Electron Spin Resonance Study of the Cobalt(II) Species formed after Room-temperature Photolysis of Aqua(*sec*-butyl)bis(dimethylglyoximato)cobalt(III) in the Presence of *N*-Donor Bases†

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The cobalt(II) species resulting from room-temperature photolysis of aqua(*sec*-butyl)bis(dimethylglyoximato)cobalt(III) $[Co^{III}(Hdmg)_2Bu^s(H_2O)]$ solutions in the presence of various amounts of each of 27 different *N*-donor bases L were studied by electron spin resonance spectroscopy and the ESR spectra compared, when possible, with those of irradiated solutions of the corresponding $[Co^{III}(Hdmg)_2Bu^s(L)]$ compounds. From the ESR results, the bases could be grouped according to the position of the substituents. Both base strength and steric effects seem to play a role in the formation of 1:1 and 1:2 cobalt(II) adducts although no definite correlation between the ESR parameters determined for the various species and basicity was found.

Cobaloximes, bis(dimethylglyoximato)cobalt(III) complexes of general formula $[Co^{III}(Hdmg)_2L(X)]$ where L and X are neutral and mononegative ligands and H_2dmg = dimethylglyoxime, are well known compounds not only because of their interesting chemistry,[1] but also because they have been widely used as models of coenzyme B_{12} and related compounds.[2] Alkylcobaloximes with *N*- and *P*-donor bases have been particularly used to study electronic and steric effects on *trans* labilization of the cobalt–carbon bond.[3,4]

In previous studies concerning the ESR characterization of the photolysis products of alkylcobaloximes with co-ordinated symmetric phosphorus bases[5] and alkyl(pyridine)cobaloximes[6] with various alkyl groups, different results emerged for the two groups of bases. For the set of phosphorus bases, ESR spectra characteristic of a cobalt(II) species with *one* co-ordinated phosphorus base were observed, regardless of the nature of the alkyl group and the temperature of irradiation. The same spectra were observed for an irradiated solution of an alkyl(aqua)cobaloxime with the phosphorus base added in a 1:1 molar ratio and for a solution of an authentic $[Co(Hdmg)_2L]$ (L = phosphorus ligand) compound. For alkyl(pyridine)cobaloximes, an ESR spectrum characteristic of the five-co-ordinated species was only observed when photolysis was performed in a frozen matrix, although superimposed on that of the alkyl radical.[6] When photolysis was performed at room temperature, only ESR spectra characteristic of 2:1 pyridine–cobaloxime compounds were observed. An ESR spectrum assigned to the six-co-ordinated species was observed for an irradiated toluene–methanol solution of an alkyl(aqua)cobaloxime with added pyridine in a 1:1 molar ratio and also for a solution of $[Co^{II}(Hdmg)_2(py)]$ (py = pyridine) in the same solvent mixture.[6]

The ability of phosphorus and nitrogen bases to form 1:1 and/or 1:2 adducts with low-spin cobalt(II) compounds, together with attempts to identify which factors could be determinant for their formation has been the object of much research during past years.[7–24] The purpose of the present work is to study the behaviour of the cobaloximes formed after the addition of 27 nitrogen bases, in different amounts, to a toluene–methanol solution of aqua(*sec*-butyl)cobaloxime $[Co^{III}(Hdmg)_2Bu^s(H_2O)]$. After irradiating the solutions with visible light, the paramagnetic species formed were monitored by electron spin resonance spectroscopy. This study allowed us to get some insight into the ability of the different nitrogen bases to form 1:1 and 1:2 adducts with a cobalt(II) low-spin complex. The results are compared with those of a similar study using the same cobalt compound but with a series of phosphorus bases.[22] Attempts are also made to correlate the behaviour of the bases with base strength.

Experimental

Sample Preparation.—Toluene, dichloromethane and methanol were obtained from Merck and were dried and purified according to standard procedures[25] and kept over 4A molecular sieves prior to use. All other chemicals were from Aldrich and used without further purification. Aqua(*sec*-butyl)cobaloxime, $[Co^{III}(Hdmg)_2Bu^s(H_2O)]$ and all alkyl(pyridine)cobaloximes were prepared by the method described by Toscano *et al.*;[26] $[Co^{II}(Hdmg)_2(py)]$ was prepared by that of Schrauzer and Lee.[27]

The ESR sample preparations were carried out under an inert atmosphere of dry nitrogen. Solvents were deoxygenated with dry nitrogen and all solids and nitrogen bases degassed under vacuum/nitrogen. Samples were prepared by: (*a*) adding known amounts of the appropriate nitrogen base to a solution of $[Co^{III}(Hdmg)_2Bu^s(H_2O)]$ in molar ratios, base:cobaloxime, ranging from 1 to 10:1, both in toluene–methanol (2:1) and in toluene–dichloromethane (1:1); or (*b*) dissolving the desired alkyl(pyridine)cobaloxime in the same solvent mixtures. Cobaloxime solutions were then irradiated in ESR quartz tubes with a Hg lamp (Philips HP/T 250 W, maximum intensity at λ = 560–580 nm) under anaerobic conditions at 300 K for about 20 to 30 min and then immediately frozen in liquid nitrogen.

ESR Measurements.—The ESR spectra were recorded at X-band frequency at 103 K, on a Varian E-109 spectrometer with a

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† *Non-SI unit employed:* G = 10^{-4} T.

Varian E-257 variable-temperature unit; the spectra were calibrated with diphenylpicrylhydrazyl (dpph) and the magnetic field by using Mn^{2+} in MgO.

Results and Discussion

Solutions of alkylcobaloximes in toluene–dichloromethane or in toluene–methanol are ESR silent and remain so for a few days when kept in the dark, as expected for low-spin cobalt(III) compounds, but when exposed to light show room-temperature ESR spectra with g_{iso} *ca.* 2.10, significantly higher than the free electron value.

Photolysis of Cobaloximes.—The purpose of this work was to study the behaviour of cobalt fragments resulting from photolysis of alkylcobaloximes with bound *N*-donor bases. Anaerobic photolysis of alkyl(pyridine)cobaloximes and of alkylcobalamins in frozen matrices have been extensively studied in protic[28,29] and aprotic solvents[30] and the results obtained were interpreted assuming that on light absorption an electron from the equatorial ligand system moves into the $Co(d_{z^2})$ σ^* orbital. The antibonding character of this orbital is then relieved by bond fission, following the proposed sequence given in equations (1)–(3) (R = alkyl, solv = solvent), where

$$R\text{–}Co^{III}(Hdmg)_2(py) \longrightarrow [R^{\cdot}] + [Co^{II}(Hdmg)_2(py)] \quad (1)$$

$$[R^{\cdot}] + Hsolv \longrightarrow RH + [solv^{\cdot}] \quad (2)$$

$$[R^{\cdot}] \longrightarrow R^{\cdot} \quad (3)$$

the brackets represent cage trapping.[29] In accordance with this mechanism, ESR spectra of frozen solutions of several alkyl(pyridine)cobaloximes photolysed at 113 K in chloroform solutions show bands due to an alkyl radical and to a cobalt(II) complex co-ordinated to the axial pyridine.[30] Our results for alkylcobaloximes with pyridine irradiated and observed at 77 K in toluene–dichloromethane or in toluene–methanol should conform to this mechanism as the ESR spectra of the photolysed solutions show bands that are identical to those of the five-co-ordinated cobalt(II) complexes referred to above, and a strong narrow signal at $g = 2$ superimposed on that of the cobalt(II) species. These results were interpreted to provide conclusive evidence that photolysis of cobaloximes with *N*-donor ligands (L) cleaves the Co–C bond homolytically and produces a radical and a cobalt(II) complex [equation (4)].

