An Electron Spin Resonance Spectral Study of Bis(dimethylglyoximato)-cobalt(II) and some Phosphine and Phosphite Adducts†

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E.s.r. spectra, at both *X*- and *Q*-band frequencies, were measured for frozen solutions of [Co(Hdmg)$_2$] (H$_2$dmg = dimethylglyoxime) and its adducts with a range of fourteen phosphines and phosphites. All spectra were indicative of a $^2A_1$ $[a(d_{z^2}) + b(d_{x^2-y^2})]$ ground state, and from analysis of the cobalt and phosphorus hyperfine tensors and the *g* tensor, wavefunction and bonding parameters were calculated. The *Q*-band results unambiguously reveal rhombic symmetry for all adducts, with the formation of 1 : 1 adducts for all the bases with identical substituents and 1 : 2 adducts for the bases with mixed substituents. Attempts to assign the ground state to the [Co(Hdmg)$_2$] complex in a diamagnetic matrix of [Ni(Hdmg)$_2$] were also made.

Bis(dimethylglyoximato)cobalt(III) complexes are interesting because of their extensive co-ordination chemistry[1] and also as models for the organocobalamins[2] which are important cofactors for many enzymatic processes. Despite extensive structural and kinetic studies on cobaloximes,[1,3] the cobalt(II) species formed upon cleavage of the Co–C bond are not well characterized.[4,5] Cobaloximes with phosphine or phosphite donor bases have played an important role in the assessment of steric contributions to the *trans* labilization of the Co–C bond[3] in B$_{12}$ model compounds. In our earlier studies concerning the photoinduced cleavage of the Co–C bond in alkylcobaloximes it was found that different behaviours occurred in solution for cobaloximes having P or N donor bases. Whilst almost all cobaloximes with N-bound bases gave rise to six-co-ordinate species in solution, the corresponding cobaloximes with P-bound bases normally produced five-co-ordinate species as inferred from only one ^{31}P splitting in their *X*-band e.s.r. spectra. Most of P-base adducts with cobalt(II) complexes having Schiff bases or macrocyclic ligands are five-co-ordinate,[6–14] a situation that we find only with phosphines and phosphites having local C_{3v} symmetry, whereas six-co-ordination is the rule for bases having mixed substituents as inferred from the coupling to two ^{31}P atoms in the *Q*-band e.s.r. spectra.

While for the adducts of low-spin cobalt(II) complexes with Schiff bases it is well established that the ground state is $^2A_1$, there has always been some controversy about the ground state of the four-co-ordinate complexes, with some workers proposing $^2B_2$ and others $^2A_1$.[15–21]

Experimental

Sample Preparation.—The compound [Co(Hdmg)$_2$] (H$_2$dmg = dimethylglyoxime) was prepared under an inert atmosphere according to the method described by Schrauzer and Lee.[22] A solid solution of [Co(Hdmg)$_2$] in a [Ni(Hdmg)$_2$] matrix was prepared by the same method using mixtures of cobalt(II) and nickel(II) acetates in the proportions 1 : 100, 1 : 200, 1 : 500, and 1 : 1 000.

The phosphine and phosphite ligands (Aldrich) were used without any further purification with the exception of triphenylphosphine which was recrystallized twice from ethanol. All solvents were purified according to methods described in the literature,[23] kept under nitrogen, and deaerated with a stream of nitrogen gas for 30 min prior to use. The adducts with phosphorus ligands were prepared by adding known amounts (1 : 1 and 1 : 4) of the appropriate phosphine or phosphite to a solution of [Co(Hdmg)$_2$] in toluene–ethanol (10 : 1).

E.s.r. sample preparation was carried out under an inert atmosphere of dry nitrogen. The spectrum of [Co(Hdmg)$_2$] was obtained in mixtures of toluene with either CH$_2$Cl$_2$, CH$_3$OH, C$_2$H$_5$OH, dimethyl sulphoxide (dmso) or dimethylformamide (dmf) in a molar ratio of 10 : 1.

E.S.R. Measurements.—E.s.r. spectra were recorded at 100 and 293K at *X*- and *Q*-band frequencies on a Varian E-109 and a Bruker ER 200 (with a ER053 QRD bridge) spectrometer respectively. The spectra were calibrated with diphenylpicrylhydrazyl (dpph) and the *X*-band magnetic field was calibrated using Mn^{2+} in MgO. The *Q*-band spectra were calibrated using dpph.

Results

Upon addition of phosphorus Lewis bases, L [PR$_3$, P(OR)$_3$, PR$_{3-x}$R'$_x$, or P(OR)$_{3-x}$R'$_x$] to solutions of [Co(Hdmg)$_2$], new species formulated as [Co(Hdmg)$_2$L] and [Co(Hdmg)$_2$L$_2$] were formed as shown by e.s.r. spectra having hyperfine coupling to one or two equivalent phosphorus atoms. It is important to point out that 1 : 1 or 1 : 2 adduct formation is independent of base concentration up to a cobalt/base molar ratio of 1 : 4 as inferred by the absence of any e.s.r. spectral change. However, for all recorded species, no hyperfine coupling with the equatorial nitrogen atoms was observed. Formation of 1 : 1 adducts was observed for all bases with identical R groups, whereas formation of 1 : 2 adducts was observed with non-symmetrical bases.

