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Characterization of the photolysis products of *sec*-butylcobaloximes with imidazole and benzimidazole bases

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Abstract

The products obtained on the photolysis, under anaerobic conditions, of *sec*-butylcobaloximes with bound N-donor Imidazole and Benzimidazole bases, and *sec*-(C_4H_9)Co($DH)_2$L are identified and characterized. The results are compared with those obtained for other alkylcobaloximes, mainly in terms of the involvement of the photolysis primary products in further reactions with the species in solution, namely the ability to form adducts with the base L. Electron paramagnetic resonance (EPR) spectroscopy was chosen to monitor the photolysis process, to obtain relevant information about the electronic structure of the cobalt(II) complexes, and to determine the extent of spin density delocalized into the ligands. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cobaloximes; Photolysis; Cobalt(II) complexes; EPR

1. Introduction

The structural characterization of B_{12} systems has revealed the existence of a cobalt–carbon (Co–C) bond, and the subsequent studies have demonstrated that the cleavage of this bond is a key step in the enzymatic mechanisms in which coenzyme B_{12} and methyl B_{12} are involved [1]. Although it has not been possible to find a class of model compounds that mimic the physical properties of cobalamines, several groups of compounds have been widely studied [2–11]. Additionally, decisive information on the development of methods for understanding the B_{12} properties, especially the factors that stabilize/labilize the Co–C bond have been provided. Cleavage of the Co–C bond in model compounds may be induced either by photolysis or thermolysis, and the study of photolysis products of cobaloximes has received particular attention [12–18].

The relevance of electronic and steric effects in Co–C bond cleavage mechanisms has been clearly demonstrated in model compounds by investigations concerning the influence of the ligand *trans* to the alkyl group in a series of alkylcobaloximes and Costa-type compounds, with nitrogen [2–4] and phosphorous donor ligands [2,7]. Most of this work has been performed with cobalt(III) compounds, and much less information is available on the structure and reactivity of the cobalt(II) species formed resulting from the homolysis of the Co–C bond.

Information on the structure and reactions in which the cobalt(II) species participate has been obtained by studying the photolysis products of B_{12} compounds and the related models using electron paramagnetic resonance (EPR) and XAFS spectroscopies. Recently an in situ X-ray absorption spectroelectrochemical study on hydroxocobalamin allowed the structural characterization of the cobalt center in the three oxidation states [19].

The chemistry of cobaloximes, compounds with the general formula $XCo^{III}(DH)_2L$ where X and L are neutral mononegative ligands and DH_2 the dimethylglyoxime, has been extensively developed owing to its connection with the B_{12} chemistry [1–5].

The studies regarding the characterization of the products of anaerobic photolysis in protic and aprotic solvents of alkylcobaloximes, compounds with the general formula $RCo^{III}(DH)_2L$ where R is an alkyl group,

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L a neutral ligand and DH_2 the dimethylglyoxime, with pyridine [10–16] and phosphorus [17] bases showed that the nature and reactivity of the species formed depend on the Lewis base and the alkyl group. Photolysis products of alkylcobaloximes with symmetric phosphorus donor bases were shown to be independent of the alkyl group and photolysis induces, in all cases, the homolytic cleavage of the Co–C bond. The products obtained are alkyl radicals and cobalt(II) five-coordinate species, and these latter complexes are not involved in the subsequent reactions and are stable in the temperature range of 77–300 K [18]. For alkylcobaloximes with the pyridine-derived bases, it has been shown that the products observed upon photolysis depend on the alkyl group and also that the photolysis primary products undergo further reactions in solution giving rise to secondary products that remain in solution even after the various thermal cycles [16,17].

In order to compare the behavior of pyridinecobaloximes with that of the other alkylcobaloximes in which the nitrogen base is different, we studied the photolysis of solutions of *sec*-butylcobaloximes with imidazole and benzimidazole bases. We also investigated the photolysis of solutions of aqua-(*sec*-butyl)bis(dimethylglyoximato)cobalt(III) in the presence of Lewis bases added in molar ratios of 1:1 and 1:10. This study allows getting insight on the ability of the bases to form 1:1 and 1:2 adducts with a common equatorial moiety and the factors that may contribute to the predominance of each type of adduct. According to the results obtained for phosphorus and pyridine cobaloximes the type of adducts formed is dependent on the sterical deformations induced by the base on the equatorial plane.

EPR spectroscopy was used to monitor the photolysis process; to obtain relevant information about the electronic structure of the cobalt(II) complexes; to determine the extent of spin density delocalized into the neighboring atoms; and to map the distribution of the unpaired electron spin density over the molecule (Fig. 1).