$$[Co^{III}(Hdmg)_2R(L)] \longrightarrow R^{\cdot} + [Co^{II}(Hdmg)_2L] \quad (4)$$

The same mechanism for Co–C bond homolysis must be operative at room temperature, as has been observed for alkylcobaloximes with *P*-donor ligands.[5] However, for pyridine cobaloximes the final photolysis products depend markedly on the temperature of irradiation and on the alkyl substituent, as the cobalt(II) fragments can be involved in subsequent reactions.[6]

Reaction of $[Co^{III}(Hdmg)_2Bu^s(H_2O)]$ *with* N-*Donor Bases.*—It has been shown previously that addition of base to a solution of aqua(alkyl)cobaloximes results in the fast replacement of water molecules by those of stronger bases, and thus provides a path to base-bound cobaloximes that avoids the need to isolate the compounds.[5] This substitution of ligated water molecules can be easily monitored by optical spectroscopy and/or by NMR spectroscopy.

This method worked well in toluene–methanol and in toluene–dichloromethane for the bases used in this study, except for pyridines with substituents in 2 position and for pyrrole. The reported photolysis results are thus valid both for base-bound alkylcobaloximes, and for solutions of aquacobaloximes and base as long as the molar concentration of base is not lower than that of the cobaloxime.

For pyridines with substituents in the 2 position and for pyrrole a different situation occurs, since the extent of water replacement by base depends markedly on the base and on the molar ratio base:aquacobaloxime. In toluene–methanol equimolar solutions of $[Co^{III}(Hdmg)_2Bu^s(H_2O)]$ and of pyridines with substituents in the 2 position show *partial* or *no* replacement by base, as shown by their NMR spectra, and the solutions to be irradiated contain, most often, a mixture of $[Co^{III}(Hdmg)_2Bu^s(H_2O)]$ and $[Co^{III}(Hdmg)_2Bu^s(L)]$. In the presence of excess base, water replacement is more extensive and for most of the studied pyridines only $[Co^{III}(Hdmg)_2Bu^s(L)]$ is detected in solution. This situation must be contrasted with that found in pure solutions of $[Co^{III}(Hdmg)_2Bu^s(L)]$ in both solvent mixtures where only one type of cobaloxime is present.

In toluene–dichloromethane(1:1) the behaviour is different, as $[Co^{III}(Hdmg)_2Bu^s(H_2O)]$ is not soluble in this solvent and only $[Co^{III}(Hdmg)_2Bu^s(L)]$ was found in solution.

The results reported relate to photolysis of solutions of (*a*) $[Co^{III}(Hdmg)_2Bu^s(H_2O)]$ in the presence of base; and (*b*) of $[Co^{III}(Hdmg)_2Bu^s(L)]$. Nevertheless, in all cases the Co–C bond is cleaved homolytically at room temperature, following the mechanism detailed above, and the resulting cobalt(II) fragments were characterized by analysis of their ESR spectra.

ESR Spectra: General Description of Species present after Photolysis at Room Temperature.—Solutions of both $[Co^{III}(Hdmg)_2Bu^s(H_2O)]$ in the presence of *N*-donor bases L, and of the corresponding $[Co(Hdmg)_2Bu^s(L)]$ exhibit, after photolysis, ESR spectra whose features are largely dependent on the base and on the solvent used, and a summary of the results is given in Tables 1 and 2.

Alkyl(aqua)cobaloximes. A solution of $[Co^{III}(Hdmg)_2Bu^s(H_2O)]$ in toluene–methanol after irradiation with visible light exhibits an ESR signal, and the spectrum recorded at 103 K is shown in Fig. 1. The spectrum exhibits large *g*-tensor anisotropy and is typical of a low-spin d^7 ($S = \frac{1}{2}$) (d_{z^2}) species thus implying a formal oxidation state of +2 for the cobalt centre. In the high-field region, the spectrum clearly shows the interaction of the unpaired electron with the cobalt atom with no further hyperfine interaction between the latter and ligand atoms (type A). The spectrum in Fig. 1 is identical to the one observed by us for the compound $[Co(Hdmg)_2]$ in a toluene–methanol solution[22] that was assigned to a roughly square-planar compound weakly solvated by methanol. These results mean that, as had already been observed for other alkylcobaloximes,[5] room-temperature anaerobic photolysis induces the homolytic

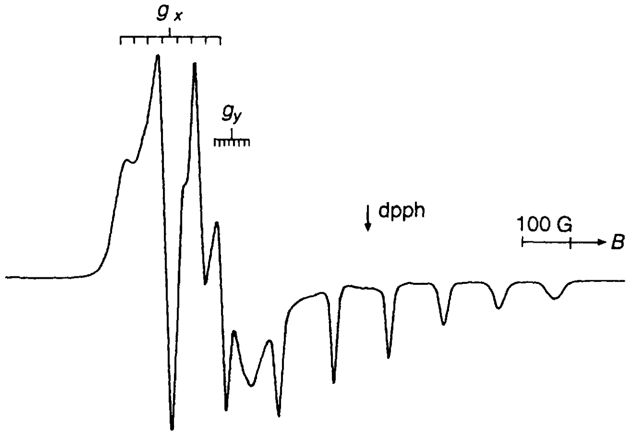


Fig. 1 Frozen-solution ESR spectrum (103 K) observed after room-temperature photolysis of a toluene–methanol solution of $[Co^{III}(Hdmg)_2Bu^s(H_2O)]$

Table 1 Predominant type of adducts formed and their co-ordination number (c.n.) after room-temperature photolysis of *sec*-butylcobaloxime in toluene–methanol solutions