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† *Supplementary data available* (No. SUP 56788, 7 pp.): e.s.r. theory. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

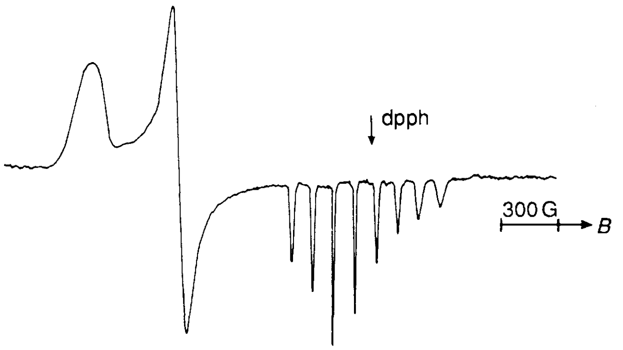

Figure 1. Q-Band spectrum of [Co(Hdmg)$_2$] in toluene–ethanol at 103 K

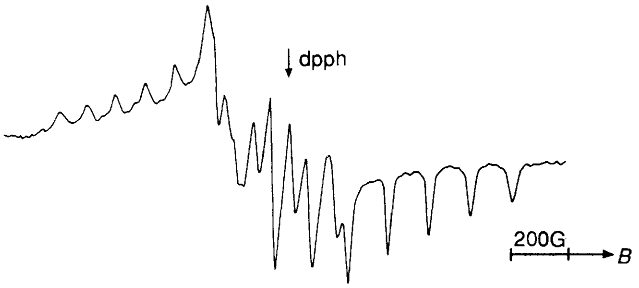

Figure 2. X-Band spectrum of [Co(Hdmg)$_2$] in [Ni(Hdmg)$_2$] at 103 K

In all cases analysis of the X- and Q-band spectra allows us to obtain the principal values of the g, $A(^{59}Co)$, and $A(^{31}P)$ tensors by computer simulation (see SUP 56788).

E.S.R. Spectra of [Co(Hdmg)$_2$] *in Solution.*—Frozen-solution e.s.r. spectra of [Co(Hdmg)$_2$] were recorded in toluene–CH_2Cl_2, –CH_3OH, and –C_2H_5OH (all in 10:1 molar ratio) and show no dependence on the solvent used. Q-Band spectra recorded under the same conditions clearly exhibit three well spaced g features (Figure 1).

E.S.R. Spectra of [Co(Hdmg)$_2$] *in* [Ni(Hdmg)$_2$].—The spectra of [Co(Hdmg)$_2$] coprecipitated in a diamagnetic matrix of [Ni(Hdmg)$_2$] are very different from those observed in solution. The X-band spectrum extends over a wider range of magnetic field and is shown in Figure 2.

Adduct E.S.R. Spectra.—1:1 *Adducts.* Frozen-solution X-band e.s.r. spectra recorded at 103 K were usually well resolved but in most cases three g features could not be clearly seen. In all spectra the high-field region (g_z) exhibits cobalt hyperfine coupling (^{59}Co, $I = \frac{7}{2}$) and phosphorus superhyperfine coupling (^{31}P, $I = \frac{1}{2}$). For this region it was possible to obtain directly from the spectra good values of g_z and of the cobalt and phosphorus hyperfine couplings. At lower fields the lines also exhibit hyperfine coupling to cobalt and phosphorus atoms but it was not possible directly to get good values either for the g tensor or for the hyperfine couplings (Figures 3 and 4).

A satisfactory simulation of these spectra requires the input of 12 parameters [the three principal values of the g, A(Co), and A(P) tensors, and the anisotropic linewidths] and unambiguous

