Photolysis Primary Products of Alkylcobaloximes Controlled by the Cobalt−Carbon Bond Strength

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Anaerobic photolysis of several methyl- and benzylpyridinecobaloximes was studied by electron spin resonance spectroscopy in aprotic solvents, at three temperatures of irradiation and with use of visible and UV light sources. Homolysis of the cobalt−carbon bond is photochemically induced when irradiation with visible light is performed at room temperature, giving rise to Co(II) five-coordinate species and organic radicals. Irradiation with visible light of fluid (250 K) or frozen (77 K) solutions does not cause homolysis of the cobalt−carbon bond, in contrast with the results reported for other alkylpyridinecobaloximes. Homolysis of the cobalt−carbon bond is achieved at all temperatures if a UV light source is used, and the results are rationalized in terms of the values of the cobalt−carbon bond dissociation energies. The results obtained at 250 K for a series of isotopically substituted methylpyridinecobaloximes allowed the definitive assignment of the spectrum obtained upon photolysis at 250 K to a cobalt(III) nitroxide radical and not to a Co(II) center as has been proposed earlier.

Introduction

The chemistry of cobaloximes, compounds of general formula [LCo(Hdimethylglyoxime)$_2$R], has been extensively studied since they have been proposed as B$_{12}$ models.[1] Although it is now recognized that these and other models[2] have little relevance to the understanding of B$_{12}$ biochemistry,[3] cobaloximes have played its role in helping to understand the reactivity of the cobalt−carbon bond. As a large number of different alkyl groups and bases may be bound to the [Co(Hdimethylglyoxime)$_2$] equatorial moiety, it was possible to study the influence of steric and electronic effects of the axial ligands on cobaloxime structure and reactivity.[4]

The cleavage of the cobalt−carbon bond, which is a central issue in B$_{12}$ chemistry, has been studied in model compounds, and several reports have appeared in the literature concerning anaerobic photolysis in protic and aprotic solvents of alkylcobaloximes with nitrogen[5−8] and phosphorus[9] donor bases. It has been demonstrated that the photolysis products of alkylcobaloximes with symmetric phosphorus donor bases are independent of the alkyl group and that at all temperatures irradiation gives rise to a cobalt(II) five-coordinate species and an organic radical, thus implying the homolytic cleavage of the Co−C bond.[9]

For alkylcobaloximes with nitrogen bases it has been reported that the products observed upon photolysis with visible light depend (a) on the ligand *trans* to the alkyl group, as it may induce deformations on the equatorial moiety that control the reactivity of the photolysis primary products,[7,8] and (b) on the alkyl group,[5] as photolysis at 250 K of methyl- and benzylpyridinecobaloximes was claimed not to induce homolysis of the cobalt−carbon bond but reduction of the metal center. However, it must be pointed out that this conclusion was based on results obtained only for two compounds and that the analysis of the ESR spectra was controversial.[6a] Also, irradiation at lower temperatures and with use of other light sources was not investigated.

In this work we characterize the products obtained upon anaerobic photolysis in aprotic solvents of a set of pyridinecobaloximes with methyl and benzyl alkyl groups (Chart 1). Photolysis has been performed with visible and UV light sources, both in fluid (300 and 250 K) and frozen (77 K) solution. Electron spin resonance (ESR) spectroscopy was used to monitor the photolysis process, to identify the paramagnetic species formed,[5−9]

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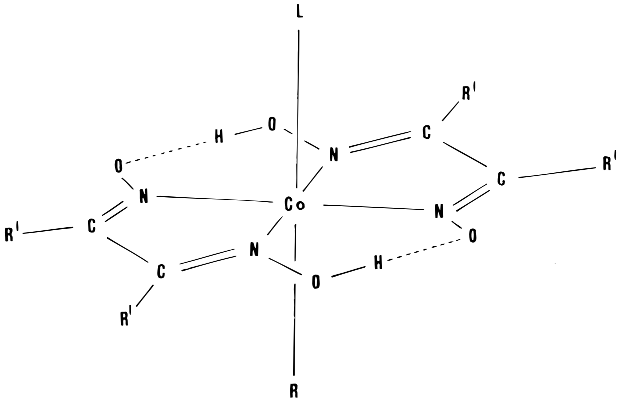
Chart 1. Alkylcobaloximes, Compounds of General Formula [RCo(Hdioxime)$_2$L]