2. Experimental

2.1. Reagents

The solvents, obtained from Merck, were dried and purified according to the standard procedures [20] and kept over 4A molecular sieves prior to use. All other chemicals were from Aldrich and used as received.

2.2. Instrumentation

The EPR measurements were made on a Varian E-109 or on a Bruker ESP 300E spectrometer, both operating at 9 GHz and equipped with variable temperature units (Varian E-257 and Bruker B-VT2000). The

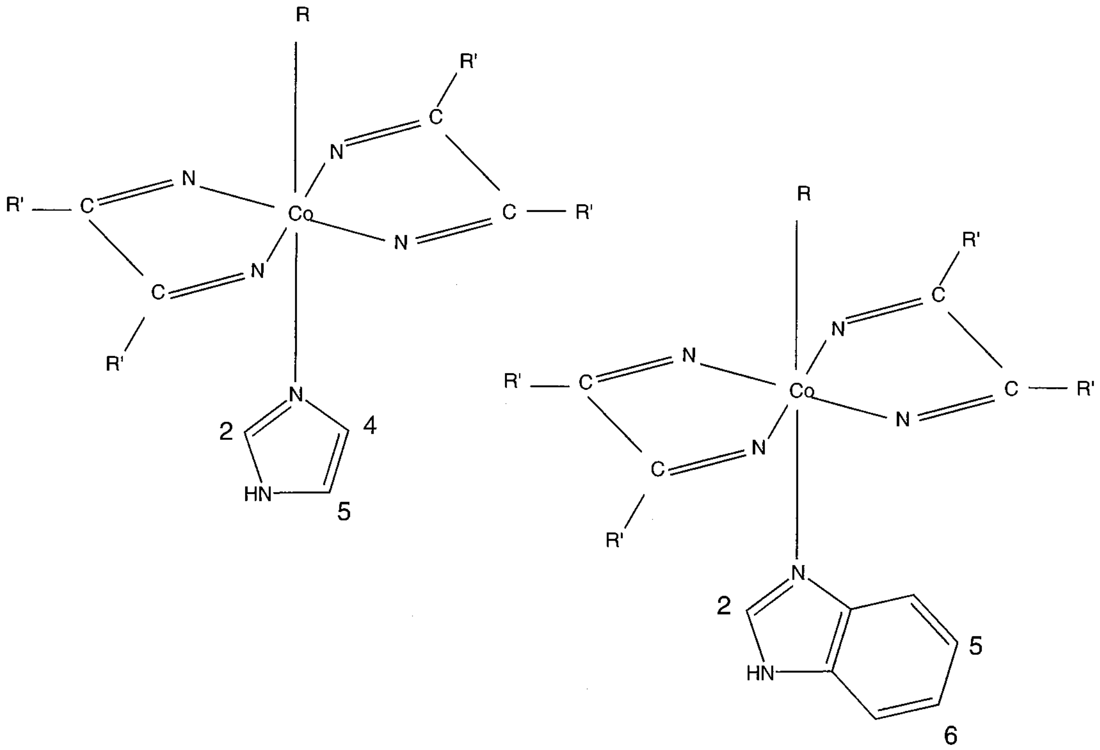

Fig. 1. Structure and formula of the cobaloximes studied.