Base (L)	p.a.[a]/kJ mol^{-1}	c.n. of base-bound cobaloxime	c.n. of cobaloxime in solution Molar ratio M : L 1 : 1	1 : 4	1 : 10
py	924	6	6	6	6
2-Substituted pyridines NC_5H_4R-2					
R = CN	878	*b*	4	4	4
OH	*c*	*b*	4	4	4
Cl	897	*b*	4	6	6
Br	898	*b*	4	6	6
NH_2	936	5	5	6(5)	6
Me	942	5	4/5	4/5	6
Et	946	*b*	4	4	6
3-Substituted pyridines NC_5H_4R-3					
R = CN	882	6	6	6	6
OH	*c*	6	6	6	6
Cl	899	6	6	6	6
Br	900	6	6	6	6
NH_2	925	6	6	6	6
Me	938	6	6	6	6
Et	937	6	6	6	6
4-Substituted pyridines NC_5H_4R-4					
R = CN	882	6	6	6	6
OH	*c*	6	6	6	6
NH_2	936	6	6	6	6
Me	942	6	6	6	6
Et	940	6	6	6	6
NMe_2	970	6	6	6	6
Disubstituted pyridines $NC_5H_3R(R')$					
3,5Me_2-py	943	6	6	6	6
2,4Me_2-py	951	6	4/5	6	6
2,6Me_2-py	955	*b*	4	4	6
2NH_2-6Me-py	*c*	*b*	4	4	6
Non-aromatic bases					
Pyrrole	875	*b*	4	*d*	*d*
Pyrrolidine	940	6	6	6	6
Piperidine	945	6	6	6	6

[a] Proton affinity (p.a.) values from ref. 31 or adapted from refs. 32–34. [b] Cobaloxime not prepared. [c] Values not found in the literature. [d] See text.

cleavage of the cobalt–carbon bond with consequent formation of cobalt(II) species.

Alkyl(base)cobaloximes. Solutions of the prepared alkyl(base)cobaloximes (Table 1) in toluene–methanol or in toluene–dichloromethane, except when the base is 2-amino- or 2-methylpyridine, yield ESR spectra that are all of the same type with each cobalt hyperfine line split into five lines with relative intensity 1 : 3 : 5 : 3 : 1 (type B), implying interaction of each cobalt atom with *two* molecules of nitrogen base (^{14}N, $I = 1$) (Fig. 2), thus indicating that co-ordination of two equivalent nitrogen ligands took place with the formation of a six-co-ordinate compound, $[Co^{II}(Hdmg)_2L_2]$.

Photolysis of solutions of $[Co^{III}(Hdmg)_2Bu^s(L)]$ (L = 2-amino- or 2-methyl-pyridine) yield ESR spectra where each cobalt hyperfine line is split into three lines with relative intensity 1 : 1 : 1 (type C). This spectrum is indicative of an interaction of the cobalt atom with one nitrogen atom (^{14}N, $I = 1$) (Fig. 3), thus supporting the formation of an axially five-co-ordinated species of formula $[Co^{II}(Hdmg)_2L]$. It must be noted that other pyridinecobaloximes in which the base has a substituent in position 2 were not prepared successfully.

Alkyl(aqua)cobaloximes in the presence of N*-donor bases*. In toluene–dichloromethane, the spectra obtained for the photolysis products of $[Co^{III}(Hdmg)Bu^s(H_2O)]$ in the presence of *N*-donor bases are similar to those reported for alkyl(base)cobaloximes, as expected, since in this solvent mixture only these latter compounds are present in solution (see above). In all cases spectra of type B were observed indicating the presence in solution of $[Co^{II}(Hdmg)_2L_2]$.

In toluene–methanol, when solutions of $[Co^{III}(Hdmg)_2Bu^s(H_2O)]$ in the presence of added *N*-donor base (L) are irradiated, depending on the type and amount of base added one of five main different types of ESR spectra, where the proposed classification is based on the hyperfine structure, were obtained. With pyridine and substituted pyridines that have no substituents groups in the 2 position, spectra of type B were always observed, whereas for pyridines with substituents in the 2 position, several situations were observed. For 2-hydroxy- and 2-cyano-pyridines, spectra of type A were always recorded; solutions of 2-chloro-, 2-bromo-, 2-ethyl-, 2,6-dimethyl- and 2-amino-6-methyl-pyridine with $[Co^{III}(Hdmg)_2Bu^s(H_2O)]$ in a 1 : 1 molar ratio exhibit after irradiation spectra of type A, but in the presence of excess base always yield ESR spectra of type B. The new type of spectra, where bands due to at least two species were observed, occurred only when the base was 2-amino-, 2-methyl- or 2,4-dimethyl-pyridine; for other bases the spectra are similar to those reported for $[Co^{III}(Hdmg)_2Bu^s(L)]$ (Table 1). For molar ratios base : aquacobaloxime of 1 : 1,

Table 2 ESR parameters of the alkylcobaloxime cobalt(II) species formed after photolysis at room temperature. The units of A_x, A_y, A_z, $-kP$ and P are 10^{-4} cm^{-1}. The parameters are defined in the text

Base L	g_x	g_y	g_z	A_x	A_y	A_z	a^2	b^2	$-kP$	P	ρ_{3d}	ρ_{4s}	ρ_L	ρ_{tot}
[Co(Hdmg)$_2$L$_2$]														
py	2.197	2.181	2.016	25	42	83	0.9892	0.0108	0.0040	89	0.35	0.06	0.10	0.60
2-substituted pyridines NC$_5$H$_4$R														
R = Cl	2.214	2.188	2.013	35	25	82	0.9982	0.0018	0.0036	93	0.37	0.05	0.09	0.60
NH$_2$	2.200	2.175	2.009	35	25	88	0.9985	0.0015	0.0038	100	0.39	0.06	0.09	0.63
Me	2.206	2.186	2.012	25	30	85	0.9988	0.0012	0.0035	101	0.40	0.06	0.09	0.63
Et	2.195	2.174	2.012	27	45	84	0.9864	0.0136	0.0043	86	0.34	0.06	0.10	0.60
3-substituted pyridines NC$_5$H$_4$R														
R = CN	2.203	2.176	2.012	25	35	84	0.9957	0.0043	0.0037	95	0.37	0.06	0.07	0.58
OH	2.207	2.181	2.011	35	25	79	0.9978	0.0022	0.0036	86	0.34	0.05	0.09	0.57
Cl	2.181	2.174	2.009	26	40	84	0.9928	0.0072	0.0040	87	0.34	0.06	0.07	0.54
Br	2.192	2.166	2.011	35	25	85	0.9982	0.0018	0.0038	93	0.37	0.06	0.09	0.60
NH$_2$	2.217	2.187	2.010	35	25	76	0.9976	0.0024	0.0035	82	0.32	0.05	0.09	0.55
Et	2.207	2.179	2.012	35	25	79	0.9979	0.0021	0.0036	86	0.34	0.05	0.09	0.57
Me	2.195	2.176	2.012	26	35	84	0.9967	0.0033	0.0038	93	0.37	0.06	0.10	0.62
4-Substituted pyridines NC$_5$H$_4$R														
R = CN	2.192	2.185	2.024	22	38	88	0.9926	0.0074	0.0039	104	0.41	0.06	0.09	0.65
OH	2.202	2.179	2.011	35	25	79	0.9976	0.0024	0.0036	85	0.33	0.05	0.09	0.57
NH$_2$	2.220	2.190	2.020	25	30	81	0.9984	0.0016	0.0034	98	0.39	0.05	0.09	0.62
Et	2.210	2.183	2.014	35	25	77	0.9977	0.0023	0.0036	84	0.33	0.05	0.09	0.56
Me	2.220	2.190	2.020	25	30	81	0.9984	0.0016	0.0034	98	0.39	0.05	0.09	0.62
NMe$_2$	2.220	2.190	2.020	25	30	81	0.9984	0.0016	0.0034	98	0.39	0.05	0.09	0.62
Disubstituted pyridines NC$_5$H$_3$R(R′)														
3,5Me$_2$-py	2.194	2.178	2.016	26	35	84	0.9969	0.0031	0.0038	94	0.37	0.06	0.10	0.63
2,4Me$_2$-py	2.194	2.169	2.011	35	25	84	0.9981	0.0019	0.0040	90	0.35	0.06	0.09	0.59
2,6Me$_2$-py	2.187	2.174	2.009	26	38	85	0.9937	0.0063	0.0040	91	0.36	0.06	0.07	0.55
Non-aromatic bases														
piperidine	2.190	2.162	2.010	35	25	84	0.9982	0.0018	0.0040	90	0.35	0.06	0.09	0.59
[Co(Hdmg)$_2$L]														
py	2.395	2.180	2.006	20	5	105	0.9962	0.0038	0.0006	205	0.81	0.06	0.09	0.05
2 NH$_2$-py	2.277	2.191	2.017	5	5	96	0.9984	0.0016	0.0011	177	0.70	0.06	0.06	0.82
2 Me-py	2.280	2.188	2.016	8	5	110	0.9988	0.0012	0.0013	201	0.79	0.06	0.06	0.92
[Co(Hdmg)$_2$]														
a	2.296	2.194	2.016	24	8	107	0.9989	0.0011	0.0012	199	0.78	0.06	0.00	0.85
b	2.377	2.216	2.006	51	31	124	0.9996	0.0004	0.0034	186	0.73	0.08	0.00	0.81
c	2.598	2.253	1.993	127	62	130	0.9920	0.0008	0.0070	135	0.53	0.09	0.00	0.62