1, $CH_3Co(DH)_2py$
2, $CD_3Co(DH)_2py$
3, $CH_3Co(DH)_2(3\text{-pic})$
4, $CH_3Co(DH)_2(3,5\text{-lut})$
5, $C_6H_5CH_2Co(DH)_2py$
6, $C_6H_5CH_2Co(DH)_2(3\text{-pic})$
7, $C_6H_5CH_2Co(DH)_2(3,5\text{-lut})$
8, $CH_3Co(PH)_2py$
9, $CH_3Co(DH)_2(^{15}Npy)$
10, $C_6H_5CH_2Co(DH)_2(^{15}Npy)$
11, $CH_3Co(GH)_2py$

and to get relevant information about the structure of the cobalt(II) complexes.[10]

The results obtained confirm that methyl- and benzylpyridinecobaloximes exhibit a photochemical behavior that is different from that reported for (a) pyridine cobaloximes with other alkyl groups and (b) methyl- and benzylcobaloximes with phosphine bases.

The results obtained in fluid solution at 250 K definitively allowed the identification of the photolysis product as a cobalt(III) nitroxide radical, which implies that, in these conditions, photolysis does not induce homolytic cleavage of the cobalt−carbon bond or reduction of the metal center but abstraction of one hydrogen atom from the cobaloxime bridge.

The results obtained with an UV light source show that homolysis of the cobalt−carbon bond is achieved at all temperatures and are rationalized in terms of cobalt−carbon bond dissociation energies (BDEs). The analysis suggests that the cobalt−carbon bond strength controls the primary photolysis products of alkylpyridinecobaloximes and that a difference of about 10 kcal mol^{-1} in BDE may be responsible for the observation of different photolysis products.

Experimental Section

The solvents, obtained from Merck, were dried and purified according to standard procedures[11] and kept over 4A molecular sieves prior to use. [^{15}N]Pyridine (99% isotopic enrichment) was from American Radiolabeled Chemicals. All other chemicals were from Aldrich and were used as received.

Instrumentation. The ESR measurements were made on a Varian E-109 or on a Bruker ESP 300E spectrometer, both operating at 9 GHz and equipped with a variable temperature unit (Varian E-257 and Bruker B-VT2000). The spectra were calibrated with diphenylpicrylhydrazyl (dpph) and the magnetic field calibrated using Mn^{2+} in MgO. The instrumental parameters used for each spectrum are given in the figure captions.

Sample irradiation was performed under anaerobic conditions in the ESR quartz tubes using either (a) a 250 W Philips HP/T Hg lamp, $\lambda_{max} = 560-580$ nm, (b) a 2 W Ar laser using the lines at 514.4 nm or at 484.4, or (c) a Hanovia UVS/100 UV lamp. With the laser beam the irradiation times used were 20, 8, and 4 min at 77 K, 250 K, and room temperature, respectively, whereas with any of the lamps the irradiation times were 60, 40, and 20 min.

Synthesis. Alkylcobaloximes, compounds of general formula $RCo(Hdioxime)_2L$, were prepared by the procedure described by Toscano et al.;[12] the dioximes were, glyoxime (GH_2), dimethylglyoxime (DH_2), and diphenylglyoxime (PH_2). For all prepared compounds the expected stoichiometry was confirmed by elemental analysis.

Sample Preparation. All manipulations were carried out under nitrogen; solvents were deoxygenated by reflux/distillation under nitrogen and the solids degassed under vacuum prior to use. Samples for photolysis were prepared by making solutions of the desired compounds in toluene/dichloromethane (1:1) or (1:2); these solutions were then irradiated in the ESR sample tubes.

Spectra Simulation and Spin Hamiltonian Parameters. ESR spectra of the radical species were simulated by using the package supplied by Bruker "WIN-EPR SimFonia", and the spin Hamiltonian parameters given in the text are those obtained by computer simulation of the corresponding spectra. For the cobalt(II) species, the spin Hamiltonian parameters were obtained by computer simulation with a program that uses Pilbrow's and McGarvey's formalisms, and that has been fully described elsewhere.[10]

Results

Freshly prepared solutions of all reported cobaloximes (Chart 1) are ESR silent and remain so for a few days when kept in the dark, as expected for low-spin Co(III) compounds. After being exposed to visible light or to a laser source, at room temperature, these solutions exhibit ESR spectra with signals typical of Co(II) species, thus implying the homolytic cleavage of the Co−C bond, as has been observed for other alkylcobaloximes.[5−9] When irradiation is performed in frozen matrix (77 K), the same solutions are ESR silent, which is indicative that the cleavage of the bond was not induced at this temperature. Irradiation performed at 250 K yields ESR spectra that reveal that cleavage of the cobalt−carbon bond did not occur. Although paramagnetic species are observed at 250 K, the spectra are not those expected for the products of homolysis of the cobalt−carbon bond but are typical of radical species.