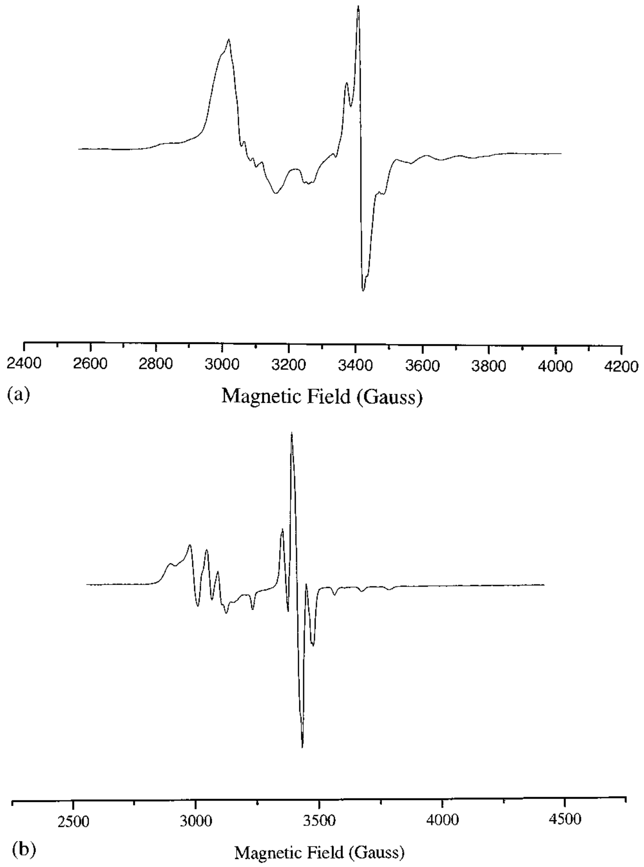

Fig. 2. (a) Frozen solution EPR spectrum of a toluene–methanol solution of *sec*-C_4 $H_9Co(DH)_2(2,5,6\text{-}Me_3Bz)$ irradiated at 77 K and recorded at 100 K. (b) Frozen solution EPR spectrum of a toluene–methanol solution of *sec*-$C_4H_9Co(DH)_2(2\text{-}MeBz)$ irradiated at 77 K and recorded at 100 K.

spectra were calibrated with diphenylpicrylhydrazyl (dpph) and the magnetic field was calibrated using Mn^{2+} in MgO.

2.3. Synthesis

Alkylcobaloximes, compounds with the general formula $RCo(DH)_2$ L, were prepared by the method outlined by Toscano et al. [21] For all the prepared compound the expected stoichiometry was confirmed by elemental analysis.

2.4. Sample preparation

All manipulations were carried out under nitrogen; solvents were deoxygenated by reflux/distillation under nitrogen and all solids degassed under vacuum prior to use. Samples for photolysis were prepared by making solutions of the desired compounds, in toluene–methanol (1:1), or by dissolving the aquacobaloxime and adding stoichiometric amounts (1:1 and 1:10) of the Lewis base.

2.5. Photolysis

Sample irradiation was performed under anaerobic conditions keeping the solutions in EPR quartz tubes and using a 250 W Philips HP/T Hg lamp as the light source, $\lambda_{max} = 560–580$ nm. The irradiation times used are given in Table 1 and were about 15–30 min for samples kept at 300 K and 60 min for samples at 77 K.

3. Results and discussion

The purpose of this work is to study the products obtained on the photolysis of *sec*-butylcobaloximes with bound N-donor Imidazole and Benzimidazole bases, under anaerobic conditions. The work involves the identification and characterization of photolysis primary products and monitoring the reactivity of the latter towards species present in solution. Previous studies on pyridinecobaloximes revealed that the cobalt(II) primary products are quite reactive and undergo further reactions in solution in contrast with those obtained from phosphinecobaloximes, for which the Co(II) primary products are maintained in solution at room temperature.

The photolysis process is monitored by EPR as freshly prepared cobaloxime solutions are, as expected for low-spin Co(III) compounds, EPR silent but become active if the homolytic cleavage of the Co–C bond occurs. Characterization of the photolysis primary products is achieved by photolysing the solutions in the frozen matrix and observing the EPR spectra at the same temperature. The possible involvement of the primary products in secondary reactions is tested by allowing the matrix to relax as the temperature is slowly raised to room temperature and the complete characterization of the products formed is obtained by analyzing of the EPR spectra exhibited after re-cooling at 77 K. These results are compared with those obtained for the photolysis performed on solutions kept at room temperature.

3.1. Photolysis in the frozen matrix, 77 K

Cobaloxime solutions irradiated at 77 K yield EPR spectra that exhibit a narrow signal at $g = 2.00$, a broad band at $g = 2.14$ and a signal that is spread over a wider range of magnetic field values and with substantial g tensor anisotropy ($g_{av} = 2.15$). The latter is assigned to a paramagnetic metal center as can be inferred from the observed hyperfine splitting in the high-field region owing to the interaction of the unpaired electron with a cobalt nucleus (^{59}Co, $I = 7/2$).