[a] In methanol, ref. 22. [b] In pyrrole. [c] Doped into [Ni(Hdmg)$_2$]; the obtained ESR parameters differ from those of the other complexes as a consequence of differing ground state.[22]

the recorded spectra show bands of type A and type C, thus suggesting the existence in solution of [Co^{II}(Hdmg)$_2$] and of [Co^{II}(Hdmg)$_2$L]. Upon addition of a large excess of base, the observed spectrum is the superposition of that attributable to a compound where each cobalt hyperfine line is split into three lines with relative intensity 1 : 1 : 1, assigned to [Co^{II}(Hdmg)$_2$L], on a spectrum where each cobalt hyperfine line split into five lines with relative intensity 1:3:5:3:1, that is due to [Co^{II}(Hdmg)$_2$L$_2$], thus suggesting the simultaneous presence of five- and six-co-ordinate cobalt(II) complexes. For 2,6-dimethyl- and 2-amino-6-methyl-pyridine the ESR spectra characteristic of [Co^{II}(Hdmg)$_2$L$_2$] were observed in the presence of a very large excess of base. In all these situations the analysis of the ESR spectra recorded after irradiation enables the characterization of the paramagnetic species in solution for each of the bases considered.

Influence of the Nitrogen Bases on the Fragments formed.— Pyridine. Solutions of [Co^{III}(Hdmg)$_2$Bu^s(py)] irradiated at room temperature exhibit frozen-solution (103 K) ESR spectra of type B, thus revealing the presence of only one type of paramagnetic species, [Co^{II}(Hdmg)$_2$(py)$_2$]. This is a surprising result since (*a*) photolysis in a frozen matrix yields a spectrum of type C and that is attributable to [Co^{II}(Hdmg)$_2$(py)], although superimposed on that of an alkyl radical; (*b*) room-temperature photolysis of the corresponding cobaloximes with *P*-donor atoms yields the five-co-ordinated complex [Co^{II}(Hdmg)$_2$(PR$_3$)] (R = alkyl or aryl)[5] and (*c*) the presence of six-co-ordinated complexes requires the abstraction of pyridine molecules from other species since there was no pyridine in excess in the solution of [Co^{III}(Hdmg)$_2$Bu^s(py)] before the irradiation process as checked by NMR spectroscopy.

Abstraction of pyridine molecules can occur either from molecules of [Co^{III}(Hdmg)$_2$Bu^s(py)] still present in solution as photolysis is not complete, or from Co^{II}(Hdmg)$_2$(py) fragments which are, together with the organic radical, the primary products of the photolysis.[6] Although the first hypothesis seems plausible, since pyridine molecules *trans* to the alkyl group in cobaloximes have been shown to be labile[35] and also because five-co-ordinate compounds [Co^{III}L′(R)] (L′ = equatorial