Homolysis of the cobalt−carbon bond is achieved at all temperatures, when cobaloxime solutions are irradiated with UV light for long periods of time, as confirmed by ESR spectra that exhibit signals which are characteristic of a cobalt(II) complex and of an organic radical.

Irradiation of solutions of the compound with glyoxime produces a precipitate, probably due to polymerization of the photolysis products. Thus it was not possible to obtain ESR spectra of such solutions.

Characterization of Products Resulting from Irradiation at Room Temperature. Solutions of methyl-, deuteromethyl-, and benzylpyridinecobaloximes, **1−10**, irradiated with visible or UV light at room temperature but observed at 100 K, yield ESR spectra that exhibit large **g** tensor anisotropy and are typical

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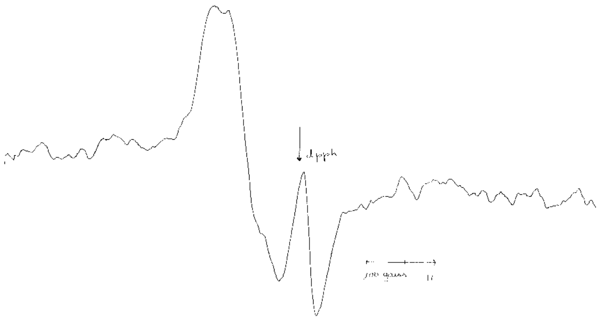


Figure 1. ESR spectrum of a toluene/dichloromethane solution of methylpyridinecobaloxime irradiated at 77 K with UV light and for 60 min: microwave power, 15 mW; modulation amplitude, 6 G; gain, 10^{-5}; scan time, 4 min; time constant, 1 s; $T = 100$ K.

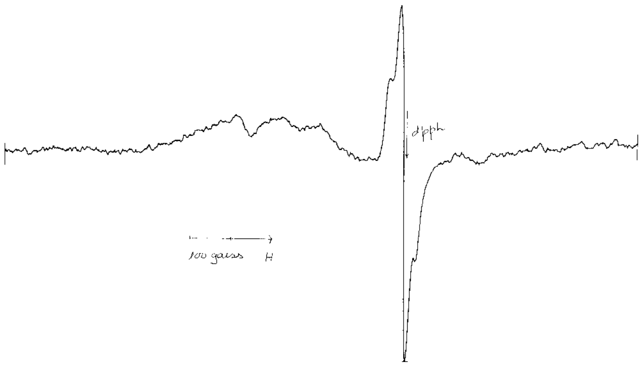


Figure 2. ESR spectrum of a toluene/dichloromethane solution of methylpyridinecobaloxime irradiated at 77 K with UV light and for 120 min: microwave power, 15 mW; modulation amplitude, 6 G; gain, 10^{-5}; scan time, 4 min; time constant, 1 s; $T = 100$ K.

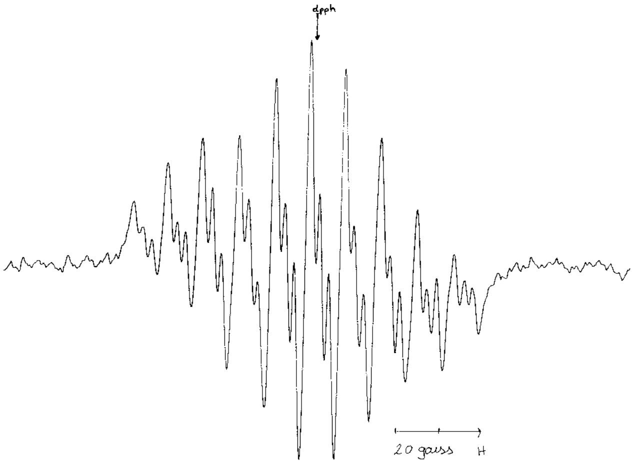


Figure 3. ESR spectrum of a toluene/dichloromethane solution of [^{14}N]pyridinemethylcobaloxime irradiated at 250 K with visible light and for 40 min: microwave power, 15 mW; modulation amplitude, 2 G; gain, 4×10^{-4}; scan time, 4 min; time constant, 1 s; $T = 250$ K.