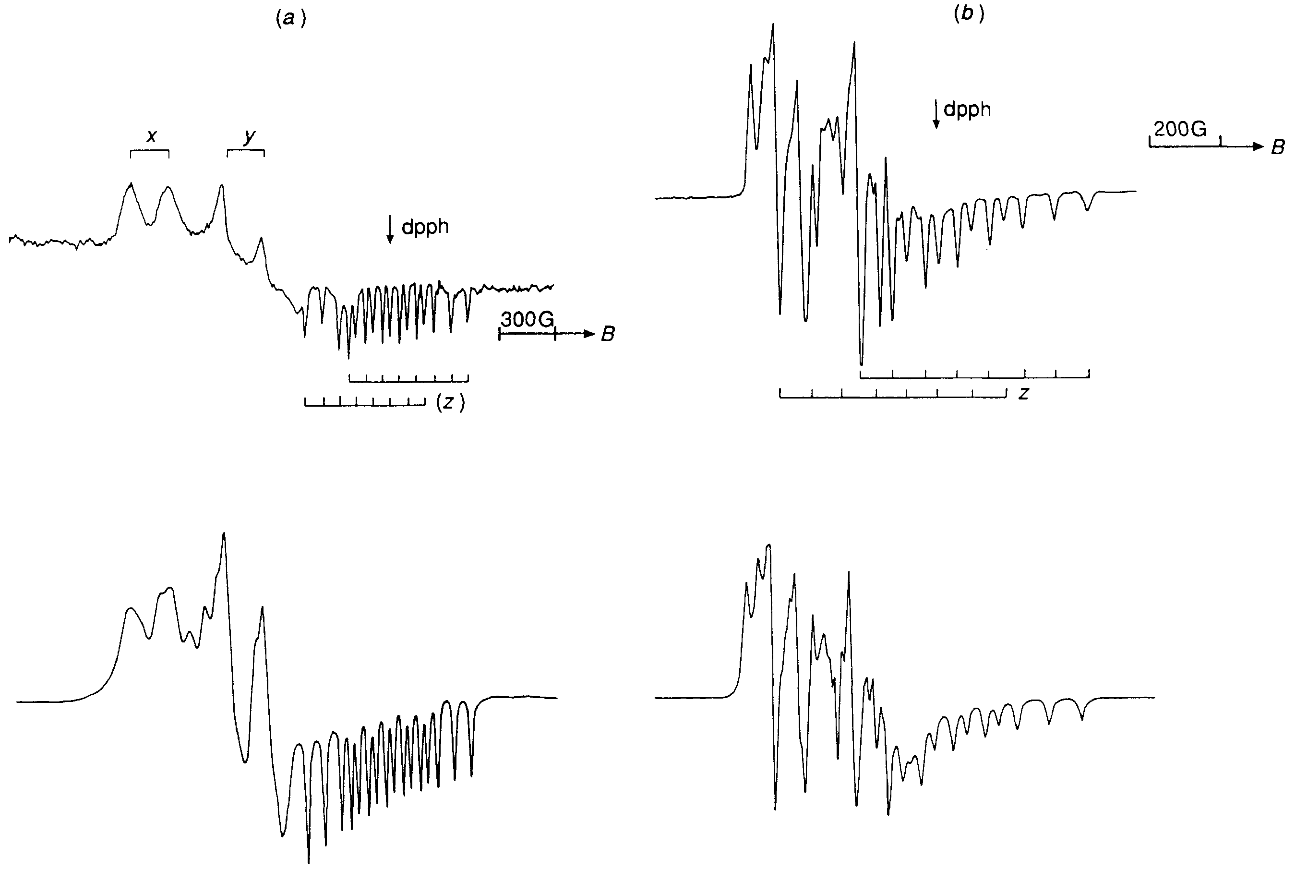

Figure 3. (a) Q- and (b) X-band spectra (with simulations below) of the adducts of $P(OPh)_3$ with [Co(Hdmg)$_2$] in toluene–ethanol at 103 K. The two sets of eight lines in the stick spectrum indicate the resolved hyperfine spitting from ^{31}P and ^{59}Co

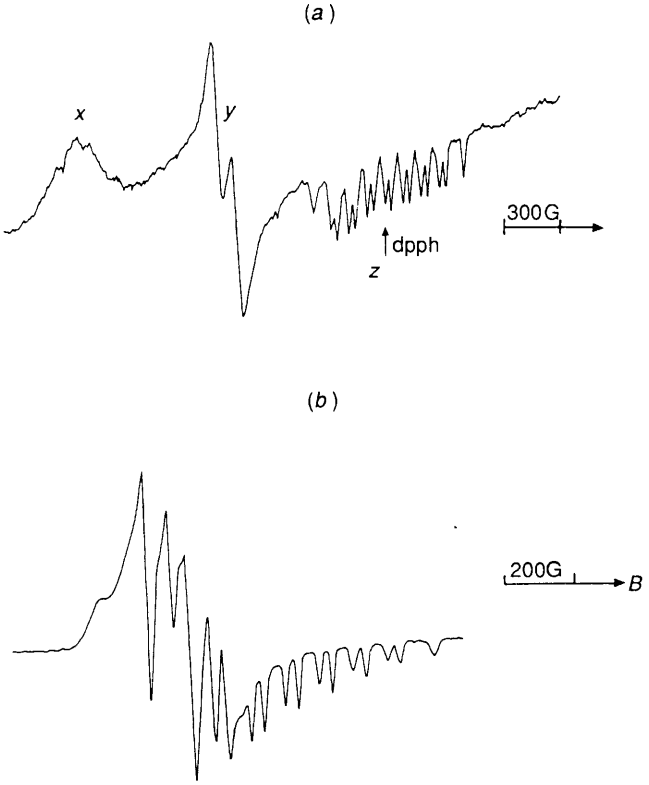

Figure 4. (*a*) *Q*- and (*b*) *X*-band spectra of the adducts of PPh_3 with $[Co(Hdmg)_2]$ in toluene–ethanol at 103 K

results could only be obtained by combining results from *X*- and *Q*-band data, since the latter clearly show three well spaced *g* features. At *Q*-band frequencies the high-field region shows very well resolved cobalt and phosphorus couplings and all the parameters can be measured. The middle *g* feature, g_y, yield the *g* value and the hyperfine coupling to phosphorus. The lower-field feature, g_x, gives the *g* value, but resolved hyperfine coupling to phosphorus is only seen in phosphite adducts. In these two latter regions no coupling to cobalt was resolved. Starting values for the parameters not obtained from direct inspection of the experimental spectra (the cobalt hyperfine coupling at the g_x and g_y features as well as for phosphorus hyperfine coupling at g_x feature) were estimated from linewidth measurements.

Isotropic spectra were recorded at just above the freezing point of the solvent mixture. Spectra were poorly resolved, but showed a single pair of lines attributed to coupling to one phosphorus atom.

1:2 *Adducts.* Frozen-solution *X*-band e.s.r. spectra recorded at 103 K were usually well resolved although there was considerable overlap of hyperfine components of phosphorus with those of cobalt. By contrast with the 1:1 adducts, their *Q*-band spectra showed partial superposition of the *x* and *y* features, and the well resolved g_z feature contained twelve lines instead of the sixteen observed in the 1:1 case (Figure 5). This latter observation can be understood by assuming a phosphorus hyperfine coupling approximately double that of cobalt, and under these circumstances an interaction with one phosphorus would produce twelve lines with relative intensities 1:1:1:1:2:2:2:2:1:1:1:1. If there were two equivalent phosphorus atoms, the observed relative intensites would be 1:1:3:3:4:4:4:4:3:3:1:1. Our results clearly fit the latter case, and the situation was confirmed by computer simulation.

The isotropic spectra were again poorly resolved, but at least in one case $[P(OMe)Ph_2]$ a well resolved 1:2:1 triplet showed the presence of two equivalent phosphorus atoms.

Discussion

Analysis of Frozen-solution E.S.R. Spectra.—All spectra clearly showed an interaction of the unpaired electron with the cobalt atom (d^7, $S = \frac{1}{2}$) and, for the adducts, with the axial ligands. Analysis of the *Q*-band spectra revealed unambiguously a rhombic symmetry for all the compounds studied, as opposed to early claims in the literature which assumed axial symmetry[14] (because *X*-band spectra did not resolve the small rhombic distortion). The components of the spin-Hamiltonian parameters were obtained by computer simulation of the *X*- and *Q*-band spectra, and the results obtained confirmed that the spectra must be interpreted in terms of three *g* values.