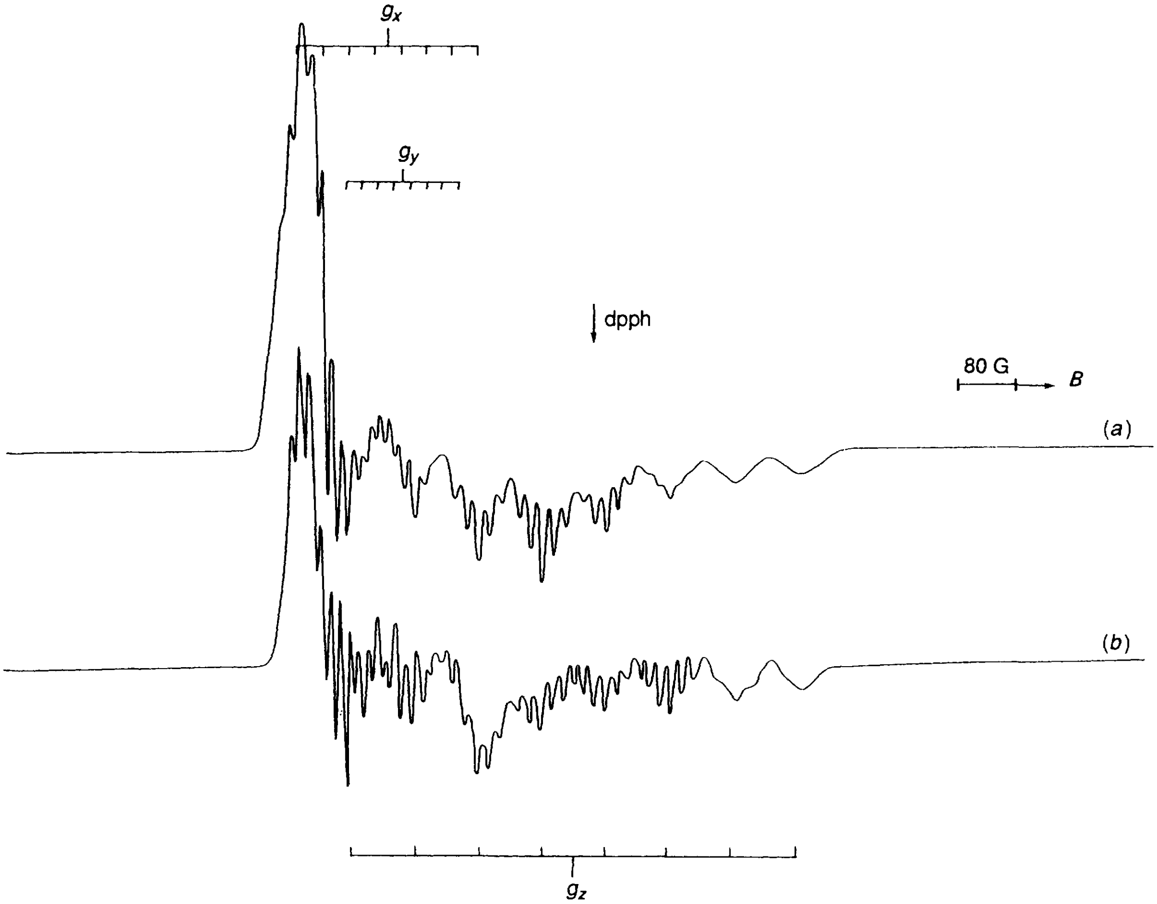


Fig. 2 (*a*) Frozen-solution ESR spectrum (103 K) observed after room-temperature photolysis of a toluene–methanol solution of $[Co^{III}(Hdmg)_2Bu^s(H_2O)]$ to which 3-chloropyridine was added in a 1 : 10 molar ratio. The simulated spectrum is depicted in (*b*)

ligand) have been isolated for other B_{12} model compounds,[36] it must be pointed out that some evidence supports preferential abstraction from other $Co^{II}(Hdmg)_2(py)$ fragments in solution. First, it must be noted that the ESR spectrum of a solution of an authentic sample of $[Co^{II}(Hdmg)_2(py)]$ shows coupling to two nitrogen atoms and thus is characteristic of species $[Co^{II}(Hdmg)_2(py)_2]$ although no spectroscopic evidence was found for the presence of $[Co^{II}(Hdmg)_2]$ in solution, as expected from abstraction of pyridine molecules from $[Co^{II}(Hdmg)_2(py)]$. Furthermore, the amount of $[Co^{II}(Hdmg)_2(py)_2]$ formed is reduced when the time of exposure to radiation increases, which can only take place if pyridine is being abstracted from cobalt(II) species [see equations (5) and (6) below]. The absence of ESR bands due to $[Co^{II}(Hdmg)_2]$ can be accounted for by assuming the formation of dimeric diamagnetic species, and support for the occurrence of magnetically coupled dimers of $[Co^{II}(Hdmg)_2]$ can be gathered by noting that (*a*) the ESR spectrum of a toluene–dichloromethane solution of $[Co^{II}(Hdmg)_2(py)]$ reveals only lines due to the six-co-ordinate complex $[Co^{II}(Hdmg)_2(py)]$ and (*b*) the magnetic moment of $[Co^{II}(Hdmg)_2(py)]$ in fluid solutions, determined by the Evans method,[37] is smaller than the value obtained for the solid (Gouy method, 1.72 μ_B), thus suggesting some form of magnetic coupling between $Co^{II}(Hdmg)_2$ entities in solution.

The ESR spectrum characteristic of the five-co-ordinated compound $[Co^{II}(Hdmg)_2(py)]$ was only observed when photolysis of the cobaloxime was performed in a frozen matrix, thus implying this compound is highly reactive and gives rise to new species as the temperature of the sample is raised above the freezing point of the solution. If the sample is brought to room temperature and cooled again to 77 K the ESR spectrum observed is identical to the one in Fig. 2 characteristic of the six-co-ordinated compound, $[Co^{II}(Hdmg)_2(py)_2]$.

The results described above for the anaerobic photolysis of pyridine alkylcobaloxime solutions can be interpreted according to the following mechanism [equations (5) and (6)], where

$$[Co^{III}(Hdmg)_2R(L)] \longrightarrow [Co^{II}(Hdmg)_2L] + R^{\bullet} \quad (5)$$

$$4\,[Co^{II}(Hdmg)_2L] \rightleftharpoons 2[Co^{II}(Hdmg)_2L_2] + [\{Co^{II}(Hdmg)_2\}_2] \quad (6)$$

the species $[\{Co^{II}(Hdmg)_2\}_2]$ is ESR silent. For bases without bulky non-co-ordinating substituents in position 2, equilibrium (6) is displaced completely to the right and no evidence for five-co-ordinate species was obtained in fluid solution.

3- *and* 4-*substituted pyridines* NC_5H_4R. The cobaloximes with 3- and 4-substituted pyridine bases behave exactly like those with pyridine despite exhibiting different values for their proton affinities. Even when the base is added in a 1 : 1 molar ratio the ESR spectra of the solutions, after being irradiated, are characteristic of six-co-ordinate species. According to these results, inductive effects do not seem to play an important role in the type of adduct formed.

2-*Substituted pyridines* NC_5H_4R. For cobaloximes with this group of bases, the influence of both stereochemical and electronic effects is evident. When the bases are added in a 1 : 1 molar ratio, the ESR spectra of the corresponding solutions are identical to the spectrum shown in Fig. 1 except for R = Me or NH_2 for which spectra of type C superimposed on type A are observed (Fig. 4). These two bases are stronger than pyridine itself and the presence of an electron donating (+I) substituent in position 2 favours co-ordination despite the steric hindrance.