of metal complexes with a d^7 ($S = {}^1/_2$) electron configuration, thus implying a +2 formal oxidation state for the cobalt atom and providing evidence for reduction of the metal center. In the high-field region it is possible to identify lines due to hyperfine coupling of the unpaired electron with the cobalt (^{59}Co, $I = {}^7/_2$) and with the nitrogen (^{14}N, $I = 1$) atoms. Each of the eight lines arising from coupling to cobalt is further split into five with relative intensities 1:2:3:2:1, due to superhyperfine coupling with two equivalent axially bound nitrogen atoms. This spectrum is assigned to a low-spin cobalt(II) compound with two axially bound pyridine or substituted pyridine molecules, $[Co(DH)_2L_2]$. As has been pointed out for other alkylcobaloximes with pyridine bases, the cobalt(II) compound resulting from homolysis, $[Co(DH)_2L]$, is quite reactive and is able to abstract pyridine molecules from other cobalt species in solution in order to form compounds with two bound pyridine bases.[7,8] The ESR parameters of the species $[Co(DH)_2L_2]$ are identical to those reported for cobaloximes with the same Lewis base.[7]

Characterization of Products Resulting from Irradiation at 77 K. Solutions of compounds **1**−**10**, irradiated with *visible light* in a frozen matrix of toluene/dichloromethane at 77 K and observed at the same temperature are ESR silent. The room temperature ^{1}H NMR spectrum is the same before and after irradiation.

The same solutions irradiated with *UV light* for 60 min exhibit ESR spectra with a narrow signal at $g = 2.00$ and a strong broad band at $g = 2.14$ (Figure 1). On raising the temperature, the signals are lost and if observed again at 100 K the solutions are ESR silent. The room temperature ^{1}H NMR spectrum obtained after the cycle is identical to that before irradiation. The ESR signals observed immediately after irradiation at 77 K are assigned to an organic radical and the broad band observed at $g = 2.14$ to a strongly exchanged coupled system $\{[R^{\bullet}\cdots Co^{II}(DH)_2L]\}$, which is kept immobilized by the lattice.[6b] Longer irradiation times yield solutions for which the ESR spectra exhibit not only the narrow signal at $g = 2.00$ and the band at $g = 2.14$, but also a new signal spread over a wide range of magnetic field (Figure 2). This latter signal is assigned to the cobalt(II) photolysis primary product, $[Co(DH)_2L]$, due to its similarity to that typically observed for (a) pyridinecobaloximes with isopropyl and *sec*-butyl groups[11,12] and (b) methylcobaloximes with phosphorus ligands.[6] The observation of this signal is a clear indication that the cobalt−carbon bond was homolytically cleaved, and the ESR parameters obtained are identical to those reported for cobaloximes with the same Lewis base.[7]

In summary irradiation in frozen matrix with visible light does not induce homolytic cleavage of the cobalt−carbon bond, whereas irradiation with UV light for about 2 h does produce the photolysis primary products, thus implying bond homolysis.

Characterization of Products Resulting from Irradiation at 250 K. Solutions of methyl-, deuteromethyl-, and benzylpyridinecobaloximes, **1**−**8**, irradiated with *visible light* at 250 K exhibit, at the same temperature, identical ESR spectra; that of methylpyridinecobaloxime is presented in Figure 3. Identical spectra were also obtained for solutions of cobaloximes incubated in dichloromethane/D_2O, for which quantitative replacement of the hydrogen atoms of the dimethylglyoxime bridges by deuterium atoms took place, as checked by ^{1}H NMR. All spectra clearly show ten regularly spaced lines (17 G apart) that are further split into three (4 G apart). For solutions of cobaloximes **9** and **10**, synthesized with [^{15}N]pyridine (^{15}N, $I = {}^1/_2$), the observed spectrum (Figure 4) is composed of the same ten lines (17 G apart), but split into two (7 G apart). Both types of spectra can be observed in the tempera-