Spin-Hamiltonian parameters were analysed assuming a $^2A_1$ ground state comprising a mixture of the d_{z^2} and $d_{x^2-y^2}$ metal orbitals of the form $\psi = ad_{z^2} + bd_{x^2-y^2}$ (taking the point-group symmetry to be C_{2v}).

Computer Simulation and Data Analysis.—The simulations of the e.s.r. spectra were carried out using a program based on Pilbrow's formalism[24] which uses a spin Hamiltonian of the type (1) where the hyperfine term was deduced assuming C_2

$$\mathcal{H} = \mathcal{H}\,(\text{Zeeman}) + \mathcal{H}\,(\text{hyperfine}) + \mathcal{H}\,(\text{ligand}) \quad (1)$$

point-group symmetry at the cobalt centre and non-coincidence of the *g* and *A*(cobalt) tensor axis in the *xy* plane. As we never observed interaction of the unpaired electron with the nitrogen atoms of the equatorial plane, the ligand term includes only the phosphorus axial interaction and, as suggested by Pilbrow and Winfield,[24] it was assumed that the phosphorus tensor has the same principal axis as that of the *g* tensor.

For the simulation of the e.s.r. spectra of the compounds reported, the best fit was observed for collinear *x* and *y* axes (rhombic symmetry) with neglect of any quadrupolar contribution to the spin Hamiltonian, since the observation of different line spacings, in the *X*-band but not in the *Q*-band spectra suggests that for these compounds the quadrupolar interaction does not exist or has no detectable effects. The computer-simulated spectra are shown with the experimental ones.

The spin-Hamiltonian parameters [*g*, *A*(Co) tensors] were analyzed using McGarvey's model[15] which uses perturbation theory extended to third order and includes the contribution of low-lying quartet states. To solve the McGarvey equations, the same method and assumptions developed by one of us[13,14] for a series of phosphine and phosphite adducts of cobalt(II) complexes with Schiff bases was applied.

In Table 1 the spin-Hamiltonian parameters for the compounds studied as well as the values of the anisotropic hyperfine coupling *P*, isotropic hyperfine coupling $-\kappa P$, the spin densities on the cobalt atom, and the energies of excited states are summarized.

The g *tensor.* For all compounds studied, the *g* tensor has three different components which implies rhombic symmetry. The observation that the lowest *g* value (taken to be g_z) is larger than 2.0 has been interpreted as indicating that coupling of the quartet states with the ground state is important. The other two *g* values lie between 2.1 and 2.3, as normally observed for phosphorus adducts of low-spin Co$^{\text{II}}$ with various equatorial ligands with N, O, S, or Se donor atoms.[9,10,13,14]

The values of Δ_{xy} ($g_x - g_y$) (Table 1), usually taken as a measure of rhombic distortion, are similar to those obtained for phosphorus adducts of cobalt(II) complexes with equatorial

Table 1. The g and ^{59}Co hyperfine tensors and deduced parameters. The units of A_x, A_y, A_z, P, and $-\kappa P$ are 10^{-4} cm^{-1}. The parameters are defined in the text and equations.

												Coefficients (cm^{-1})			Spin densities			Excited-state Energy		
Complex	Axial ligand	g_x	g_y	g_z	Δ_{xy}	$-A_x$	$-A_y$	A_z	P	$-\kappa P$	a^2	b^2	c_1	c_2	c_3	ρ_{3d}	ρ_{4s}	ρ_l	ΔB_1	ΔB_2	ΔQ
[Co(Hdmg)$_2$L]	P(OPh)$_3$	2.251	2.139	2.016	0.112	15	10	86	176	0.000 0	0.995 7	0.004 3	0.023 2	0.036 3	0.092 0	0.70	0.05	0.12	15 919	10 174	4 014
	P(OMe)$_3$	2.230	2.139	2.010	0.081	15	10	84	171	0.000 1	0.997 3	0.002 7	0.025 1	0.034 2	0.091 2	0.67	0.05	0.09	14 303	10 497	3 895
	P(OEt)$_3$	2.233	2.153	2.016	0.081	13	10	83	167	0.000 2	0.997 9	0.002 1	0.023 5	0.033 2	0.101 0	0.66	0.05	0.12	14 894	10 542	3 465
	P(OBu)$_3$	2.230	2.139	2.010	0.091	15	10	82	162	0.000 1	0.996 7	0.003 3	0.023 8	0.034 5	0.072 9	0.64	0.04	0.13	14 286	9 855	4 664
	PPh$_3$	2.326	2.152	2.011	0.164	10	10	90	200	−0.000 7	0.994 2	0.005 8	0.029 1	0.048 3	0.084 9	0.79	0.05	0.09	14 433	8 696	4 947
	P(C$_6$H$_4$Me-*m*)$_3$	2.326	2.152	2.011	0.164	10	10	90	200	−0.000 7	0.994 2	0.005 8	0.029 1	0.048 3	0.084 9	0.79	0.05	0.09	14 433	8 696	4 947
	P(C$_6$H$_4$Me-*p*)$_3$	2.326	2.152	2.011	0.164	10	10	90	200	−0.000 7	0.994 2	0.005 8	0.029 1	0.048 3	0.084 9	0.79	0.05	0.09	14 433	8 696	4 947
	P(C$_6$H$_{11}$)$_3$	2.347	2.172	2.004	0.175	10	10	75	174	−0.001 1	0.993 4	0.006 6	0.032 6	0.052 5	0.065 1	0.69	0.04	0.09	11 288	7 009	5 653
	PBu$_3$	2.268	2.191	2.017	0.077	10	10	81	175	−0.000 3	0.998 7	0.001 3	0.031 3	0.040 4	0.097 0	0.69	0.05	0.09	11 725	9 084	3 784
	PEt$_3$	2.258	2.181	2.009	0.077	10	10	75	157	−0.000 3	0.998 7	0.001 3	0.030 8	0.040 2	0.073 3	0.62	0.04	0.09	10 697	8 195	4 508
[Co(Hdmg)$_2$L$_2$]	PPh$_2$Me	2.149	2.121	2.01	0.028	20	5	80	144	0.000 7	0.994 3	0.005 7	0.020 5	0.021 6	0.067 2	0.57	0.04	0.12	14 732	13 981	4 494
	PPh$_2$Bu	2.177	2.125	2.014	0.052	15	10	85	157	0.000 6	0.998 4	0.001 6	0.019 9	0.026 0	0.081 9	0.62	0.05	0.09	16 533	12 654	4 017
	PPh$_2$(OMe)	2.174	2.130	2.014	0.044	15	10	85	157	0.000 6	0.998 4	0.001 6	0.020 7	0.025 7	0.081 8	0.62	0.05	0.09	15 894	12 802	4 022
	PPh$_2$(OEt)	2.174	2.130	2.014	0.044	15	10	85	157	0.000 6	0.998 4	0.001 6	0.020 7	0.025 7	0.081 8	0.62	0.05	0.09	15 894	12 802	4 022
[Co(Hdmg)$_2$] in solution		2.296	2.194	2.016	0.102	24	−8	107	199	0.001 2	0.998 9	0.001 1	0.029 6	0.049 6	0.097 8	0.78	0.06		14 045	8 382	4 250
[Co(Hdmg)$_2$] in [Ni(Hdmg)$_2$]		2.598	2.253	1.993	0.363	127	62	130	135	0.007 0	0.992 0	0.008 0	0.039 6	0.112 4	0.090 7	0.53	0.09		7 146	2 518	3 120
[{Co(salen)}$_2$][17]		2.690	2.310	2.000	0.380	126	58	110	130	0.005 7	0.988 3	0.011 7	0.050 1	0.132 8	0.127 2	0.51	0.08		5 449	2 056	2 146