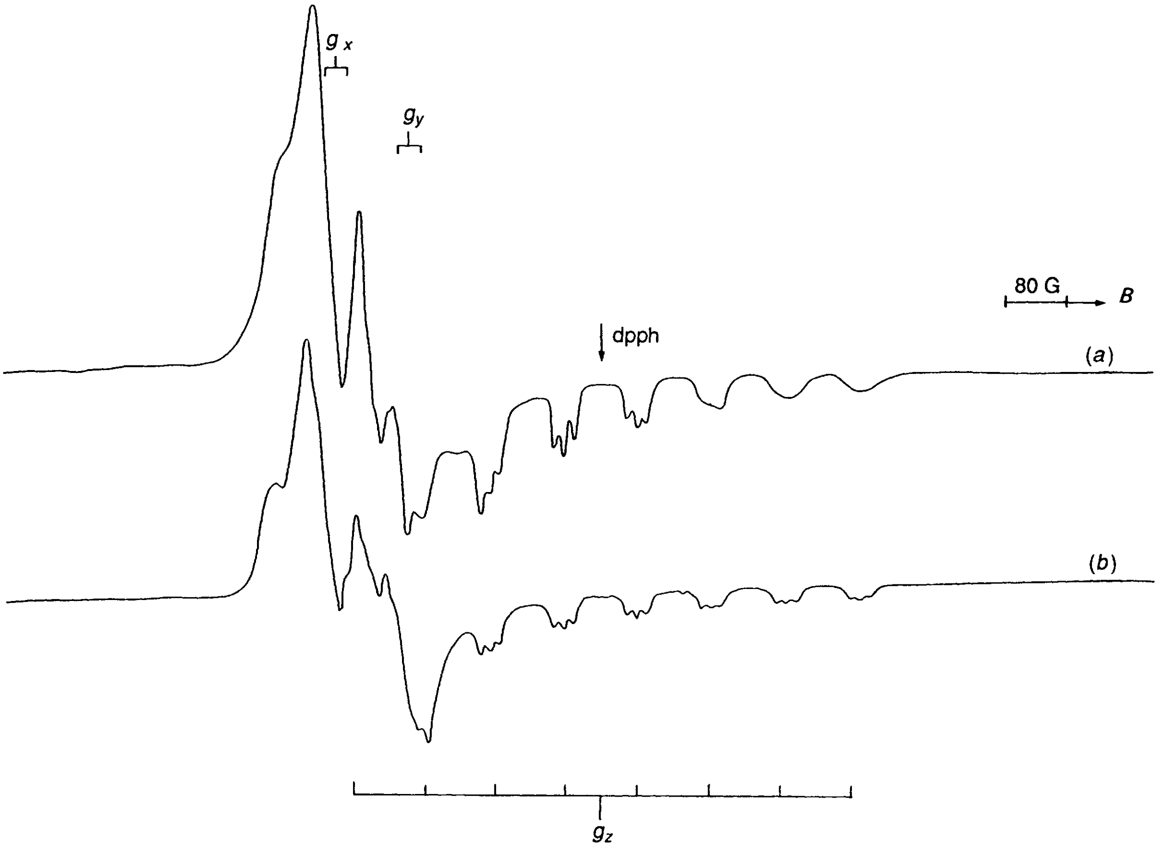


Fig. 3 (*a*) Frozen-solution ESR spectrum (103 K) observed after room-temperature photolysis of a toluene–methanol solution of $[Co^{III}(Hdmg)_2Bu^s(2NH_2\text{-}py)]$. The simulated spectrum is depicted in (*b*)

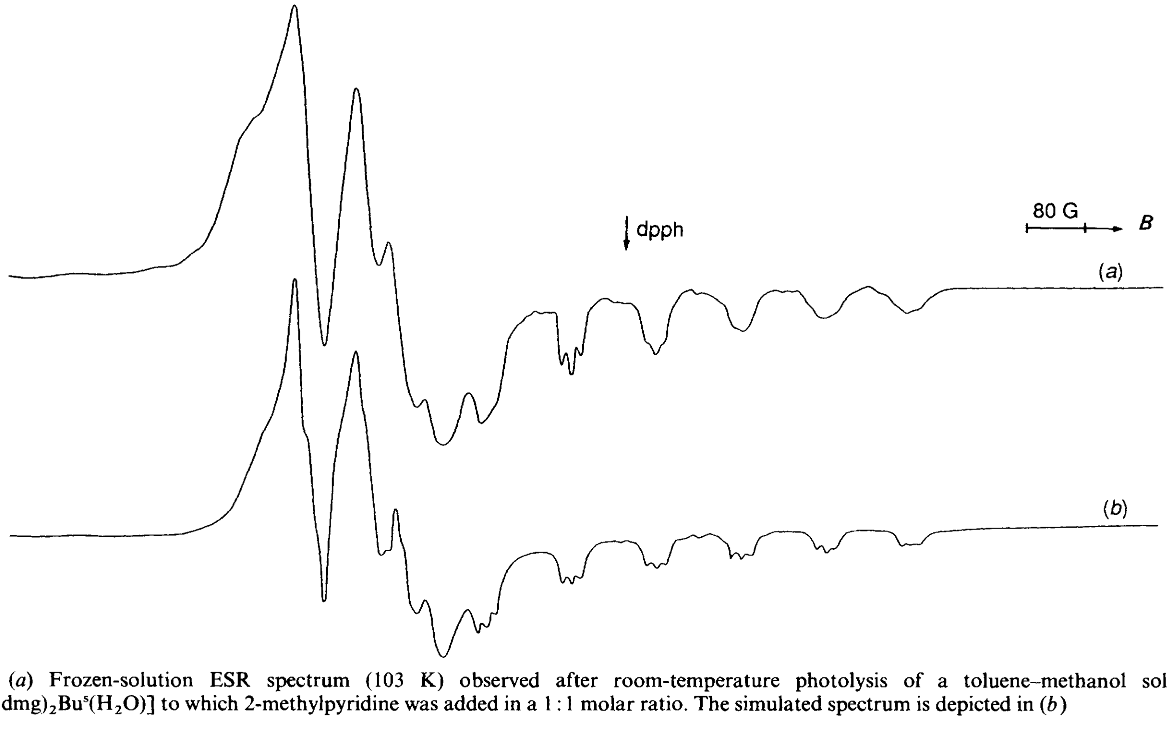


Fig. 4 (*a*) Frozen-solution ESR spectrum (103 K) observed after room-temperature photolysis of a toluene–methanol solution of $[Co^{III}(Hdmg)_2Bu^s(H_2O)]$ to which 2-methylpyridine was added in a 1 : 1 molar ratio. The simulated spectrum is depicted in (*b*)

Stereochemical effects also induce deformations in the equatorial plane and allow the observation of the five-co-ordinated species in solution. The other bases are either not strong enough (−I) (R = CN, OH, Cl or Br) or have bulkier groups (R = Et) which hinder co-ordination. For bases (R = Me or NH_2) added in excess (4 : 1 molar ratio), ESR spectra of type C superimposed on type B are observed, in which the five-co-ordinated species is present but the six-co-ordinate species is also detectable.

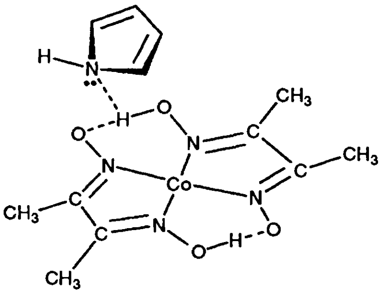
Upon addition of base in large excess (except for the weakest bases, R = CN or OH) the ESR spectra exhibited by the frozen solutions are similar and show superhyperfine coupling to two equivalent nitrogen atoms indicative of a six-co-ordinated species (Fig. 2) thus implying the formation of the 1 : 2 adduct in solution.

It must be remembered that for the 2-substituted pyridines it was only possible to isolate the 2-amino- and 2-methyl-pyridine alkylcobaloximes and that room-temperature photolysis yields only five-co-ordinate species.

2,4-, 2,6- *and* 3,5-*disubstituted pyridines* $NC_5H_3R(R')$. The cobaloximes with 3,5-dimethylpyridine behave exactly like pyridine, forming the 1:2 adduct when added in a 1:1 molar ratio. The 2,4-substituted base (R = R' = Me) forms the 1:1 adduct in a 1:1 molar ratio; in 1:4 molar ratio, it gives rise to ESR spectra in which the five-co-ordinated species is dominant but the six-co-ordinated species is already detectable, and forms the 1:2 adduct when added in a larger amount (*i.e.*, it behaves identically to 2-methylpyridine).

