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Reduction of hexaazacyclophane complexes of Co(II) and Cu(II) by $^{\bullet}CH_2OH$ and e_{sol}^-; a pulse radiolysis study

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Abstract

The reactions of $^{\bullet}CH_2OH$ and e_{sol}^- with hexaazacyclophane complexes of Co(II) and Cu(II) in methanol and or methanol–water mixed solvents were investigated by pulse radiolysis. The primary products from the reduction of the macrocyclic complexes were assigned a radical nature by comparing their optical spectra with those of related Co(I) and Cu(I) species. Such metal–ligand radical products undergo disproportionations. The product of the disproportionation was assigned as a Co(III)–hydride complex. Although a similar hydride could be produced in the disproportionation of the Cu(II)–ligand radical, the optical spectrum of the product is in accordance with the hydrogenation of a double bond in the ligand. Interception of the metal–ligand radical intermediates with CO_2 resulted in the formation of adducts.

Keywords: Pulse radiolysis; Reduction; Cobalt complexes; Copper complexes; Hexaazacyclophane complexes

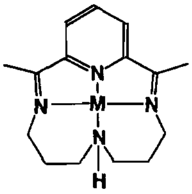
1. Introduction

Phthalocyanine and porphyrin radicals coordinated to various transition metal ions have been reported in the literature [1,2]. Most of these species are short-lived reaction intermediates of photochemical or thermal reactions that have been detected by ESR and/or time-resolved optical spectroscopy. There are, however, a number of metal–ligand radical complexes, e.g. derivatives of Ru(II) and Rh(III) phthalocyanines, which exhibit sufficient kinetic and/or thermal stability to be isolated as products [3–6]. There are more sparse observations of similar radicals in reactions of complexes with macrocyclic ligands less unsaturated than phthalocyanines and porphyrins. In the reduction of $M(Me_2\text{-}3,4,5\text{-pyo-}[14]trieneN_4)^{2+}$ (I), M = Cu(II), Ni(II), the reduction potential of e_{aq}^- allows the rapid reduction of the macrocycle, Eq. (1), in the same manner as the metallophthalocyanines [7].

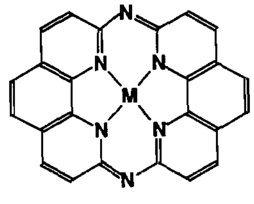
$$\begin{aligned} &M^{II}(Me_2\text{-}1,3,5\text{-pyo-}[14]trieneN_4)^{2+} + e_{aq}^- \longrightarrow \\ &\quad M^{II}(Me_2\text{-}1,3,5\text{-pyo-}[14]trieneN_4)^+ \longrightarrow \qquad (1) \\ &\quad M^{I}(Me_2\text{-}1,3,5\text{-pyo-}[14]trieneN_4)^+ \end{aligned}$$

The addition of OH radicals to the $Me_2\text{-}3,4,5\text{-pyo-}[14]trieneN_4$ macrocycle produces radicals which function as intermediates for the oxidation, i.e. Co(II) to Co(III), and reduction, i.e. Cu(II) to Cu(I), of the metal center [8].

The redox reactions of the hexaazacyclophane complexes have not been previously investigated. In terms of the delocalization of π orbitals through the ligand, complexes of the hexaazacyclophane macrocycle, **II**, can be placed somewhere between the phthalocyanines and $Me_2\text{-}3,4,5\text{-pyo-}[14]trieneN_4$ complexes. Based on their structural relationship to these macrocycles [9], it could be expected that ligand radicals could also be intermediates in their electron transfer processes. The chemical reactions initiated when powerful reducing



(I)



(II)

M = Cu(II), Ni(II), Co(II)

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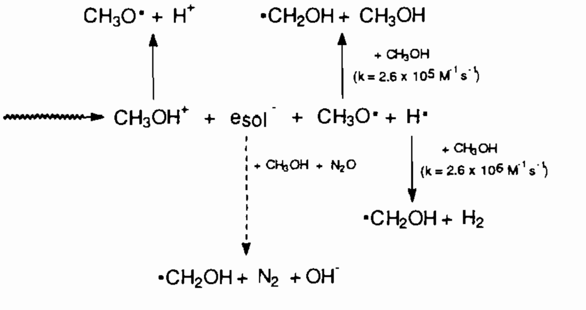
species, i.e. e_{sol}^- and $^\bullet CH_2OH$, react with Cu(II) and Co(II) complexes of the hexaazacyclophane have been investigated in this work.