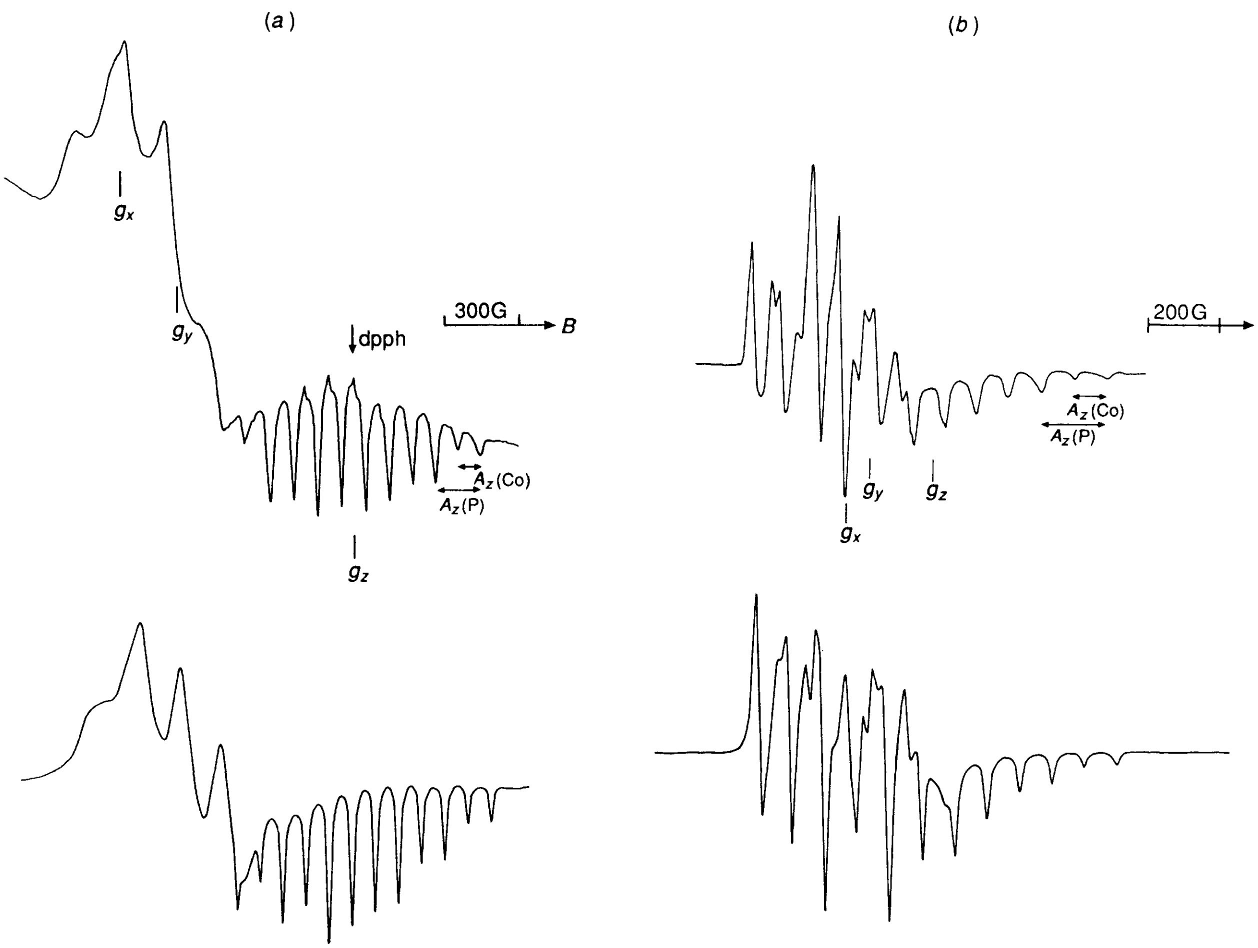

Figure 5. (*a*) *Q*- and (*b*) *X*-band spectra (with simulations below) of the adducts of $PPh_2(OMe)$ with $[Co(Hdmg)_2]$ in toluene–ethanol at 103 K

Schiff bases.[9,10,13,14] For the same type of axial ligand, the values of Δ_{xy} reflect the asymmetry of the equatorial ligand which in turn will influence the π bonding to the phosphorus and cause the phosphorus tensor to be no longer axial. In terms of energy levels, the effect of σ bonding, between the phosphorus and cobalt atoms, will destabilize the d_{z^2} orbital while π bonding will stabilize 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.