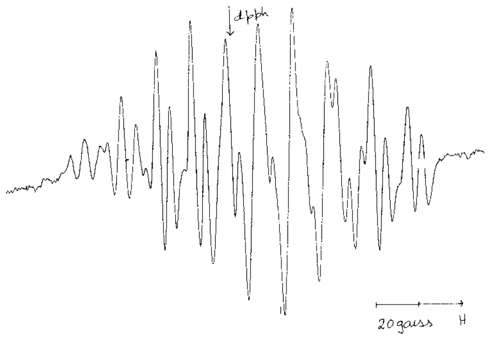


Figure 4. ESR spectrum of a toluene/dichloromethane solution of [^{15}N]pyridinemethylcobaloxime irradiated at 250 K with visible light and for 40 min: microwave power, 15 mW; modulation amplitude, 2 G; gain, 4 × 10^{-4}; scan time, 4 min; time constant, 1 s; $T = 250$ K.

ture range 190−300 K, but above this latter temperature the signal starts to broaden and at 320 K is completely lost. Decreasing the temperature of observation makes the spectra detectable again. On cooling the solutions below 190 K, when the solution freezing point is approached, the signal also starts to broaden and is lost in frozen solutions. If this solution is warmed and becomes fluid, the same signal is observed with no loss in amplitude.

The spectral shape, the line width trends, and the experimental parameters that can be obtained visually from these spectra ($g = 2.007$, hyperfine coupling constants equal to 17 G and 4 G) seem to indicate that the signal does not arise from cobalt(II) species but rather from a radical of the nitroxide type confined to the equatorial ligand and with weak hyperfine coupling to cobalt. The ten lines may be ascribed to interaction of the unpaired electron with the cobalt atom ($I = {}^{7}/_{2}$) and with one nitrogen atom (^{14}N; $I = 1$) of the equatorial plane both having, in this particular case and by an accidental coincidence, identical or very close values of the hyperfine coupling constant. The third splitting arises from an interaction with the nitrogen atom of the pyridine molecule in the axial position, as the ten lines are split into three of equal intensity when we use [^{14}N]-pyridine ($I = 1$) or into two of equal intensity for [^{15}N]-pyridine ($I = {}^{1}/_{2}$).

The ESR spectra were simulated assuming these interactions, and the best fitting was obtained with the following parameters: $g = 2.0058$, $A_{\mathrm{Co}} = 15.5 \times 10^{-4}$ cm^{-1}, $A_{\mathrm{N}}(\mathrm{eq}) = 15.3 \times 10^{-4}$ cm^{-1}, and $A_{\mathrm{N}}(^{14}\mathrm{Npy}) = 3.7 \times 10^{-4}$ cm^{-1} for the compound with [^{14}N]pyridine; and $g = 2.0075$, $A_{\mathrm{Co}} = 16.4 \times 10^{-4}$ cm^{-1}, $A_{\mathrm{N}}(\mathrm{eq}) = 15.3 \times 10^{-4}$ cm^{-1}, and $A_{\mathrm{N}}(^{15}\mathrm{Npy}) = 6.8 \times 10^{-4}$ cm^{-1} for the compound with [^{15}N]pyridine.

The uncertainties associated with the g values are ≈1.0 × 10^{-4}, calculated from the experimental errors in field and frequency accuracy. In what concerns the uncertainties in the A values, they are mainly controlled by the modulation amplitude used in the accquisition of the experimental spectrum, and in this case the value used was 2 G, which means an error of ±1, in the worst situation. However, it must be pointed out that if the values of A_{Co} and of $A_{\mathrm{N}}(\mathrm{eq})$ are changed by more than $\pm 0.05 \times 10^{-4}$ and $\pm 0.3 \times 10^{-4}$ cm^{-1}, respectively, it is not possible to get a good fitting of the experimental spectra.

The results above support the proposal that for methyl, deuteromethyl-, and benzylpyridinecobaloximes, irradiation with visible light at 250 K does not induce homolytic cleavage of the cobalt−carbon bond or reduction of the cobalt center.

Solutions of methyl-, deuteromethyl-, and benzylpyridinecobaloximes, **1**−**10**, irradiated with UV light at 250 K exhibit ESR spectra that clearly show that two species are present in solution: (a) the cobalt(III) radical species previously observed with irradiation with visible light and (b) another one which is typical of a cobalt(II) species and for which the ESR spectra are identical to those observed for room temperature photolysis. This result shows that, with high-energy radiation, the same molecules undergo homolysis of the cobalt−carbon bond, and it has also been observed that the extension of homolysis increases with longer irradiation times.