2. Experimental

2.1. Radiolytic procedures

Optical pulse radiolysis measurements were carried out with a system similar to that described earlier [10]. The apparatus makes use of a 10 MeV linear accelerator. Thiocyanate dosimetry was carried out at each experimental section. In this procedure, the output signal of a secondary emission monitor was calibrated against $(SCN)_2^-$ radical concentrations produced in the radiolysis cell by the electron pulse. A flow system was used to ensure that fresh solution was brought to the reaction cell between electron pulses. Solutions for the irradiation were prepared by adding the solid compounds to liquids previously deaerated with streams of O_2 free gasses, i.e. N_2O, N_2 and CO_2. The solvents, i.e. CH_3OH, H_2O or their mixtures, were allowed to equilibrate with a given gas or gas mixture for 12 h. The anaerobic handling of the solutions was required in order to avoid radical reactions with O_2 and the oxidation of Co(hexaazacyclophane).

Radiolysis with ionizing radiation of CH_3OH and CH_3OH/H_2O mixtures has been reported elsewhere in the literature [11,12]. These studies have shown that pulse radiolysis can be used as a convenient source of e_{sol}^- and $^\bullet CH_2OH$ radicals according to Scheme 1 [13,14]. Since these products have large reduction potentials, i.e. -2.8 V versus NHE for e_{sol}^- and -0.92 V versus NHE for $^\bullet CH_2OH$ in aqueous solution, they can be used for the reduction of coordination complexes and for the study of electron transfer reactions. The yield of e_{sol}^- in CH_3OH ($G \approx 1.1$) is about a third of the G value in the radiolysis of H_2O ($G \approx 2.8$) [12]. In solutions where e_{sol}^- was scavenged with N_2O [13], the $^\bullet CH_2OH$ radical appears to be the predominant product (yield $>90\%$) of the reaction between CH_3OH and OH [13]. A dose of ~0.5 Krad/pulse was used for most of the spectroscopic measurements. Reaction kinetics were investigated as a function of the reactants concentrations. In order to generate various concentrations of the reaction intermediates, the dose was adjusted to a given value between 0.2 and 0.5 Krad/pulse. Curve-fitting procedures have been reported elsewhere [7,8].



Scheme 1. Reactions of primary radicals in the irradiation of methanol by ionizing radiation.

2.2. Materials

The hexaazacyclophane complexes of Cu^{II}, Ni^{II} and Co^{II}, M(hexaazacyclophane), were prepared by a modification of a literature procedure [15,16]. The purity of the compounds was assessed by means of their spectra and elemental analysis. Reagent grade anhydrous trifluoromethane sulfonic acid, HTFMS, its potassium salt, KTFMS, and O_2 free gasses, N_2O, CO_2 and N_2, were used without further purification.

3. Results and discussion

3.1. Species in solution

The hexaaza complexes of Cu(II), Ni(II) and Co(II) are sparingly soluble in MeOH and/or H_2O. However, their solubility in these solvents is greatly enhanced by the addition of acids. In order to investigate the effect of HTFMS on the complexes, UV–Vis spectra were recorded for various values of the quotient between the acid, C_{AH}, and complex, C_{ML}, concentrations. While $C_{ML} \approx 2.25 \times 10^{-5}$ M in all the solutions, the value of C_{AH} was varied between 5.62×10^{-5} and 0.56×10^{-5} M and the ionic strength kept at 5.62×10^{-5} M with KTFMS. No further spectral changes were observed when C_{AH}/C_{ML} was above 2.5, Fig. 1. Recorded changes of the complexes optical spectra with acid concentration denote modifications in the structure of the hexaazacyclophane ligand. For example, a band at 280 nm appears in the Cu^{II}(hexaazacyclophane) spectrum at high acid concentrations. Such a spectral feature and shoulders at longer wavelengths correlate well with absorptions in the literature spectrum of $Cu(dmp)_2^{2+}$ in CH_3OH. The optical density changes recorded at various wavelengths, i.e. 220, 250, 280, 300 and 320 nm, reveal that most of such changes take place when $C_{AH}/C_{ML} \leq 1$. Less than a 16% change is recorded for relationships of the acid to complex concentration, $1 < C_{AH}/C_{ML} \leq 2.5$. These results suggest that the principal reaction is a single protonation of the bridging aza groups in the macrocycle, Eq. (2).