For the six-co-ordinated species the values of Δ_{xy} observed are significantly smaller, almost half of those observed for the five-co-ordinated species, as has been observed for the adducts of [Co(salphen)] [salphen = *o*-phenylenebis(salicylideneiminate)][25] and $[Co(Hdmg)_2]$[26] with pyridine. This decrease is associated with the inevitable movement of the Co atom into the plane defined by the equatorial atoms, thus decreasing the energy separation d_{xz}–d_{yz}. There is a consequent reduction in the π interaction with the axial ligand and a better σ interaction with the equatorial ligand. Similar observations have been made by Hitchman[17,18] concerning the decrease in Δ_{xy} values across the series [Co(salen)], $[\{Co(salen)\}_2]$, and [Co(salen)]·py [salen = *N,N'*-ethylenebis(salicylideneiminate), py = pyridine].

The values of the energy separations ΔB_1 (d_{z^2}–d_{xz}), ΔB_2 (d_{z^2}–d_{yz}), and ΔQ (average energy of quartet states) were calculated from the McGarvey coefficients (c_1, c_2, c_3) considering $c_i = (\rho_{3d}\lambda)/\Delta E_i$ where ρ_{3d} is the spin density in the d_{z^2} orbital calculated as P/P^{2+}, with $P^{2+} = 0.0254$ cm^{-1},[27] and the free-ion spin–orbit coupling parameter (λ) for the Co^{2+} ion was chosen to be 533 cm^{-1}.[27] The values obtained, ΔB_1 = 10 000—16 000, ΔB_2 = 7 000—13 000, and ΔQ = 3 500—5 000 cm^{-1}, are in the range of those reported for phosphorus adducts of other cobalt(II) complexes with equatorial Schiff bases.[9,10,13,14] The relative energies of the various excited states stress the importance of low-lying quartet states and that their contribution must be included in the calculations.

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 observed. Upon addition of base the visible spectrum changed from one with two 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.

The cobalt hyperfine tensor and cobalt spin densities. The Cobalt hyperfine tensor was analyzed using McGarvey's theory for d^7 ions with no assumptions concerning the sign of the cobalt hyperfine coupling constants.[15] For the adducts, as in related work,[9,10,13,14] the only reasonable fit of the experimental data was obtained when A_z is positive and A_x and A_y are negative, whereas for $[Co(Hdmg)_2]$ the only reasonable assumption was for A_z and A_x positive and A_y negative.

The calculated values of the anisotropic (P) and the isotropic ($-\kappa P$) components of the nuclear hyperfine interaction as well as the values for the spin density of the cobalt are included in Table 1. For values of a approaching unity, the unpaired spin density in the d_{z^2} orbital ($\rho_{3d_{z^2}}$) can be obtained as the ratio P/P^{2+}, where $P^{2+} = 254 \times 10^{-4}$ cm^{-1} [27] is the value for the free ion Co^{2+}. Cobalt 4*s* spin densities (ρ_{4s}) were estimated according to equation (2)[28] where c_{4s}^2 is the real spin density

$$-\kappa P = c_{4s}^2 A_{iso}(4s) + c_{3d}^2 A(3d\,\text{polarization}) \quad (2)$$

Table 2. ^{31}P Hyperfine tensors and deduced parameters. The units of hyperfine coupling are Gauss

	Experimental hyperfine coupling				Anisotropic hyperfine tensor			Principal values of decomposed tensors		Spin densities on ^{31}P				
Axial ligand	A_x	A_y	A_z	A_{iso}	A_{xx}	A_{yy}	A_{zz}	A_{xx}	A_{zz}	ρ_{3p}	ρ_{3s}	ρ_l	η	θ
$P(OPh)_3$	210	221	242	224	−13	−2	16	−8	12	6	6	12	1	102
$P(OMe)_3$	190	201	223	205	−15	−5	18	−8	14	7	6	13	1	
$P(OEt)_3$	182	193	217	197	−14	−3	18	−8	14	7	5	12	1	104
$P(OBu)_3$	179	190	216	195	−15	−4	19	−8	16	8	5	13	2	105
PPh_3	98	112	133	114	−15	−1	17	−10	12	6	3	9	2	107
$P(C_6H_4Me\text{-}m)_3$	98	112	133	114	−15	−1	17	−10	12	6	3	9	2	107
$P(C_6H_4Me\text{-}p)_3$	98	112	133	114	−15	−1	17	−10	12	6	3	9	2	107
$P(C_6H_{11})_3$	95	107	124	109	−14	−2	15	−8	12	6	3	9	2	107
PBu_3	112	151	166	143	−31	8	23	−26	10	5	4	9	1	102
PEt_3	113	153	168	145	−32	8	23	−26	10	5	4	9	1	102
PPh_2Me	159	159	184	169	−7	−7	15	—	—	7	5	12	1	104
PPh_2Bu	163	163	181	169	−5	−5	10	—	—	5	5	10	1	102
$PPh_2(OMe)$	163	164	181	169	−5	−4	10	−1	9	5	5	10	1	102
$PPh_2(OEt)$	163	164	181	169	−5	−4	10	−1	9	5	5	10	1	102

in the cobalt 4*s* orbital, $A_{iso}(4s) = 1\,232 \times 10^{-4}$ cm^{-1}, c_{3d}^2 is the spin density in the 3*d* orbital, and A (3*d* polarization) is the value estimated by McGarvey[29] for the polarization contribution to A_{iso} (-84×10^{-4} cm^{-1}) from an electron entirely in a 3*d* orbital.