On warming the solutions to 100 K the band at $g = 2.14$ vanishes, but the other two remain detectable (Fig. 2). These two bands are assigned to an organic

Table 1
Type of Co(II) species formed upon photolysis of cobaloximes

sec-$C_4H_9Co(Hdmg)_2L$			*sec*-$C_4H_9Co(Hdmg)_2H_2O+L$					
				1:1		1:1		1:10
	hv, 77 K	Coordination number		*hv*, 77 K	Coordination number	*hv*, room temperature.	Coordination number	Coordination number
Im	60 min	Five	Im	60 min	Five	15 min	Five	Six
2-Me–Im	60 min	Five	2-Me–Im	60 min	Five	15 min	Five	Five+six
2-Et–Im	60 min	Five	2-Et–Im	60 min	Five	15 min	Five	Five+six
2-Et–4Me–Im	60 min	Five	2-Et–4Me–Im	60 min	Five	15 min	Five	Five+six
N–Me–Im	60 min	Five	N–Me–Im	60 min	Five	15 min	Five	Six
4–Me–Im	60 min	Five	4-Me–Im	60 min	Five	30 min	Low resolution	Five+six
4,5 Cl_2–Im	60 min	Four+five	4,5Cl_2–Im	60 min	Four+five	30 min	Four+five	Four+five
2-Me-5-Nitro–Im	60 min	Four	2-Me-5-Nitro–Im	60 min	Four	30 min	Four	Four
Bz	60 min	Five	Bz	60 min	Five	30 min	Five	Six
5,6 Me_2–Bz	60 min	Five	5,6 Me_2–Bz	60 min	Five	30 min	Five	Six
2,5,6 Me_3–Bz	60 min	Five	2,5,6 Me_3–Bz	60 min	Five	30 min	Five	Six

radical (R) and to a Co(II) species, and the broad band that was observed at $g = 2.14$ must be owing to the strongly exchanged coupled system $\{[R^\bullet]\cdots[Co^{II}\text{-complex}]\}$ which is kept immobilized by the lattice [15].

This result shows that, for all cobaloximes, photolysis induces the homolytic cleavage of the Co–C bond originating the corresponding alkyl radical and a Co(II) complex. The results are interpreted as mentioned earlier [16–18] for alkylcobaloximes with pyridine and phosphorus bases according to the mechanism proposed by Symons [14] which assumes that on light absorption an electron from the equatorial plane 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:

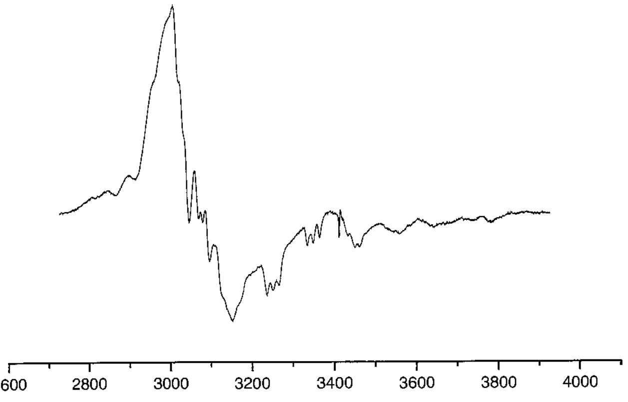

Fig. 3. Frozen solution EPR spectrum of a toluene–methanol solution of *sec*-$C_4H_9Co(DH)_2(2,5,6\text{-}Me_3Bz)$, irradiated at 77 K and recorded at 100 K, after being warmed to room temperature and frozen to 100 K. Spectrum of type A.

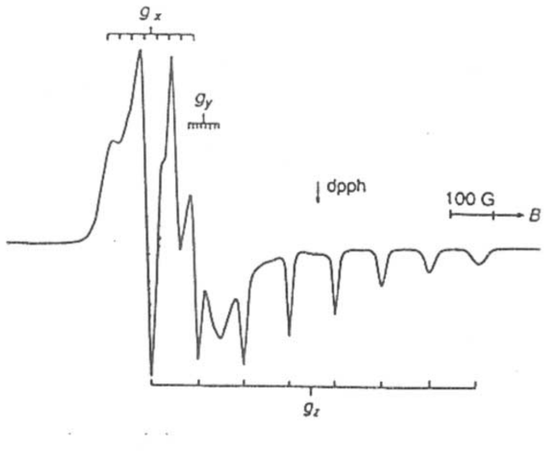

Fig. 4. Frozen solution EPR spectrum of a toluene–methanol solution of *sec*-$C_4H_9Co(DH)_2(2\text{-}Me\text{-}5\text{-}NO_2Im)$, irradiated at 77 K and recorded at 100 K, after being warmed to room temperature and frozen to 100 K. Spectrum of type B.

$$R\text{–}Co^{III}\text{complex} \rightarrow [R^\bullet] + [Co^{II}\text{complex}]$$

$$[R^\bullet] + \text{Hsolvent} \rightarrow RH + [\text{solvent}^\bullet]$$

$$[R^\bullet] \rightarrow R^\bullet$$

where the brackets represent cage trapping.