Discussion

Pyridinecobaloximes with methyl and benzyl radicals show a photolytic behavior that is different from that of (a) pyridinecobaloximes with isopropyl or *sec*-butyl groups[5,7,8] and (b) methyl- and benzylphosphinecobaloximes.[9] For all these latter compounds, irradiation with *visible light* induces cobalt−carbon bond cleavage and originates as primary products of photolysis a five-coordinate cobalt(II) complex and an alkyl radical, both at 77 K and at room temperature. For the methyl- and benzylpyridinecobaloximes **1**−**10**, homolysis of the cobalt−carbon bond is observed when photolysis is performed with *UV light*, but with *visible light* homolysis is only observable if irradiation takes place at temperatures higher than ≈270−280 K. When homolysis occurs, the resulting products are identical to those of isopropyl- or *sec*-butylpyridinecobaloximes, and the mechanism proposed for cobalt−carbon bond cleavage in these compounds[6,7] is also operative for methyl- and benzylpyridinecobaloximes.

Characterization of the Spectra Obtained at 250 K. The intriguing result about photolysis of methyl- and benzylcobaloximes is the observation of a novel type of spectrum when solutions are irradiated at 250 K. Similar spectra for the photolysis products of these compounds, obtained in conditions comparable to ours but with a much poorer resolution, have been reported by Giannotti et al.[5a] several years ago. These authors claimed that the spectra of the methyl and benzyl derivatives were not identical and were composed of 11 lines split into three for the methyl and of 10 lines split into three for the benzyl compound. They concluded further that photolysis did not induce homolytic cleavage of the cobalt−carbon bond but that reduction of the metal center took place. The resulting species were assumed to be cobalt(II) paramagnetic complexes, in which all six initial ligands were maintained, and the spectra were interpreted assuming the signals show hyperfine interaction of the unpaired electron with the cobalt atom, with the pyridine nitrogen atom, and with the protons of the methyl and benzyl groups. Symons[6a] has questioned this interpretation, claiming the spectrum to be due to a radical confined to the equatorial ligand and with hyperfine interaction to the cobalt atom, as observed for some cobalt(III) nitroxide derivatives.[13,14]

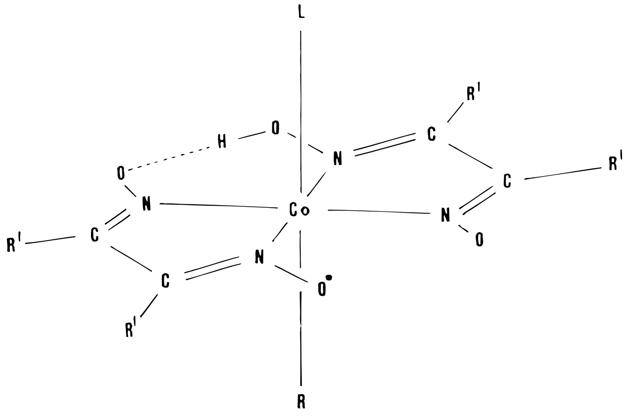
Recognition that cobaloximes with methyl-, deuteromethyl-, and benzyl- groups (**1**−**8**) exhibit identical ESR spectra with the same number of lines, invalidates Giannotti et al.'s[5a] view of coupling to the hydrogen atoms of the alkyl group, since the number of lines should be different for each of the three radicals which have a different number of protons or different magnetic nuclei.

The ESR spectra obtained for compounds **1**−**8** clearly exhibit 10 lines (as confirmed by its second derivative), with each one split into three, and have a shape and line width pattern typical of a radical signal. The value determined for the cobalt hyperfine coupling constant (17 G) is quite small and of the same order of magnitude as those observed for cobalt(III) nitroxide radicals[13,14] and superoxocobalt complexes.[15] Comparison of this value with those observed for the isotropic hyperfine coupling in the cobalt(II) complexes (90−100 G) indicates that the unpaired electron must not reside on the cobalt atom, so reduction of the cobalt center did not occur, and implies that a cobalt(III) radical must have been formed. Furthermore, the spectrum in Figure 3 is very similar to the one reported by Swanwick and Waters[13] for species formed upon reaction of bis(dimethylglyoximato)cobalt(II) with 2,3,5,6-tetrachloronitrosobenzene, and that was assigned to a cobalt nitroxide radical. This latter spectrum also exhibits 10 lines (16 G apart) with relative intensities 1:2:3:3:3:3:3:3:2:1 and was interpreted as arising from the interaction of the unpaired electron with one cobalt atom and with one nitrogen atom bound to the cobalt, both having by an accidental coincidence the same value of the hyperfine coupling constant (16 G). This similarity can be extended further to indicate that the same splitting scheme is operative for compounds **1**−**10**, and thus the 10 observed lines must be due to coupling to a nitrogen atom of the equatorial ligand and to the cobalt(III) center.

