3$	210	256	284	250	−39	7	32	16	−30	0.068	0.079	0.147	1.16	102° 36′
[Co(mosalen)]	P(OMe)$_3$	198	250	290	246	−47	5	42	24	−34	0.067	0.119	0.186	1.78	105° 42′
	P(OEt)$_3$	198	245	286	243	−44	3	41	25	−31	0.066	0.124	0.190	1.87	105° 6′
	P(OPh)$_3$	212	270	298	260	−47	11	36	16	−38	0.071	0.079	0.150	1.12	101° 19′
	P(OEt)$_2$Ph	183	233	274	230	−46	4	42	25	−33	0.063	0.124	0.186	1.98	106° 30′
	PBu$_3$	129	175	206	170	−40	6	34	18	−30	0.046	0.089	0.135	1.93	105° 18′
	PPh$_3$	106	158	186	150	−43	9	34	16	−34	0.041	0.079	0.120	1.94	105° 22′
	dppe	102	158	195	155	−52	14	38	16	−43	0.042	0.079	0.121	1.88	105° 7′
[Co(salphen)]	P(OMe)$_3$	195	247	290	244	−48	4	44	26	−34	0.066	0.129	0.195	1.94	105° 21′
	P(OEt)$_3$	195	246	288	243	−47	4	43	26	−33	0.066	0.129	0.195	1.95	105° 23′
	P(OPh)$_3$	210	264	294	256	−45	9	36	18	−36	0.070	0.089	0.159	1.28	102° 17′
	P(OEt)$_2$Ph	190	240	272	234	−43	7	36	19	−33	0.064	0.094	0.158	1.48	103° 21′
	PBu$_3$	134	180	208	174	−39	7	32	16	−30	0.047	0.079	0.127	1.67	104° 16′
	PPh$_3$	105	155	184	148	−42	8	34	17	−32	0.040	0.084	0.124	2.09	106° 54′
	dppe	104	170	200	158	−53	13	40	18	−43	0.043	0.089	0.132	2.07	106° 51′

We would like to point out that in most publications reporting a strongly asymmetric ligand hyperfine tensor, the authors rarely correct for indirect dipolar coupling nor decompose the tensor into two axial tensors, merely taking the largest positive value for subsequent calculations of spin densities. Such calculations are wrong. Our results and calculations are given in Table 2.

Spin polarisation of phosphorus p_x and p_z π electrons by an unpaired electron in a Co–P σ orbital must be contrasted with the much more common spin polarisation of σ electrons (*e.g.* α C–H) by an unpaired electron in a C $p_z(\pi)$ orbital as frequently found in organic radicals. In our molecules, the d_{z^2} (α-spin) unpaired electron polarises each of the pairs of electrons in the $3d_{xz}$(Co)–$3p_x$(P) and $3d_{yz}$(Co)–$3p_y$(P) π bonds to give some β spin in the $3p_x$ and $3p_y$ orbitals on phosphorus (see Figure 4). Likewise, there will be some polarisation of the non-bonding $2p_x$ and $2p_y$ electron pairs on phosphorus but this is likely to be a much smaller effect. If the d_{xz} and d_{yz} cobalt orbitals are equal in energy, then they will be polarised equally and transmission of apparent spin density onto $3p_x$ and $3p_y$ phosphorus orbitals will be equal and effectively cancel each other out. The result will be an axially symmetric phosphorus hyperfine tensor. On the other hand, if the d_{xy} and d_{yz} cobalt orbitals are different in energy, then polarisation of the electron pairs in these orbitals will be to different extents with the result that the apparent spin density in the $3p_x$ and $3p_y$ phosphorus orbitals will be different. This difference in apparent spin density in the x and y directions will contribute to the anisotropic hyperfine tensor such as to reduce its symmetry from axial. Our attempts to decompose the corrected anisotropic hyperfine tensor in all cases yield two possible pairs of tensors. Using the example of [Co(salphen){P(OMe)$_3$}], the corrected anisotropic hyperfine tensor is (in Gauss: x, y, z) −48, 4, 44, which decomposes into either (a) −13, −13, 26 G (tensor 1) and −34, 17, 17 G (tensor 2) or (b) −31, −31, 62 G (tensor 1) and −17, 34, −17 G (tensor 2). In (a) the principal value of tensor 1, A_{zz}, 26 G (z), is positive and represents 12.9% spin density in the phosphorus $3p_z$ orbital, whilst the principal value A_{xx} of tensor 2, −34 G (x), is negative and arises from the imbalance (difference) in the polaris-