Comparing the EPR spectra recorded at 100 K it is discernible that they are not identical for all the cobaloximes studied although all of them exhibit characteristics of Co(II) spectra. For the compounds with the Lewis bases Im, 2-Me–Im, 2-Et–Im, 2-Et–4-Me–Im, *N*-Me–Im, 4-Me–Im, Bz, 5,6-Me_2–Bz, 2,5,6-Me_3–Bz the EPR spectrum shows the cobalt hyperfine lines further split into three of equal intensity (1:1:1) thus indicating the interaction of the unpaired electron with one axially bound nitrogen atom (^{14}N, $I = 1$), (Fig. 2a). Cobaloximes with the bases 4,5-Cl_2–Me–Im, 2-Me–5-NO_2–Im, exhibit spectra in which cobalt hyperfine lines are observed but no axial interactions were detected (Fig. 2b). The spectra recorded for the latter set are identical with the one obtained when a solution of the aquacobaloxime is irradiated in the same conditions.

When the samples are further warmed, the radical signal looses intensity and vanishes near the glass-softening point and the cobalt(II) signal begins to broaden and converges into a single line at 300 K. After recooling the solutions to 100 K, three types of EPR spectra (A, B and C) are observed. Cobaloximes with the bases Im, 2-Me–Im, 2-Et–Im, 2-Et-4-Me–Im, N–Me–Im, 4-Me–Im, Bz, 5,6-Me_2–Bz, and 2,5,6-Me_3–Bz, exhibit spectra of type A (Fig. 3), with a large g tensor anisotropy and in which three g features may be distinguished (type A). In the high-field region the hyperfine coupling of the unpaired electron with the cobalt (^{59}Co, $I = 7/2$) and nitrogen (^{14}N, $I = 1$) atoms is clearly detected. Each of the eight lines arising from coupling to cobalt is further split into three with relative intensities 1:1:1, resulting from the superhyperfine coupling with *one* axially bound nitrogen atom. This spectrum is assigned to a low-spin cobalt(II) compound with one axially bound imidazol or substituted imidazol base, $[Co(DH)_2L]$. On the other hand cobaloximes with the base 2-Me-5-NO_2–Im show spectra (Fig. 4) with a large g tensor anisotropy and in which three g features are also discernible, exhibiting hyperfine coupling of the unpaired electron with the cobalt (^{59}Co, $I = 7/2$) atom (type B) in the high-field region. The eight lines arising from coupling to cobalt are not split further, thus indicating that there is no axially bound nitrogen base. This spectrum is assigned to a low-spin cobalt(II) compound, $[Co(DH)_2]$. Finally, the cobaloxime with the base 4,5-Cl_2–Me–Im exhibits a spectrum of type C (Fig. 5), which is a superposition of spectra of types A and B thus implying the presence of two cobalt species in solution, $[Co(DH)_2L]$ and $[Co(DH)_2]$ (type C).

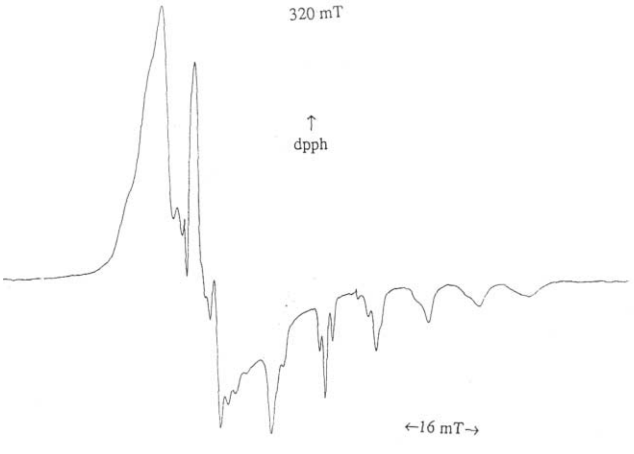

Fig. 5. Frozen solution EPR spectrum of a toluene–methanol solution of *sec*-$C_4H_9Co(DH)_2(4,5\text{-}Cl_2Im)$, irradiated at 77 K and recorded at 100 K. Spectrum of type C.

The results obtained for the photolysis of cobaloximes are summarized in Table 1 together with those obtained for the photolysis of solutions of the aquacobaloxime to which the imidazole bases have been added in a 1:1 ratio. The results are identical for a given L base and the same primary and secondary photolysis products are observed thus confirming that for the imidazole bases also the solutions are equivalent [16].