The optical density data are in accordance with an equilibrium constant, $\log K \approx (4.4 \pm 0.1)$, for the protonation equilibrium.

$$\text{M(hexaazacyclophane)} + H^+ \rightleftharpoons \text{M(hexaazacyclophaneH)}^+ \qquad (2)$$

$M = Cu^{II}$, Co^{II}

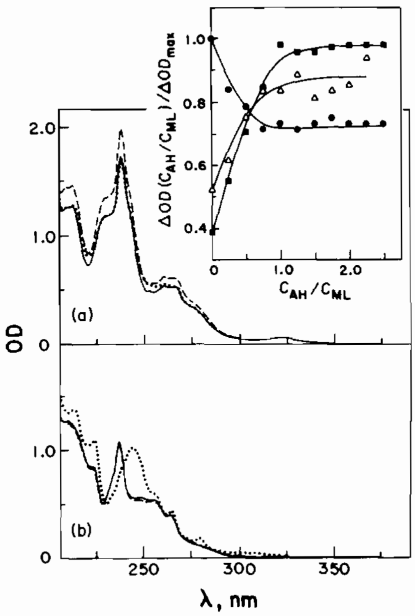


Fig. 1. Effect of the acid concentration on the spectrum of hexaazacyclophane complexes: (a) 2.25×10^{-5} M Co(hexaazacyclophane) or (b) 2.25×10^{-5} M Cu(hexaazacyclophane) in HTFMS 5.63×10^{-5} M (——), 4.5×10^{-5} M (·····), 1.12×10^{-5} M (- - -). The insert shows the dependence of the optical density changes on C_{AH}/C_{ML} as they were measured at 340 (△) and 280 (●) nm with Co(hexaazacyclophane) and 280 (■) nm with Cu(hexaazacyclophane).

It must be noted that this value lies between those of similar amino groups, e.g. log $K=8.6$ for *N*-phenylpiperazine and log $K=4.57$ for *o*-toluidine. The basicity exhibited by Co^{II}(hexaazacyclophane), log $K\approx(5.3\pm0.1)$, is slightly larger than in the Cu(II) complex. The spectra recorded with Ni^{II}(hexaazacyclophane) for various relationships of acid to complex concentrations, $0.0\leqslant C_{AH}/C_{ML}\leqslant2.5$, suggest more than one equilibria. It is possible that a second protonation of the ligand, Eq. (3), becomes noticeable at larger acid concentrations than in the Co(II) and Cu(II) compounds.

$$\text{Ni(hexaazacyclophaneH)}^+ + \text{H}^+ \rightleftharpoons \text{Ni(hexaazacyclophaneH}_2)^{2+} \qquad (3)$$

In solutions saturated with CO_2, the spectra of the macrocyclic complexes in methanol are similar to those recorded under N_2 with concentrations of HTFMS making $C_{AH}/C_{ML}\geqslant1.5$. The conductance of these methanol solutions was measured in order to verify that spectra under CO_2 were related to the protonation of the complexes, Eq. (1). Data in Table 1 show a large conductance of the Cu(hexaazacyclophane) solutions saturated with CO_2 by comparison to those saturated with N_2. Since such a conductance is uncharacteristic of CO_2-saturated methanol, Table 1, it must be attributed to protonation of the complexes. Minor spectral differences between solutions acidified with CO_2 and HTFMS probably reflect differences in ion pairing.

Table 1
Conductance values for solutions of hexaazacyclophane complexes

Compound (concentration)	Medium conditions	Λ (μS)
Methanol	N_2 (1 atm.)	1.15
	CO_2 (1 atm.)	1.60
	CO_2 (0.5 atm.) N_2O (0.5 atm.)	1.30
Cu(hexaazacyclophane) (1.8×10^{-5} M in methanol)	N_2O (1 atm.)	2.3
	CO_2 (1 atm.)	9.65
	CO_2 (0.5 atm.) N_2O (0.5 atm.)	8.30
Ni(hexaazacyclophane) (1.8×10^{-5} M in methanol	CO_2 (0.5 atm.) N_2O (0.5 atm.)	6.30