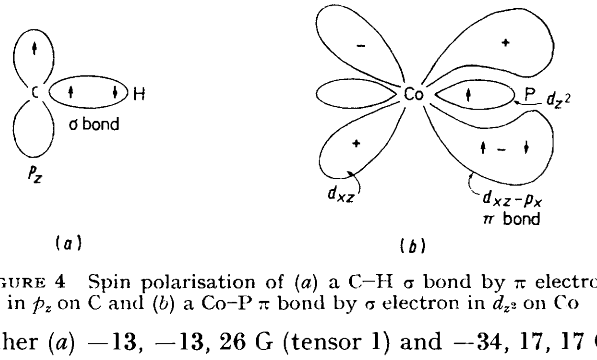

FIGURE 4 Spin polarisation of (a) a C–H σ bond by π electron in p_z on C and (b) a Co–P π bond by σ electron in d_{z^2} on Co

ation of the $3p_x$ and $3p_y$ orbitals. In the alternative pair of decomposed tensors, (*b*), the principal value, A_{zz}, 62 G (z) is suspiciously high and would represent 31% spin density in the phosphorus $3p_z$ orbital. Furthermore, the principal value of the second tensor, A_{yy}, 34 G (y) is positive. Since there is no mechanism for positive spin density to get into the p_x or p_y orbitals on phosphorus, and this value is far too high anyway ($\equiv$17% spin density in $3p_y$ orbital), then we reject (*b*) as a possibility.

Polarisation of the Co–P bonding electrons by the d_{z^2} electron will also contribute to the polarisation of $3p_x$ and $3p_y$ orbitals. In an axially symmetric system, $3p_x$ and $3p_y$ are degenerate and they will be equally polarised, but in lower symmetry, there will be polarisation to differing extents and this will contribute to the tensors (*a*) described above.

In summary, we see that there are several electron pairs involved in spin polarisation by the d_{z^2} electron, some of which are very close to the d_{z^2} electron. It would seem that the magnitude of polarisation could be very large although our numbers represent differences in polarisation in the x and y directions. These values at first sight seem rather large, especially in comparison with the more common types of polarisation seen in organic and inorganic radicals. Hunter and Symons [17] have shown for these classes of radicals that spin polarisation rarely exceeds 4% of the spin density in the adjacent atom π orbital, so our values of 10—20% spin polarisation are very high, but perhaps not unreasonably high in view of the comments above. To our knowledge this situation has not been noted before.

The magnitude of the spin polarisation tensor, A_{x} (being a difference in the polarisations in the x and y directions), must be related to the rhombic distortion in the molecule, since it disappears in axially symmetrical molecules. The amount of rhombic distortion may be calculated from the cobalt hyperfine and g tensors. Some of the parameters deduced in solving the McGarvey [6] equations are related to the energy of excited states. In particular, the excited doublet state ^2E (in C_{4v} symmetry) is split in rhombic symmetry to $^2B_1(d_{xz})$ and $^2B_2(d_{yz})$ $[C_{2v}(z)]$. The energies above the ground state of these two states, Δ^2B_1 and Δ^2B_2, are given by equations (2) and (3), where C_1 and C_2 are deduced

$$C_1 = \frac{\lambda C_{3d}{}^2\beta_{b1}{}^2}{\Delta^2B_1} \qquad (2)$$

$$C_2 = \frac{\lambda C_{3d}{}^2\beta_{b2}{}^2}{\Delta^2B_2} \qquad (3)$$

parameters in McGarvey's equation, the β^2 terms approximate to 1, and λ is the free-ion spin–orbit coupling constant for Co^{2+} (533 cm^{-1}). The energy difference $C_1 - C_2$ we call Δ. We have plotted A_{xx} against Δ for all the results in this and the previous paper and calculated the correlation coefficient for the data. We have calculated Δ for each adduct using the different assumptions involved in the solution of the McGarvey equations; these results are summarised in Table 3. It is immediately apparent that there is a good correlation (0.78—0.84) in three of the cases considered.

Spin Density on Phosphorus.—From the principal value of the first decomposed tensor (A_{zz}), the unpaired-electron spin density $C_p{}^2$ in the phosphorus $3p$ orbital is given by $A_{zz}/A_p{}^{100}$, where $A_p{}^{100} = 202$ G.[11] The value of $C_s{}^2$, the spin density in the phosphorus $3s$ orbital, is given by $A_{iso.}/A_p{}^{100}$ where $A_s{}^{100} = 3\,676$ G.[11] The ratio $C_p{}^2/C_s{}^2 = \lambda^2$ and gives the hybridisation in the orbital concerned. This value of λ was then used in the Coulson [11] equation for calculating the angle R–P–R(θ) in symmetrical C_{3v} groups like PR_3 co-ordinated to a metal. The calculation for those complexes involving $P(OEt)_2Ph$ and dppe adducts yields a less meaningful effective angle. Differences between θ for any one phosphine or phosphite when co-ordinated to the similar Schiff bases [Co(salphen)] and [Co(mosalen)] are negligible. With [Co(sacsac)$_2$], the angle is smaller and may result from some steric interaction with the equatorial ligands.