No co-ordination was observed for 2,6-dimethylpyridine (R = R' = Me) or 2-amino-6-methylpyridine when added in a 1:1 molar ratio and the ESR spectra are characteristic of the six-co-ordinate compound only if base is added in large excess. Stereochemical effects are evident when the bases are added in a 1:1 molar ratio but are not able to prevent 1:2 adduct formation if the base is added in a larger amount.

Non-aromatic Bases.—The results obtained for cobaloximes with piperidine and pyrrolidine are identical to those of pyridine. Pyrrole, the weakest base studied, exhibited a very different behaviour. As with some of the 2-substituted pyridines it was not possible to isolate the species $[Co^{III}(Hdmg)_2Bu^s(C_4H_4NH)]$. The ESR spectra recorded upon addition of base in 1:1, 1:1.5 and 1:10 molar ratios to $[Co^{III}(Hdmg)_2Bu^s(H_2O)]$ followed by irradiation are shown in Fig. 5. Upon addition of pyrrole in a 1:1 molar ratio, the ESR spectrum [Fig. 5(*a*)] is identical to that in Fig. 1 and is assigned to the species $[Co^{II}(Hdmg)_2]$ in solution. Upon addition of base in a 1:1.5 ratio some extra peaks appear [Fig. 5(*b*)] in both the high- and low-field features of the ESR spectrum. Addition of more base in a molar ratio of ⩾4:1 gives a different ESR spectrum [Fig. 5(*c*)] consisting of the superposition of two spectra with quite different values of A_z (132 and 114 G). One of the signals is identical to that in Fig. 1 and the other shows larger values of g_x and A_z and does not exhibit any hyperfine splitting due to interaction with an *N*-donor base in the axial co-ordination positions. The weakness of pyrrole as a base suggests that there is little likelihood of adduct formation and this is verified by the absence of hyperfine coupling to N. Nevertheless, an unambiguous interaction is observed in the ESR spectrum showing g_x and g_y widely different, suggesting a significant distortion in the *x*-*y* plane. We propose that solvation by pyrrole occurs by hydrogen bond interaction with the $Co(Hdmg)_2$ hydroxyl groups.



ESR Spectra Analysis.—*Analysis of frozen-solution ESR spectra.* All spectra clearly showed an interaction of the unpaired electron with the cobalt atom (^{59}Co, $I = \frac{7}{2}$) and, for the adducts, also with the axial ligands (^{14}N, $I = 1$). The spin-Hamiltonian parameters were obtained by computer simulation which also confirmed that all compounds have rhombic symmetry, although this rhombic distortion is smaller than that for the phosphorus analogues.[22]

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 $\Phi = ad_{z^2} + bd_{x^2-y^2}$ (taking the point-group symmetry to be C_{2v}).[38]

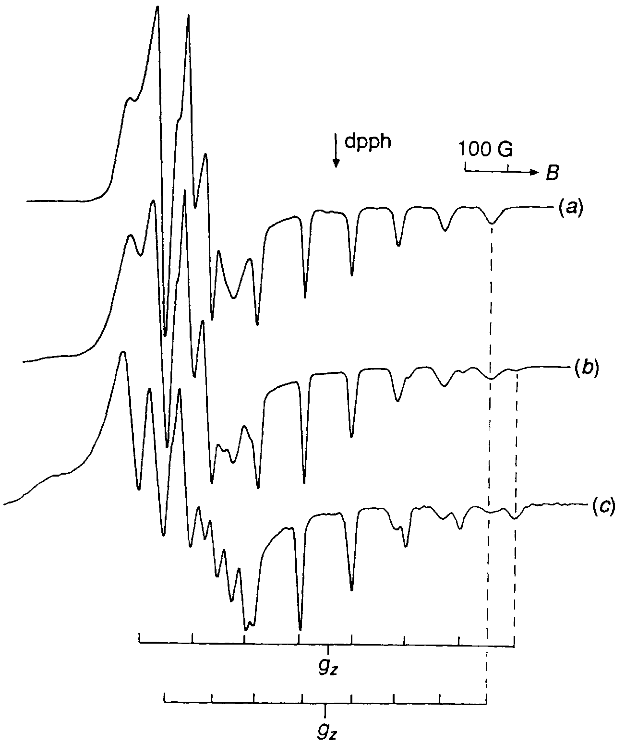


Fig. 5 Frozen-solution ESR spectrum (103 K) observed after room-temperature photolysis of a toluene–methanol solution of $[Co^{III}(Hdmg)_2Bu^s(H_2O)]$ to which pyrrole was added in a 1:1 (*a*), 1:1.5 (*b*) or 1:10 molar ratio (*c*)

Computer simulation. The simulations of the ESR spectra were carried out using a program based on Pilbrow and Winfield's formalism[39] which uses a spin Hamiltonian of the type $H = H(\text{Zeeman}) + H(\text{hyperfine}) + H(\text{ligand})$. The hyperfine term was deduced assuming a C_{2v} point-group symmetry at the cobalt centre and non-coincidence of the g and A_{Co} tensor axes 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 nitrogen axial interaction and it was assumed that the nitrogen tensor has the same principal axis as that of the g tensor. For the simulation of the ESR spectra of the compounds reported, the best fit was obtained for collinear g and A tensors in the x and y plane (rhombic symmetry) with neglect of any quadrupolar contribution to the spin Hamiltonian. The spin–Hamiltonian parameters for the compounds studied are summarized in Table 2.

Ligand spin density. No hyperfine coupling was observed to the equatorial nitrogen atoms, but from the observed hyperfine coupling to the axial donor nitrogen atoms, spin density on base N 2s and 2p orbitals can be determined. For the 1:2 adducts hyperfine couplings to axial N donor atoms are all the same within experimental error with A_z = 17 G and $A_x = A_y$ = 14 G. These values yield A_{aniso} of *ca.* 2G representing *ca.* 5.9% of the electron in the 2p orbital and A_{iso} = 15 G representing 2.7% of the electron in the 2s orbital. The p:s ratio of 2.2:1 is close to that expected on a pyridine nitrogen. For the 1:1 adducts the values of the hyperfine coupling to the axial N donor atom are smaller, A_z = 14 G and $A_x = A_y$ = 12 G. These values yield A_{aniso} of *ca.* 2 G representing *ca.* 5.9% of the electron in the 2p orbital and A_{iso} = 12 G representing 2.2% of the electron in the 2s orbital.

Cobalt spin densities. Analysis of the cobalt hyperfine coupling and g tensors allows deduction of the unpaired spin density in the metal 3d and 4s orbitals. The procedures for this have been described by one of us fully[20,21] and are based on those of McGarvey.[38] The signs of the x and y components of the cobalt hyperfine tensor are both positive for all adducts and were chosen by solving the McGarvey equations for the different possibilities and taking into account the values of total unpaired spin densities around the cobalt atom. The results are summarized in Table 2.