3.2. Reduction of the macrocycles by $^{\bullet}CH_2OH$

Pulse radiolysis of Cu(hexaazacyclophane) and various concentrations of HTFMS, $C_{AH}\leqslant10^{-4}$ M, was carried out in methanol equilibrated under N_2O [13]. Reaction kinetics for the formation of the reduction product from Cu(hexaazacyclophane) and the spectrum of that product were interpreted in terms of Eq. (4).

$$\begin{array}{l}\text{M(hexaazacyclophane)} + {}^{\bullet}\text{CH}_2\text{OH} \longrightarrow \\ \qquad\qquad \text{M(hexaazacyclophane)}^- + \text{CH}_2\text{O} + \text{H}^+ \\ \uparrow\downarrow \\ \text{M(hexaazacyclophane)}^+ + {}^{\bullet}\text{CH}_2\text{OH} \longrightarrow \\ \qquad\qquad \text{M(hexaazacyclophaneH)} + \text{CH}_2\text{O} + \text{H}^+ \\ (\text{M}=\text{Cu, Co}) \qquad\qquad\qquad\qquad\qquad\qquad (4)\end{array}$$

In solutions of Cu(hexaazacyclophane), $C_{ML}=2.25\times10^{-5}$ M, and HTFMS, $C_{AH}/C_{ML}=1.1$ or 2.2, the reaction of the radical with the complex was followed by the appearance of new absorption bands and bleaching of the solution between 240 and 450 nm, Fig. 2. Lifetimes, $\tau=1.0\pm0.4$ μs when $C_{AH}/C_{ML}=2.2$ and $\tau=1.5\pm0.4$ μs when $C_{AH}/C_{ML}=1.1$, were measured for the time-resolved spectral changes for the growth and decay of the optical density at various monitoring wavelengths between 250 and 435 nm. Such lifetimes correspond to a reaction rate that is close to the diffusion limit, i.e. $k\approx10^{10}$ M^{-1} s^{-1}, in agreement with the proposed reduction of the macrocycle [2,8]. Since the equilibrium in Eq. (3) is more displaced to the left for $C_{AH}/C_{ML}=2.2$ than $C_{AH}/C_{ML}=1.2$, the small dependence of the rate constant on C_{AH}/C_{ML} suggests a much

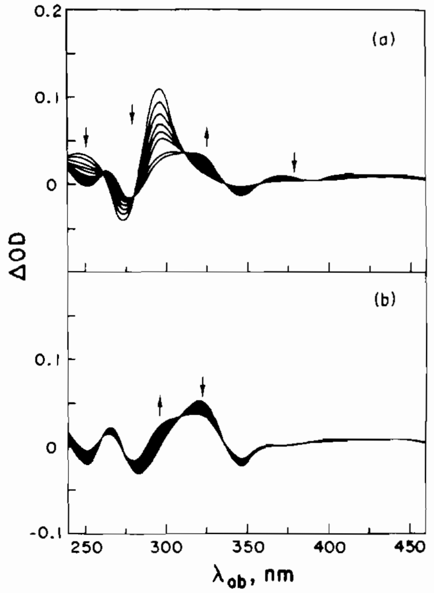


Fig. 2. Typical transient difference spectra for reactions between $^{\bullet}CH_2OH$ and 1.8×10^{-5} M Cu(hexaazacyclophane) in CH_3OH with 3.6×10^{-5} M of HTFSM. The arrows give the sense of increasing sampling intervals. In (a) difference spectra were recorded 1.2, 1.8, 3.6, 4.2, 4.8, 5.4, 6.0, 6.6 μs after the pulse irradiation. Spectra in (b) were recorded 72 μs after the pulse irradiation at 6 μs intervals.

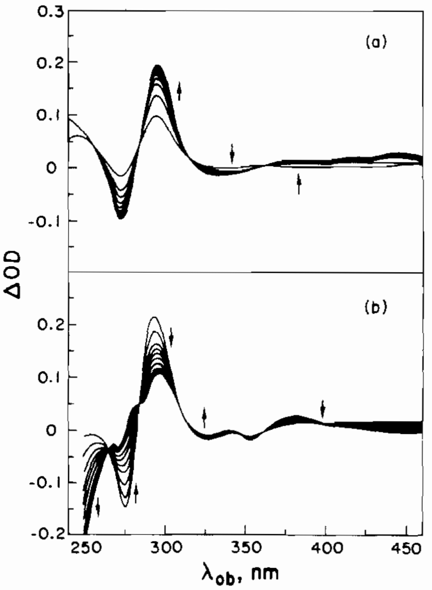


Fig. 3. Typical transient difference spectra for reactions between $^{\bullet}CH_2OH$ and 1.8×10^{-5} M Co(hexaazacyclophane) in CH_3OH with 3.6×10^{-5} M of HTFSM. The arrows give the sense of increasing sampling intervals. In (a) spectra were recorded 0.6 μs after the pulse irradiation at 0.6 μs intervals. Spectra in (b) were recorded 25 μs after the pulse irradiation at 6 μs intervals.