TABLE 3

The various assumptions in the solution of the McGarvey equations and correlation coefficients for all adducts with [Co(salphen)]

Assumptions	Range of total electron density	Average total electron density	Correlation coefficient A_{xx} *vs.* $\Delta B_1 - \Delta B_2$
$C_3 = C_1 = C_5, C_6 = 0$	0.99—1.21	1.13	0.84
$C_4 = C_5 = C_6 = 0$	1.04—1.26	1.18	0.78
$C_3 = C_4 = C_5 = 0$	0.84—1.02	0.96	0.78
$C_3 = C_4 = C_5, a^2 = 0.99$	0.85—1.17	1.02	0.57

The trends within each group reflect the known increased σ-donating power (inductive effect) in the phosphine series Bu > dppe > Ph and in the phosphite series OEt > OMe > OPh. Thus the inductive effect in PBu_3 pushes spin density in the d_{z^2} orbital away from the cobalt onto the equatorial ligands and lowers P.

Theoretical Treatment of Low-spin Cobalt(II) *in Low Symmetry.*—The theoretical treatment for the ground-state e.s.r. of low-spin Co^{II} d^7 was first worked out by Griffith [18] and subsequently extended by Maki *et al.*,[19] Engelhardt and Green,[20] Busetto *et al.*,[21] and Bentley *et al.*[22] A major improvement in the theory came when Parker [23] realised that the formal similarity assumed between d^7 and d^9 configurations did not strictly exist, mainly because the excited states for d^7 and d^9 are quite different. Parker assumed a $3d^3$ hole configuration, using a strong cubic field approach throughout. His equations incorporated terms involving quartet as well as doublet excited states. The latest approach is that of McGarvey [6] who used only the d wave functions, applying perturbation theory to third order and included these low-lying quartet states and their related doublet states which can be coupled to the doublet ground state by spin–orbit coupling. These states contribute to g only in third order or higher, but contribute to the hyperfine terms in second order and so can be as important as the excited doublet states normally included in previous calculations.

There are two approaches to the calculation of the solutions to the McGarvey equations. Either (*i*) the coefficients can be varied systematically until what appears to be the best fit with the experimental results is obtained. How good that fit is, is often a matter of opinion and is never quantified by the authors who use this method. Alternatively, (*ii*) the experimental results can be used with Powell's non-linear equations hybrid minimisation method to obtain values of the unknowns.[24] We have preferred to use the latter method since it makes use of the experimental data to the fullest extent (and these are the only facts to go on and must be used), and also because the computing is so much simpler with no less accuracy. Nevertheless, because there are 13 unknowns for the non-axial case, and only seven equations, approximations have to be made amongst the range of nine molecular orbital coefficients. It is this choice of approximations which is at the root of potential controversy, and in particular, the debate ranges over whether quartet states contribute to any significant extent.

Method (*i*) has been used by most workers and, we believe, is the root of much error and self deception. For example, McGarvey [6] tests his five equations upon the results of Walker [12] with axially symmetric adducts of cobalt tetraphenylporphyrin derivatives. Values of P so deduced range from 0.011 7 to 0.052 1 cm^{-1} for pyrene and 1,3,5-trimethoxybenzene adducts respectively. Since P for the free Co^{2+} ion is 0.026 5 cm^{-1}, then it is difficult to account for values around 0.025 4 cm^{-1}, let alone those almost twice as large. Attanasio *et al.*[16] likewise calculate a value of $P = 0.029\,3$ cm^{-1} for Co^{2+} in a single crystal of [Co,Zn(sacen)]. Pezeshk *et al.* [8] consider a range of values for the C_n parameters, testing the effect, or not, of incorporating the quartet states by using five of McGarvey's equations. The remaining equation was used to calculate A_z, which was then compared with the experimental value to determine whether suitable agreement was reached. However, they do not define what tolerance is placed on the suitable agreement. Mathematically, this is an unsound approach to solving such equations. Pezeshk *et al.* in another paper [7] use the observation that if C_3 and C_4 (see ref. 1) are both zero (*i.e.* two of the three quartet states are not considered) then $g_z < g_e$ for any value of b. They use this observation to prove that low-lying quartet states are not negligible.