The results indicate that, for all cobaloximes, the homolytic cleavage of the Co–C bond is induced on photolysis and the cobalt primary products, complexes of type $[Co^{II}(DH)_2L]$ or $[Co^{II}(DH)_2]$, remain in solution after a thermal cycle from 100 to 300 K and back to 100 K. The result is identical with the one observed for cobaloximes with symmetric phosphorus bases [18] and contrasts with the one observed for pyridinecobaloximes [16] for which the photolysis primary product $[Co^{II}(DH)_2L]$ is never observed after the thermal cycle which means that the species is involved in further reactions in solution. For cobaloximes with pyridine bases a six-coordinate complex $[Co^{II}(DH)_2L_2]$ is always present after the thermal cycle even in solutions with no free base present. A possible interpretation is the abstraction of base molecules from other cobaloximes in solution [16] and studies to clarify this mechanism using other spectroscopic and magnetic methods are in progress.

A new result that emerged with the imidazole bases is the observation of the species $[Co^{II}(DH)_2]$ as a primary product of photolysis of a cobaloxime solution, as is evident from the recording of type B spectra for compounds with the base 2-Me-5-NO_2–Im. We believe that this result is a consequence of the non-stability of the cobaloxime *sec*-$C_4H_9Co(DH)_2(2\text{-Me-5-}NO_2\text{–Im})$ in methanolic solutions.

If the result had been observed only for a solution of aquacobaloxime to which the base had been added, one could assume that base replacement did not occur and so the result is coincident with that of the aquacobaloxime itself. However, as it is observed for solutions of cobaloximes that have been isolated as powders it must be admitted that in methanol–toluene solutions the Lewis base is displaced by the solvent. In both cases the base has a substituent in a position, which is adjacent to the coordinating nitrogen atom, and as it has been shown for a set of *ortho*-pyridine bases [16] this is enough reason to prevent the coordination or induce the displacement of the base. It is well known that bases *trans* to the alkyl groups are labile and also that five-coordinate compounds have been identified for other B_{12} model compounds such as RCo^{III}(bae) and RCo^{III}(salen) [22,23].

The observation of a type C spectrum for the 4,5-Cl_2–Me–Im cobaloxime is interesting because it shows the coexistence of the species $[Co^{II}(DH)_2L]$ and $[Co^{II}(DH)_2]$ in solution.

3.2. Photolysis at 300 K

Cobaloxime solutions were irradiated at room temperature and their EPR spectra recorded at 300 and 100 K. Spectra at 300 K comprises a single broad band and spectra recorded after cooling at 100 K are identical to those obtained for samples irradiated at 77 K and warmed at 300 K. The spectra are characteristic of low-spin Co(II) species with coordination numbers five or four, $[Co^{II}(DH)_2L]$ or $[Co^{II}(DH)_2]$, and the results obtained for each base are summarized in Table 1.

3.3. Photolysis in the presence of an excess of base

The results of photolysis of aqua-*sec*-butylcobaloxime solutions to which the L base was added in a 1:10 molar ratio are summarized in Table 1.

In the above conditions, solutions of cobaloximes with bases Im, N–Me–Im, Bz, 5,6-Me_2–Bz and 2,5,6-Me_3–Bz exhibit spectra that show two well-separated g features and lines owing to the hyperfine coupling of the unpaired electron with the cobalt atom (^{59}Co, $I = 7/2$) and with two nitrogen atoms (^{14}N, $I = 1$) in the high-field region. Each of the eight lines arising from the hyperfine coupling to cobalt is split into five with relative intensities 1:2:3:2:1, resulting from the superhyperfine coupling with *two* equivalent nitrogen atoms (Fig. 6). This spectrum is assigned to a low-spin cobalt(II) species with two axially bound base molecules, $[Co(DH)_2L_2]$. Solutions of cobaloxime with 2-Me-5-NO_2–Im yield as before an EPR spectrum characteristic of the four-coordinate species and for the other bases a mixture of the five-and six-coordinate species is observed.