It is seen that of the electron density localized on the cobalt 3d orbitals, more than 99% is in the d_{z^2} orbital with only a trace in the $d_{x^2-y^2}$ orbital. The Fermi contact term K is positive in all adducts which indicates that there is strong admixture of the 4s orbital with the $3d_{z^2}$ orbital. The amount of this 4s character depends on the co-ordination geometry and varies in the range 5–9.0%.

The structure of the adducts: correlations. For the six-co-ordinated complexes in which the pyridine substituent is in the *ortho* or *para* position, there is a clear correlation between base strength and 3d unpaired spin density (P). As base strength (p.a.) of the pyridines decrease with more negative inductive effect substituents, so the value of P increases. This is as expected since the size of the lone pair orbital of the nitrogen gets smaller making the overlap of the nitrogen lone pair and Co $3d_{z^2}$ orbital less effective for bonding. As a result the Co–N σ-bonding molecular orbital (for weak bases) is largely based on nitrogen, and consequentially the corresponding antibonding molecular orbital containing the unpaired electron must be largely Co in character. The absence of adducts when the pyridine is *ortho*-substituted with CN or OH is readily explained because these bases are so much weaker. No correlation is apparent with pyridines substituted in the *meta* position since the inductive effect is much weaker.

For the five-co-ordinate compounds it is not possible to establish correlations since it was only possible to obtain ESR spectra for three bases, and for pyridine the photolysis was performed in frozen matrices. However for these three compounds the ESR spectra are spread over a wider range of magnetic field exhibiting larger values of g_x (2.3–2.4) and A_z [(98–110) × 10^{-4} cm^{-1}] and show larger differences between g_x and g_y.

Even without the full analysis of the results in terms of 3d and 4s spin densities, it is clear that six-co-ordinated complexes can be identified by large values of A_z [(70–90) × 10^{-4} cm^{-1}], small values of A_x and A_y [(25–35) × 10^{-4} cm^{-1}] and small g_x and g_y (2.16–2.21). The five-co-ordinate complexes are characterized by larger values of A_z [(98–105) × 10^{-4} cm^{-1}], smaller values of A_x and A_y [(8–20) × 10^{-4} cm^{-1}] and larger rhombic distortion ($\Delta_{xy} = g_x - g_y$).

Molecular-orbital Energy Levels.—For a cobalt macrocycle complex with a d_{z^2} ground state, as the strength of the ligand field along the z axis increases (*e.g.* with addition of axial ligands), so the energy of the d_{z^2} orbital is expected to rise substantially relative to the energies of the d_{xz} and d_{yz} orbitals. These orbitals themselves rise in energy relative to the d_{xy} and $d_{x^2-y^2}$ orbitals which have no component along the z axis. This directly affects the principal values of the g tensor since in C_{4v} symmetry, to a first approximation, the d_{z^2} orbital mixes strongly with the d_{yz} and d_{xz} orbitals by spin–orbit coupling. This causes g_x and g_y to get smaller as the ligand field strength along the z axis increases. Values of g_x and g_y for square-planar complexes will, in general, be larger than for similar complexes with one axial ligand, and larger again for a similar complex with two axial ligands.

In our complexes, there is a large difference in the values of g_x and g_y implying a large separation in the energies of the d_{yz} and d_{xz} orbitals. This lifting of the degeneracy is partly due to the N–Co–N angles of the four nitrogen atoms co-ordinating to the Co not all being equal, but also due to a marked twisting out of planarity of the CoN_4 unit. Deviations from planarity would enhance the difference in g_x and g_y.

Conclusion

Photolysis at room temperature of [Co^{III}(Hdmg)$_2$Bu^s(H$_2$O)] in the presence of *N*-donor bases yields as products adducts of the bases with bis(dimethylglyoximato)cobalt(II), thus implying homolytic cleavage of the cobalt–carbon bond.

The ESR results obtained for the photolysed solutions can be divided in two groups: one comprises pyridine derivatives with substituents in the *ortho* position; whereas the other contains pyridine, its other derivatives and non-aromatic bases. For the latter class of compounds, ESR spectra observed after room-temperature photolysis of solutions of [Co^{III}(Hdmg)$_2$Bu^s(L)] or of solutions obtained by addition of bases to [Co^{III}(Hdmg)$_2$-Bu^s(H$_2$O)], indicate that [Co^{II}(Hdmg)$_2$L$_2$] are the predominant paramagnetic species in solution. For this group of bases the cobalt(II) five-co-ordinate species, that are the photolysis primary products, are very reactive and abstraction of a second base molecule must take place, with rapid formation of the 1:2 adduct, thus preventing detection of 1:1 adducts in the ESR spectra. For bases with substituents in *ortho* positions, it is possible to detect the presence of species with only one bound base, [Co^{II}(Hdmg)$_2$L], in the photolysed solutions of [Co^{III}-(Hdmg)$_2$Bu^s(L)] or of those obtained by addition of base in a 1:1 molar ratio to aquacobaloximes, if strong enough to replace the water molecule. Groups in the *ortho* position induce deformations in the equatorial moiety, as can be gathered from the crystal structures of the corresponding alkyl(base)cobaloximes,[1,3,4] with both dimethylglyoximate fragments bending away from the occupied axial position and making the other axial position less accessible to co-ordination, thus stabilizing the five-co-ordinate species. In the presence of an excess of base, however, formation of six-co-ordinate species takes place, and the ESR spectra of solutions containing a large excess of base show only bands due to these latter species. It can be concluded that the ability of a *N*-donor base to co-ordinate at all depends on proton affinity, whilst the type of adduct formed with Co(Hdmg)$_2$ (1:1 or 1:2) depends on steric effects imposed on the equatorial ligands by the axial co-ordinated bases, and on the amount of base added since in the presence of a large excess of base formation of 1:2 compounds was always observed.

These results must be contrasted with those obtained for addition of symmetric *P*-donor bases to the same cobalt(III) compounds[22] as they form only 1:1 adducts even in the presence of a large excess of base, whereas *N*-donor bases, even those with substituents in *ortho* positions that are able to form 1:1 adducts, will in the presence of excess base co-ordinate a second molecule. It is important to bear in mind that a phosphine or phosphite molecule induces, in the equatorial plane, much larger distortions than do pyridine or substituted pyridine molecules[3,5] and so the conclusion is that for the Co(Hdmg)$_2$ system the tendency to form one type of adduct seems to be associated predominantly with the distortions the first axial ligand induces in the equatorial moiety upon co-ordination.

The possibility of the equatorial ligand to be deformed and the electronic energy changes associated with this deformation seem to be the dominant factor in determining the formation of different type of adducts. Among all macrocyclic or pseudo-macrocyclic equatorial ligands studied,[7–9,15–17,19,24] [Co-(Hdmg)$_2$] through the presence of the O–H–O bridges is the most flexible, exhibiting bending and twisting of the two dimethylglyoxime ligands. The equatorial moiety can be easily deformed but with steep changes in electronic energy, and thus for most systems the planarity is maintained which implies the occurrence of six-co-ordinate compounds.

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