This leads to the crucial decision as to what assumptions must be made to solve McGarvey's equations. Everyone agrees that C_3', C_4', and C_5' (see ref. 1) are very small and can even be made equal to zero because the corresponding energy levels are all of high energy, at least 15 000 cm^{-1} above the corresponding quartet states. The first point of controversy is whether C_3, C_4, and C_5 are zero (*i.e.* quartet states are ignored). McGarvey argues that when adducts are formed, the energy of the quartet states becomes much lower.[6] Thus for non-adduct molecules he ignores quartet states. Only Pezeshk *et al.*, in two papers on adducts of a cobalt(II) macrocyclic Schiff base (N_4 type), have made calculations on adducts.[7,8] In one paper,[7] taking C_4, C_5, and C_6 equal to 0, the deduced parameters are all quite reasonable for adducts with thiazole, pyridine, $P(OEt)_3$, and PEt_3, whilst in the other paper,[8] they argue that the values C_3, C_4, C_5, and C_6 have little effect upon the calculated values of κ, P, C_1, and C_2.

Our approach to the problem has been to consider in turn different reasonable assumptions and assess the value of each by two criteria, namely that the total calculated unpaired-electron spin density ($\Sigma C_d^2 + C_s^2 + C_L^2$) should be *ca.* 1, and that the calculated difference in energy of the excited states $^2B_1$ and $^2B_2$, which are a measure of the rhombic distortion, should be related to the phosphorus hyperfine tensor. Our first assumption that all quartet states should be ignored yields total spin densities for adducts of [Co(salphen)] which range from 0.84 to 1.02. Whilst this range seems very reasonable, and there is a good correlation between the ^{31}P spin-polarisation tensor (A_{xx}) and the energy separation of d_{xz} and d_{yz} orbitals (Δ), the results are unacceptable because the assumption is invalid. There is strong evidence that quartet states are much lower in energy in adducts than in the square-planar complexes.[6] Pezeshk *et al.* [8] have assumed that the quartet parameters C_4 and C_5 each equal zero, but not C_3. This again is incorrect because the terms C_3 and C_4 are both *equally* important in McGarvey's equations for g_x and g_y.[6] The approach used by Attanasio *et al.* [16] who took the quartet parameters $C_3 = C_4 = C_5$ and $C_6 = 0$ yielded slightly higher spin densities but a better correlation between A_{xx} and Δ. We observed that values of a^2 were all between 0.987 and 1.0. We thought the constancy of this parameter would allow us to calculate another C parameter, C_6, and we took $C_3 = C_4 = C_5$ as before, with $a^2 = 0.99$. However, although the total spin densities were good, the correlation of A_{xx} with Δ was poor (0.57). Inspection of the McGarvey equations shows that all the C parameters are very sensitive to small changes in a, and thus it is impossible to treat a as a constant. These assumptions are given in Table 3. Our results calculated in Table 1 and in Part 1 [1] use the assumption $C_3 = C_4 = C_5$ and $C_6 = 0$.

Optical spectra were recorded with the object of seeing if the predicted absorptions ΔB_1 ($d_{z^2} - d_{xz}$) and ΔB_2 ($d_{z^2} - d_{yz}$) were visible. Upon addition of base, the visible spectrum changed from one with three or four well resolved bands to one with a very broad absorption with ill defined shoulders. Whilst these shoulders were roughly in the region predicted, we felt it unwise to draw firm conclusions from the spectra.

Adducts with Complexes of Axial Symmetry.—Some phosphine and phosphite monoadducts of square-planar complexes were investigated. With cobalt(II) phthalocyaninetetrasulphonate, $[Co(pts)]^{4-}$, the only solvent which gave good resolution of the e.s.r. spectrum was dimethyl sulphoxide. The other complex was cobalt(II) dimethylglyoximate, [Co(Hdmg)$_2$], which, although not of D_{4h} symmetry, nevertheless yielded spectra which were axially symmetric. The best solvents for this complex were chloroform mixed with either toluene or *NN*-dimethylformamide. The results are given in Tables 4 and 5, and the spin-Hamiltonian parameters were processed using the equation of McGarvey.[6] In axial symmetry, the $^2B_1$ and $^2B_2$ states are degenerate thus making $C_1 = C_2$, $C_3 = C_4$, $C_3' = C_4'$, $a = 1$, and $b = 0$ (for a d_{z^2} ground state). The seven McGarvey equations now reduce to four with six unknowns, C_1, C_3, C_5, C_3', κ, and P. C_3' is taken as zero as before, since it is at high energy, and the other assumption concerns C_3 and C_5. These are two quartet states and McGarvey assumes $C_5 = 0$ in his calculations. Since the quartet states are known to be low, we have decided to make $C_3 = C_5$ as before. In the calculations of our data, the assumption of $C_5 = 0$ would make P larger by 0.000 2, κ smaller by 0.004, and C_1 and C_3 both larger by 0.001.