smaller rate of reaction of the unprotonated complex. Indeed, the measured rate constant, k_{obs}, can be expressed as

$$k_{obs}=\left[\frac{\alpha+K[H]}{1+K[H]}\right]k_{M(LH)}=fk_{M(LH)} \qquad (5)$$

where $\alpha=k_{M(L)}/k_{M(LH)}$ is the ratio of the rate constants for the reactions of $^{\bullet}CH_2OH$ with Cu(hexaazacyclophaneH)$^+$, $k_{M(LH)}$, and with Cu(hexaazacyclophane), $k_{M(L)}$. The value of the equilibrium constant, K, for protonation of the complex, Eq. (1), was given above. If one assumes that Cu(hexaazacyclophane) reacts ten times slower than Cu(hexaazacyclophaneH)$^+$, the value of f varies between 0.5 and 0.8. The change of f with C_{AH}/C_{ML} is, therefore, concurrent with measured values of k_{obs}.

Pulse radiolysis of N_2O-saturated methanol solutions of Co(hexaazacyclophane) were carried out under similar conditions, $C_{AH}\leqslant10^{-4}$ M and $C_{ML}\leqslant5\times10^{-5}$ M, reported above for Cu(hexaazacyclophane). The spectra of the products from the respective reductions of Co(hexaazacyclophane) and Cu(hexaazacyclophane) with $^{\bullet}CH_2OH$ exhibited minor differences which could be ascribed to those between the spectra of the parent complexes, Fig. 3. The rates of product formation for the reaction with Co(hexaazacyclophane), e.g. $\tau=1.0\pm0.4$ μs when $C_{AH}/C_{ML}=2.2$ and $\tau=1.2\pm0.4$ μs when $C_{AH}/C_{ML}=1.1$, were also comparable to those measured with Cu(hexaazacyclophane). The common spectra and rates of product formation suggest a radical nature for Cu(hexaazacyclophaneH)$^-$, Eq. (4), and the homologous species in the reduction of the Co(II) macrocycle. Indeed, reaction intermediates with oxidized/reduced Co and Cu metal centers or with coordinated OH_2OH must have very different absorption spectra.

Further spectral changes were observed with a delay longer than 4 μs, i.e. following the formation of the Cu(hexaazacyclophane) reduction product described above. A partial decay of the 296 nm optical density and the growth of a new absorption band with $\lambda_{max}=320$ nm were the most conspicuous spectral changes. Inspection of the oscillographic traces recorded at monitoring wavelengths between 260 and 350 nm reveals two processes. The faster of the two processes exhibited an acid concentration dependent rate, i.e. $t_{1/2}=37$ μs for $C_{AH}/C_{ML}=2.2$ and $t_{1/2}=170$ μs for $C_{AH}/C_{ML}=1.1$. This process was followed by another with a lifetime, $t_{1/2}\geqslant200$ μs. It is possible to account for these experimental observations with the reactions in Eqs. (6)–(8).

$$\mathrm{Cu^{II}(hexaazacyclophaneH)+H^+} \overset{K}{\rightleftharpoons} \mathrm{Cu^{II}(hexaazacyclophaneH_2)^+} \qquad (6)$$

$$\mathrm{2Cu^{II}(hexaazacyclophaneH_2)^+} \xrightarrow{k_1} \mathrm{Cu^{II}(hexaazacyclophaneH_2)+Cu^{II}(hexaazacyclophaneH)^+ +H^+} \qquad (7)$$

$$\mathrm{Cu^{II}(hexaazacyclophaneH_2)} \xrightarrow{k_2} \mathrm{products} \qquad (8)$$