The calculated spin densities in the cobalt 4*s* orbital ($\approx 5\%$) do not vary with the phosphorus base and lie in the range of values expected for this type of equatorial ligand,[9,10,13,14] suggesting a contribution of the 4*s* orbital to the $^2A_1$ ground state.

The spin densities in the d_{z^2} orbital depend on the number of bases co-ordinated to the cobalt and are slightly smaller for the 1:2 adducts. For the 1:1 adducts the values vary between 62 (PEt_3) and 79% (PPh_3) and for each phosphine or phosphite they follow the same order as for other related N_4 equatorial ligands. We also observe that the values of the anisotropic hyperfine coupling follow the order $P(OPh_3) > P(OMe_3) > P(OEt_3) > P(OBu_3)$ for the phosphites and $PPh_3 > PEt_3 > PBu_3$ for the phosphines.

As already found in other systems, the more the spin density is localized on the cobalt atom the larger are the spin densities on the phosphorus atom.[13,14] This fact has been interpreted in terms of strong π interactions that make the Co–P bond shorter and so allow more spin density to flow onto the phosphorus atom.

The phosphorus hyperfine tensor and phosphorus spin densities. Since the unpaired electron interacts directly with the phosphorus atom the isotropic hyperfine coupling will be positive. The values obtained from computer simulation (Table 2) are reported in Gauss (10^{-4} T).

The phosphorus tensors were corrected for indirect dipolar coupling using the point-dipolar approximation[27] with a value of 2.5×10^{-10} cm for the Co–P bond distance. When asymmetric the tensors were decomposed into two symmetrical tensors: one whose *z*-axis is defined as along the Co–P bond, and the other whose principal axis (*x*) is defined such as to give a negative principal value since it can only result from polarization.[13,14]

The magnitude of the spin polarization tensor A_{xx} must be related to the rhombic distortion, since it disappears in axial symmetry, and so is related to the energy difference $\Delta = \Delta B_1 - \Delta B_2$[13,14] and in fact a rough correlation can be obtained between A_{xx} and Δ_{xy} giving further support to this assumption. Also, the values we obtain for A_{xx} are smaller than those obtained for cobalt Schiff-base complexes, and we think this reflects a symmetry for our compounds closer to axial. The observation that the phosphorus tensors for 1:2 adducts are axially symmetric supports this proposal.

The phosphorus hyperfine coupling constants can yield spin densities on the phosphorus atom. The anisotropic couplings give the 3*p* spin density (ρ_{3p}) using the expression (3) where

$$\rho_{3p} = A_{zz}/A_p^{100} \qquad (3)$$

$A_p^{100} = 202$ G,[27] and the isotropic couplings give the 3*s* spin density (ρ_{3s}) using expression (4) where $A_s^{100} = 3\,767$ G.[27]

$$\rho_{3s} = A_{iso}/A_s^{100} \qquad (4)$$

The ratio $\rho_{3p}/\rho_{3s} = \eta$ gives the hybridization in the orbital concerned. Using the values of η in Coulson's formula,[27] $\theta = \cos^{-1}[(1.5/2\eta + 3) - 0.5]$, for C_{3v} symmetry (PR_3 groups co-ordinated to a metal) the angle R–P–R (θ) can be calculated. The calculated θ values (Table 2) are larger than those found from *X*-ray studies of the corresponding alkylcobaloximes[3] which can be explained by the expected longer Co^{II}–P bond lengths because the unpaired electron is in a d_{z^2} orbital.

The total spin densities on the phosphorus atoms range between 8 and 13% as in similar complexes,[9,10,13,14] with the larger values being observed for the phosphite adducts. In the case of the 1:1 complexes this can be explained by the stronger π interactions which shorten the Co–P bond and place more spin density on the phosphorus. The total spin densities on the phosphorus atoms are very similar for 1:1 and 1:2 adducts, although the cobalt spin densities are significantly smaller in the latter case.

Spin density on the equatorial ligand. The values of the total spin densities, calculated as the sum of the spin densities on the cobalt and phosphorus atoms, vary in the range 86—96% and suggest that most of the remaining 4—14% of the unpaired spin density must be delocalized into the equatorial ligand. However no hyperfine coupling with the equatorial nitrogen atoms has ever been observed in adducts of any other cobalt(II) complexes[6–10,13,14]

E.S.R. Spectra of $[Co(Hdmg)_2]$.—*Frozen solution.* The spectra simulation confirmed the rhombic symmetry for the complex in solution and provided the spin-Hamiltonian parameters. These parameters fit a $^2A_1$ ground state and were analysed according to McGarvey's theory. The best fit was obtained for A_z, $A_x > 0$ and $A_y < 0$. From the $-\kappa P$ and P values (Table 1) the cobalt spin densities were evaluated as $\rho_{4s} = 6\%$ and $\rho_{3d} = 76\%$, implying 18% spin density delocalized into the equatorial ligand and/or into interaction with axial solvent molecules.