The spectrum in Figure 3 shows additional splitting of the ten lines into three, which is due to interaction with other neighboring atoms, either coupling to (a) the hydrogen atoms of the alkyl groups bound to cobalt, (b) the hydrogen atoms of the dimethylglyoxime bridges, (c) the methyl groups of dimethylglyoxime, or (d) the nitrogen atom of the pyridine ligand. Hypothesis a is obviously not a possibility, as the spectra of methyl and deuteromethyl derivatives are identical. To rule out hypothesis b, we note that the ESR spectra of cobaloximes incubated in dichloromethane/D_2O, thus allowing for the replacement of the hydrogen atoms of the dimethylglyoxime bridges by deuterium atoms, are identical to that in Figure 3, thus implying a noninvolvement of the bridging hydrogen atoms in the observed coupling. The splitting also cannot be assigned to the hydrogen atoms of the dimethylglyoxime, as identical ESR spectra were obtained for compounds with dimethylglyoxime **1** and diphenylglyoxime **8**.

Finally, we synthesized compounds **9** and **10** with [^{15}N]pyridine (^{15}N, $I = {}^1/_2$) and obtained ESR spectra (Figure 4) that are similar to that in Figure 3, but in which each of the 10 lines is split into two instead of three (^{14}N, $I = 1$), thus indicating that the 4 G splitting pattern is due to the nitrogen atom of the pyridine molecule. This result also impinges on the identification of the nitrogen atom responsible for the splitting of 17 G: since it cannot be the pyridine nitrogen, it must be one residing on the equatorial ligands.

Chart 2



According to the above results, we propose that the ESR spectra obtained upon irradiation with visible light of solutions of methyl-, deuteromethyl-, and benzylcobaloximes at 250 K (Figure 4) are due to cobalt(III) nitroxide radicals in which the unpaired electron is mainly residing in a π orbital of the equatorial moiety. The computer simulation of the spectra was performed assuming an interaction of the unpaired electron with an equatorial nitrogen atom, with the cobalt atom, and with the nitrogen atom of the axial pyridine ring. The hyperfine interaction with these latter atoms can occur by spin density delocalization by pπ−dπ bonding and/or by spin polarization of the σ-bonding electrons. The magnitude of the values of the hyperfine coupling to the nitroxide nitrogen atom (17 G) is indicative of spin delocalization which is favored by the equatorial conjugated system. The observation that the value of hyperfine coupling to the nitrogen atom in a dimethylglyoxime radical obtained by γ-irradiation of solid dimethylglyoxime samples is 31.7 G[16,17] provides support for considerable delocalization onto the equatorial moiety of the cobalt(III) dimethylglyoxime radical.

To clarify the origin of this type of radical, we note (a) that the spectra of species derived from complexes with dimethyl- and diphenylglyoxime ligands are identical, thus precluding the involvement of the protons attached to carbon atoms of the chelate ring, and (b) that no changes were observed in spectra of cobaloximes in which the hydrogen bridging atoms were replaced by deuterium atoms. On the basis of these additional observations together with evidence provided by Giannotti[5c] in a study concerning the photolysis, at room temperature, of alkylcobaloximes and other B_{12} models in the presence of spin traps, we propose that the radicals are formed by abstraction of hydrogen bridging atoms (Chart 2). Giannotti's results show that upon irradiation there is evidence for hydrogen atom abstraction and also that it must take place in the hydroxyl bridges, as the other sources have been either blocked or isotopically

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replaced. Furthermore, it was shown that homolysis of the cobalt−carbon bond and hydrogen abstraction are competitive reactions, as in some cases, not only adducts of the spin trap with hydrogen atoms were observed but also adducts with the alkyl radical could be detected.[5c] This fact is also supported by our results, as irradiation at 250 K with UV light produces both the homolysis products and the cobalt(III) nitroxide radical.

We propose that by lowering the irradiation temperature, homolysis of the cobalt−carbon bond is prevented, and thus it was possible to observe the cobalt(III) radical formed upon hydrogen abstraction (contrast with the results of irradiation at room temperature).