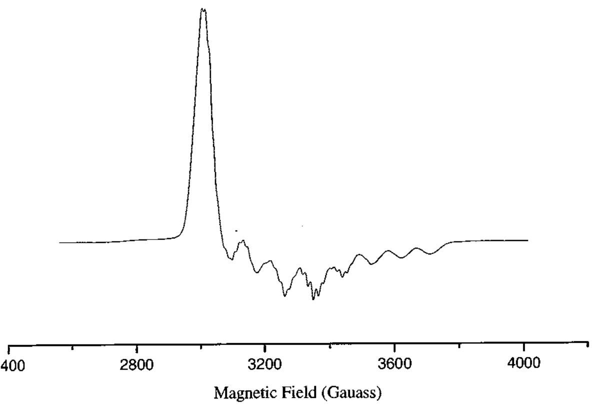

Fig. 6. Frozen solution EPR spectrum of a toluene–dichloromethane solution of of *sec*-$C_4H_9Co(DH)_2(H_2O)$ and the base (2,5,6-Me_3Bz) added in a ten-fold excess, irradiated at 77 K and recorded at 100 K, after being warmed to room temperature and frozen to 100 K.

3.4. EPR spectra analysis

The components of the spin-Hamiltonian parameters (Table 2) were obtained by the computer simulation of the experimental spectra and the results confirm that the spectra must be interpreted in terms of three different *g* values. The analysis was based on the assumption of a $^2A_1$ ground state for the cobalt(II) atom, comprising a mixture of the d_{z^2} and $d_{x^2-y^2}$ metal orbitals of the form $\Phi = a d_{z^2} + b d_{x^2-y^2}$ (taking the point-group symmetry to be C_{2v}) [24].

3.4.1. Computer simulations

The EPR spectra of cobalt(II) compounds were simulated using a program based on Pilbrow's formalism [25,26] which uses a spin-Hamiltonian of the type H = H(Zeeman) + H(hyperfine) + H(ligand). The hyperfine term was deduced assuming a C_{2v} point-group symmetry at the cobalt center and the non-coincidence of the *g* and *A*(Co) tensor axes in the *xy* plane. As no interaction of the unpaired electron with the nitrogen atoms of the equatorial plane was observed, 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. In simulating the experimental spectra, the best fit was obtained for collinear *g* and *A* tensors in the *x* and *y* plane (rhombic symmetry) with the absence of quadrupolar contribution to the spin-Hamiltonian.

3.4.2. Cobalt spin densities

The analysis of the *g* and cobalt hyperfine tensors allows the calculation of the unpaired spin density in the 3d and 4s orbitals of the metal. The procedures for these calculations have been described in Ref. [27] based on those by McGarvey [24] and the results obtained are shown in Table 2.

3.4.3. Ligand spin density

No hyperfine coupling was observed with the equatorial nitrogen atoms, but from the observed hyperfine coupling to the axial donor nitrogen atoms, spin density on base nitrogen 2s and 2p orbitals could be determined. The procedures for this have been described in Ref. [18,27] and the results are shown in Table 2.

The EPR parameters are similar to those obtained for low-spin Co(II) complexes with the same number and type of axial ligands. The values obtained are consistent with a $^2A_1$ ground state and the values of a^2 and b^2 show that it is essentially a d_z^2 state thus justifying the absence of hyperfine coupling with the nitrogen atoms of the coequatorial ligand and strong coupling with the axial ligands. The geometry is confirmed as rhombic and it is evident that the degree of anisotropy,

Table 2
EPR parameters of the Co(II) species formed upon photolysis of cobaloximes. The units of A_x, A_y, A_z, $-kP$ and P are 10^{-4} cm^{-1}

	g_x	g_y	g_z	A_x	A_y	A_z	a^2	b^2	$(-kP)$	P	ρ 3d	ρ 4s	ρ Co	ρ Total
Five coordinate														
Im	2.246	2.239	2.032	65	8	88	0.9472	0.0528	0.0037	128	0.50	0.06	0.57	0.57
2-Me–Im	2.370	2.255	2.026	40	10	92	0.9990	0.0010	0.0021	156	0.61	0.06	0.67	0.68
2-Et–Im	2.265	2.255	2.056	84	5	95	0.9238	0.0762	0.0044	150	0.59	0.08	0.67	0.67
2-Et–4Me–Im	2.242	2.196	2.009	65	18	91	0.9566	0.0434	0.0043	107	0.42	0.06	0.48	0.49
N–Me–Im	2.255	2.208	2.030	65	18	96	0.9680	0.0320	0.0045	121	0.48	0.07	0.55	0.55
Bz	2.190	2.177	2.007	90	14	91	0.8620	0.1380	0.0052	111	0.44	0.07	0.51	0.51
5,6 Me_2–Bz	2.230	2.173	2.006	66	18	90	0.9523	0.0477	0.0045	101	0.40	0.06	0.46	0.47
2,5,6 Me_3–Bz	2.220	2.191	2.006	86	18	92	0.8851	0.1149	0.0052	107	0.42	0.07	0.49	0.50
Six coordinate														
Im	2.238	2.218	2.018	25	25	70	0.9999	0.0001	0.0029	86	0.34	0.05	0.39	0.77
N–Me–Im	2.195	2.180	2.012	25	35	80	0.9958	0.0042	0.0037	87	0.34	0.05	0.40	0.80
Bz	2.185	2.169	2.011	25	35	87	0.9965	0.0035	0.0039	97	0.38	0.06	0.44	0.88
5,6 Me_2–Bz	2.220	2.172	2.011	25	35	83	0.9942	0.0058	0.0036	94	0.37	0.05	0.42	0.85
2,5,6 Me_3–Bz	2.185	2.170	2.012	25	35	85	0.9963	0.0037	0.0038	94	0.37	0.06	0.43	0.86