Diamagnetic matrix. The spin-Hamiltonian parameters obtained by computer simulation did not point unambiguously to either of the two possible ground states $^2A_1$ (d_{z^2}) and $^2B_2$ (d_{yz}). In our work we define the z axis as perpendicular to the CoN_4 plane so that d_{yz} is referred to as $^2B_2$ for consistency with other work. Attempts to choose the ground state were made using McGarvey's model[15,16] and the experimental results were also compared with Hitchman's diagrams.[17]

To test for a $^2A_1$ ground state the best fit for McGarvey's equations was obtained for A_x, A_y, and $A_z > 0$. The value of P was quite low implying 53% of spin density located in the $3d_{z^2}$ orbital. The $-\kappa P$ value was positive and larger than for the adducts, and a 9% contribution for the 4s orbital was estimated. The cobalt spin density is then 62% which means that spin density must be largely delocalized into the axial positions since 38% seems far too much to be delocalized onto the equatorial ligand. No acceptable solution was obtained for a $^2B_2$ ground state using the appropriate equations of McGarvey since the η values would be negative or the next higher state would have to be associated with a $d_{x^2-y^2}$ orbital. Also a good fit of the g values for $[Co(Hdmg)_2]$ in $[Ni(Hdmg)_2]$ can be obtained using the plots given by Hitchman[17] for an abcissa of 3.8×10^{-3} cm^{-1}, implying a $^2A_1$ ground state with the first excited state ($^2B_2$) 3 800 cm^{-1} above.

In the $[Ni(Hdmg)_2]$ crystal the molecules are stacked with the nickel atoms aligned vertically.[30,31] Since for this compound there is evidence of Ni–Ni interactions, it is probable that in the diamagnetic matrix there are also interactions between the cobalt centre and nickel atoms above and below, although this fact could not be confirmed by e.s.r. spectroscopy since the nickel atom has no nuclear magnetic moment ($I = 0$). Further support for axial interaction in solid $[Co(Hdmg)_2]$ is provided by the observation that the e.s.r. parameters of this compound in the nickel matrix are quite similar to those for $[\{Co(salen)\}_2]$.[32] We applied the McGarvey model to this latter compound and the results obtained are shown in Table 1. The similarity of the spin-Hamiltonian parameters of $[Co(Hdmg)_2]$ in $[Ni(Hdmg)_2]$ and of $[\{Co(salen)\}_2]$, namely the spin densities on the metal, makes it meaningful to compare both complexes in the solid form thus supporting the possibility of axial Co–Ni or Co–O interactions and justifying the low P values since the spin density can then be delocalized on the nickel atoms. On the other hand, for the other crystalline modification of [Co(salen)] where the molecules are planar and do not show axial co-ordination,[33] the spin-Hamiltonian parameters are very different ($g_x = 3.805$, $g_y = 1.660$, and $g_z = 1.740$; $A_x = 291 \times 10^{-4}$, $A_y = 52 \times 10^{-4}$, and $A_z = 39 \times 10^{-4}$ cm^{-1}) and are associated with a $^2B_2$ ground state.[34]

Our results seem to support a $^2A_1$ ground state for $[Co(Hdmg)_2]$ in a $[Ni(Hdmg)_2]$ matrix with the cobalt atoms exhibiting axial co-ordination. The values of the spin densities and energies of the excited states associated with this ground state are shown in Table 1.

Structural Characteristics: Formation of 1:2 *Adducts.*—The geometry of adducts of square-planar cobalt(II) complexes is largely dependent on the co-ordinated atom of the axial ligand and on the rigidity of the equatorial moiety. For N-donor bases most of the adducts formed are 1:2,[35] whereas for P-donors the formation of 1:2 adducts has been observed only for strictly planar equatorial ligands, mainly derived from porphyrins.[7]

Greenaway and co-workers[9,10] have studied two related systems involving a cobalt macrocycle with tetra-aza Schiff base ligands, one of which is strictly planar whereas the other shows a pronounced saddle shape. Since they did not observe formation of 1:2 adducts for both ligands, the results of their study were interpreted as to suggest that the planarity of the equatorial ligand is not crucial to the formation of 1:2 adducts, but that the important factor was the size of the hole for the metal. This observation agrees well with the fact that the tetra-aza ligands form 14-membered rings, whereas the porphyrin systems form 16-membered rings and a larger cavity to accommodate the metal ion. For this reason the metal ion in the tetra-aza complexes is displaced away from the plane of the equatorial nitrogen atoms, thus preventing the formation of six-co-ordinated species.

In our case the $[Co(Hdmg)_2]$ unit is more flexible; it is not a true macrocyclic ligand, and there is the possibility of tilting of the dimethylglyoxime units with respect to one another and in the cobaloximes it is usual to characterize this deformation by the dihedral angle between the two planes (α). For six-co-ordinate alkylcobaloximes with the same R group the position of the cobalt atom with respect to the plane of the four equatorial co-ordinated atoms depends largely on the axial base. For N-donor bases the cobalt atom lies essentially on that plane and the angle α is very small, whereas for symmetric phosphines and phosphites the cobalt atom lies well above the plane and $\alpha \approx 10$—$15°$.[3] In the methylcobaloximes the distance between the cobalt atom and the equatorial plane (d) is 0.11 Å for triphenylphosphine, 0.10 Å for trimethyl phosphite, and only 0.04 Å for pyridine and the corresponding values of α are 14, 10, and $\approx 0°$.[3] It seems possible that in the adducts of $[Co(Hdmg)_2]$ the symmetrical phosphines will pull the cobalt atom well above the equatorial plane, thus preventing the formation of six-co-ordinate species, whereas for the nitrogen adducts the coplanarity of the cobalt and of the equatorial co-ordinated atoms will make the sixth position readily available for co-ordination.

For non-symmetric phosphines and phosphites the formation of six-co-ordinate complexes cannot be related with the Tolman cone angle nor with the electronic Tolman parameter of the phosphorus ligands.[36] It is possible that the asymmetry of the ligands could induce deformations that favour 1:2 adduct formation and smaller deviations from square-planar localized geometry for the $Co(Hdmg)_2$ moiety. However, extensive work on other compounds with asymmetric phosphines and phosphites with different equatorial ligands would be necessary to address this question fully.

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