In this work the ESR spectrum obtained after photolysis of methyl-, deuteromethyl-, and benzylpyridinecobaloximes at 250 K was identified and characterized. The interpretation of the spectrum has been controversial for some time, but we believe that the results obtained in this work are conclusive in what concerns the assignment of the signal to a cobalt(III) nitroxide derivative. This type of spectrum is not observed upon irradiation, in the same conditions, of (a) isopropyl- and *sec*-butylpyridine cobaloximes[7,8] and (b) methyl- and benzylphosphinecobaloximes;[9] in all cases the photolysis products observed at 250 K are identical to those observed at room temperature and that are consistent with homolysis of the cobalt−carbon bond.

Influence of Cobalt−Carbon Bond Strength on the Photolysis Products. We observed that photolysis with *visible light* induces homolysis of the cobalt−carbon bond of methyl- and benzylpyridinecobaloximes only at temperatures above ≈270−280 K and that solutions photolyzed at 77 K are ESR silent. These results must be contrasted with those obtained upon irradiation with higher energy (*UV-light*), for which cleavage of the cobalt−carbon bond is induced at all temperatures, as ESR spectra of the homolysis primary products could be observed.

Although we do not present any photochemical rationale for our results, as no data on the energy of the excited states nor kinetic data for cobalt−carbon bond cleavage could be found in the literature, we must point out that it is for the alkylpyridinecobaloximes with the higher BDEs that the cobalt−carbon bond is not cleaved at 250 K.

In fact, Toscano and co-workers[18] have determined the bond dissociation energy (BDE) values for the cobalt−carbon bond in some alkylpiridinecobaloximes by a calorimetric method and obtained values of 34.6 ± 1.4 kcal mol^{-1} for the methyl and of 31.1 ± 2.2 kcal mol^{-1} for the benzyl derivatives, values much higher than the one found for the isopropyl analogue, 21.3 ± 2.0 kcal mol^{-1}. This latter value lies within the range of BDEs (18−26 kcal mol^{-1}) obtained previously, by noncalorimetric methods, for other model compounds.[19] The BDE values of the cobalt−carbon bond for the methyl- and benzylpyridine cobaloximes are about 10 kcal mol^{-1} higher than those determined for the majority of other cobaloximes. With UV light (≈5 eV) the cobalt−carbon bond is cleaved in all compounds as its energy is well above that of the Co−C bond (0.9−1.5 eV), whereas with visible light (≈2.2−2.5 eV), the stronger bonds (methyl and benzyl derivatives; BDE ≈ 1.5 eV) do not cleave.

In a recent FT-Raman spectral study of cobaloximes[17] it was shown that the Co−C stretching frequency was sensitive to the steric bulk of the axial base rather than to the electronic *trans* influence; in fact it was suggested that the BDEs are more reflective of differences in the product state than differences in the ground state. Notwithstanding this suggestion, since the bases of the complexes studied have similar steric requirements (and in fact the Co−C stretching frequencies are very similar for pyridines nonsubstituted in the 2 position), the resulting cobalt(II) fragment must have similar structures, and thus using ground-state data seems reasonable to account for the photochemical behavior in aprotic solvents of the cobaloximes studied in the present work.

No reliable values of the cobalt−carbon bond dissociation energies could be found in the literature for methyl- and isopropylcobaloximes with phosphine bases, and for these molecules it is to be expected that the product state, the cobal(II) complex, would have an extensive deformation of the equatorial moiety.[9] Thus, the observation that the Co−C stretching frequency is lower for methylphosphinecobaloxime (487 cm^{-1}) than for methylpyridinecobaloxime (522 cm^{-1}), provides indirect evidence that the BDE of the phosphine derivative must be smaller than the value reported for the analogous pyridine compound, which justifies the fact that for these compounds the methyl- and benzyl derivatives exhibit the same behavior as pyridine cobaloximes with the other alkyl groups, for which homolysis of the cobalt−carbon bond takes place.[9]

From the results obtained in this work it seems that it can be assumed that for solutions of alkylpyridinecobaloximes, in which the pyridine has no substitutents in the *para* position, photochemically induced cleavage of the cobalt−carbon bond with visible light at temperatures below 250 K only takes place in aprotic solvents if the BDE of the cobalt−carbon bond is smaller than ≈30 kcal mol^{-1}, whereas for solutions of methyl- and benzylpyridinecobaloximes irradiation with visible light at 250 K induces hydrogen abstraction from the equatorial moiety.

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