measured as $\Delta_{xy} = g_x - g_y$, is higher for the five-coordinate compound. The largest values of hyperfine coupling to cobalt are those of the A_z component and according to the results obtained as a solution for McGarvey's equations the signs of the A_x and A_y components were both taken as positive. The values of Fermi contact, $-kP$, term suggest a significant contribution of the 4s orbital to the $^2A_1$ ground state and the values of anisotropic spin density, P, lie within the range expected for this type of complexes, with the largest values being observed for the five-coordinate species.

Taking the values of the hyperfine coupling tensor with the axial ligands, spin densities on the 2s and 2p orbitals have been calculated according to the usual procedures giving values of ca. 6% for the 2p orbital and 2% in the 2s orbital.

4. Conclusions

For all the cobaloximes studied photolysis resulted in the homolytic cleavage of the Co–C bond and the cobalt primary products, complexes of type $[Co^{II}(DH)_2L]$ or $[Co^{II}(DH)_2]$, remain in solution after a thermal cycle 100–300–100 K. This result is similar to the one observed for cobaloximes with symmetric phosphorus bases [18], and contrasts with the one observed for pyridinecobaloximes [16,17] for which the photolysis primary product $[Co^{II}(DH)_2L]$ is never observed after the thermal cycle always giving rise to the compound $[Co^{II}(DH)_2L_2]$. For imidazole and benzimidazole bases the formation of the 1:2 adduct is observed only in the presence a 1:10 excess and for some of the bases the 1:1 adduct is still detected in solution. An important conclusion of this work is that the ability exhibited by pyridines to form 1:2 adducts in the present non-excess of base is not observed for all nitrogen bases and must be related to the properties of the pyridine compounds.

From X-ray data of alkylcobaloximes [2,3] with the various types of bases it is known that the phosphorus bases induce significant deformations on the equatorial moiety and thus the five-coordinate species is favored; while for the pyridine bases the absence of such stereochemical factors favor the formation of the six-coordinate compound. The results obtained with the imidazole bases, suggest that the electronic effects are in this case important, and in fact it is observed that the presence of electron-withdrawing substituents favors the presence of the species with non-bound bases. It was observed that the base 2-Me-5-NO_2–Im is never bound to cobalt in methanol–toluene solutions as EPR spectra of the four-coordinate complex $[Co(DH)_2]$ are always registered and for the base 4,5-Cl_2–Me–Im the species $[Co(DH)_2]$ is in equilibrium with the five-coordinate one $[Co(DH)_2L]$ in all the conditions studied. The presence of the six-coordinate complex $[Co^{II}(DH)_2L_2]$ is detected in solutions of cobaloximes with the non-substituted bases Im and Bz or bases with substituents having electron-donating properties, N–Me–Im, 5,6-Me_2–Bz and 2,5,6-Me_3–Bz added in a ten-fold excess.

The influence of steric factors seems to have some relevance in preventing the predominance of the six-coordinate complex in the case of imidazole bases with substituents in positions 2 or 4 as a pure spectrum of the six-coordinated species, $[Co(DH)_2L_2]$, is not observed but always a mixture of five- and six-coordinate compounds even in the presence of the base in a ten-fold excess.

In these conditions the results for the remaining bases imply that: (a) 2-Me-5-NO_2–Im is never bound to cobalt in methanol–toluene solutions as EPR spectra of the four-coordinate complex, $[Co(DH)_2]$, are always registered; (b) for the base 4,5-Cl_2–Me–Im the species $[Co(DH)_2L]$ and $[Co(DH)_2]$ exist in equilibrium in all the conditions studied; (c) for imidazole bases with substituents in positions 2 or 4 a pure spectrum of the six-coordinated species, $[Co(DH)_2L_2]$, is not observed.

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