TABLE 4

g and ^{59}Co hyperfine tensors and deduced parameters *

Complex	Axial ligand(L)	$g_\perp$	$g_\parallel$	$g_{av.}$	Hyperfine coupling $-A_\perp$	$A_\parallel$	P	κ	Coefficients C_1	C_3	Spin densities C_{3d}^2	C_{4s}^2	C_L^2	Orbital energies/cm^{-1} ΔB_1	ΔQ
[Co(pts)]$^{4-}$	P(OMe)$_3$	2.172	2.011	2.118	34	75	179	0.084	0.027	0.074	0.70	0.060	0.238	13 820	5 040
	PBu$_3$	2.177	2.012	3.122	34	80	193	0.088	0.028	0.078	0.76	0.038	0.169	14 470	5 190
[Co(Hdmg)$_2$]	P(OPh)$_3$	2.162	2.012	2.112	35	94	210	0.062	0.025	0.076	0.83	0.067	0.248	17 700	5 820
	PBu$_3$	2.154	2.018	2.109	30	75	174	0.070	0.023	0.093	0.69	0.057	0.181	15 990	3 950
	P(C$_6$H$_{11}$)$_3$	2.198	2.017	2.138	31	75	152	0.058	0.031	0.094	0.60	0.048	0.142	10 320	3 400
	PPh$_3$	2.150	2.016	2.105	32	87	193	0.052	0.023	0.087	0.76	0.060	0.119	17 610	4 660

* $A_\perp$, $A_\parallel$, and P are in cm^{-1} × 10^{-4}.

TABLE 5

^{31}P hyperfine tensors and deduced parameters *

Complex	Axial ligand(L)	Experimental hyperfine coupling $A_\perp$	$A_\parallel$	$A_{iso.}$	$A_{aniso.}$	Spin densities on ^{31}P C_{3s}^2	C_{3p}^2	total	λ^2	θ
[Co(pts)]$^{4-}$	P(OMe)$_3$	293	340	309	31	0.084	0.154	0.238	1.83	106° 57′
	PBu$_3$	193	227	204	23	0.555	0.114	0.169	2.07	106° 51′
[Co(Hdmg)$_2$]	P(OPh)$_3$	150	212	171	41	0.046	0.202	0.248	4.39	111° 53′
	PBu$_3$	140	185	155	30	0.042	0.149	0.181	3.54	110° 34′
	P(C$_6$H$_{11}$)$_3$	90	125	102	23	0.028	0.114	0.142	4.07	111° 26′
	PPh$_3$	120	145	128	17	0.035	0.084	0.119	2.41	107° 57′

* Hyperfine couplings are in Gauss.

A comparison can now be made between adducts of the less rigid Schiff bases [Co(mosalen)] and [Co(salphen)] with the much more rigid [Co(pts)]$^{4-}$ and [Co(Hdmg)$_2$]. In the former case, P and κ are both greater, ΔB_1 about the same, and the energy of the quartet states (ΔQ) lower than with the [Co(pts)]$^{4-}$ and [Co(Hdmg)$_2$] complexes. The distribution of spin density is such that in the latter two there is less localisation on the cobalt orbitals and less delocalisation onto the phosphorus. The R–P–R bond angles are larger in the square-planar complexes, although we do not have sufficient data to give a satisfactory reason for the trends other than to assume they are related to the amount the cobalt atom is above the plane of the ligands, even for [Co(pts)]$^{4-}$. In no case was there evidence for two ligands adding to the complex. The R–P–R bond angles of the large P(OPh)$_3$, PBu$_3$, and P(C$_6$H$_{11}$)$_3$ adducts of [Co(Hdmg)$_2$] are very significantly larger (*ca.* 111°) than in complexes with Schiff-base ligands.

The only other published phosphine and phosphite adducts of square-planar complexes have been by Wayland and Elmageed [10] who made adducts of cobalt(II) tetraphenylporphyrin. They analysed their data using perturbation theory to first order and their deductions are in broad agreement with ours.

We thank the S.R.C. for a grant (to G. L.).

[9/2030 *Received*, 31*st December*, 1979]

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