The product, $Kk_1 \approx 5\times10^8$ s^{-1}, of the equilibrium constant, Eq. (6), with the reaction rate constant, Eq. (7), was calculated with values of $t_{1/2}$ measured at various acid concentrations. Dose and acid concentrations were adjusted in order to induce a minimum displacement of Eq. (6) in the reaction. In Eqs. (7) and (8) Cu(hexaazacyclophaneH_2) is the product of a two-electron reduction, Eqs. (4) and (7). Absorptions in the spectrum of this species are placed in the near UV, i.e. $\lambda_{max} = 320$ nm, and have extinction coefficients, i.e. $10^3 \times M^{-1}$ cm^{-1}, which can be expected for a Cu(II) complex. Assignment of the optical transient to a Cu(I) complex is incompatible with the absence of a strong absorption band in the Vis–NIR region [17–19]. Therefore, a double bond of the macrocycle must be reduced to a single bond or a proton must be converted to a hydride ligand in Eq. (8). It must be noted that similar hydride complexes functioning as reaction intermediates in redox processes undergone by copper(II) macrocycles have been reported in the literature. By contrast to the reactions of the radical Cu(hexaazacyclophaneH), Eqs. (7) and (8), the spectral transformations observed with the homologous Co species are kinetically of first order in the Co(II)–radical concentration. Lifetimes independent of the acid concentration, $\tau = (34\pm3)$ μs for $C_{AH}/C_{ML} = 1.1$, 1.5 or 2.2 and $C_{ML} = 2.2\times10^{-5}$ or 1.1×10^{-5} M, were recorded at monitoring wavelengths between 290 and 435 nm. The 430 nm absorption band of the product from the radical decay could be assigned to an LMCT absorption of a Co^{III}–hydride species, Co^{III}(hexaazacyclophane)(H^-), Eq. (9).

$$\mathrm{Co^{II}(hexaazacyclophaneH)} \longrightarrow \mathrm{Co^{III}(hexaazacyclophane)(H^-)} \quad (9)$$

It is improbable that the spectral transformations can be ascribed to a conversion of the Co^{II}(hexaazacyclophaneH)$^+$ radical into a Co(I) complex, Co^I(hexaazacyclophaneH), Eq. (10).

$$\mathrm{Co^{II}(hexaazacyclophaneH)} \longrightarrow \mathrm{Co^{I}(hexaazacyclophane)^-} + H^+ \quad (10)$$

Indeed, the 430 nm absorption band appears much more to the UV than the MLCT transitions in the spectra of Co(I) macrocyclic complexes where ligands have isolated azomethine groups [17–20].

The effect of H_2O on the respective $^\bullet CH_2OH$ reductions of the Co(II) and Cu(II) complexes was investigated in N_2O-saturated, mixed solvent solutions. A mixture of H_2O and methanol in a 1:1 molar relationship was the solvent with the highest concentration of H_2O used in these experiments. The reduction of the complexes by $^\bullet CH_2OH$ gave the ligand radical species, Cu(hexaazacyclophaneH) and Co(hexaazacyclophaneH), described above. The rates of formation of these products are close to those measured in the absence of water under similar acid concentrations, i.e. $C_{AH}/C_{ML} = 1.1$, 1.5 or 2.2.

Although the rates of decay of the radicals to products in H_2O/CH_3OH mixtures are almost the same as those measured in CH_3OH, the optical density change followed at various wavelengths indicates that the yield of those products decreases with H_2O concentration. In a 1:1 H_2O/CH_3OH mixture the yields are nearly 50% of those in the absence of water. Decomposition of the radical in parallel to the formation of the products, Eqs. (6)–(9), accounts for these observations. Hydrolysis of the ligand radical is one possible process that will be favored by H_2O.

3.3. Reduction of the macrocycles by e_{sol}^-

The e_{sol}^- and $^\bullet CH_2OH$ are the reactive species to be concerned in pulse radiolysis of the complexes in CH_3OH deaerated with N_2. In solutions with concentrations of the complexes about 2.0×10^{-5} M, M(hexaazacyclophaneH), M = Cu or Co, was produced with the same lifetimes as the solutions saturated with N_2O (above) but with only a 50 to 70% yield. Reactions of the $^\bullet CH_2OH$ radicals, Eqs. (3) and (4), that are pulse radiolytically generated simultaneously with e_{sol}^- are the sources of such products. Since e_{sol}^- and H^+ react to give $H^\bullet$ with a rate constant $k = 2.3\times10^{10}$ M^{-1} s^{-1}, this reaction rate is slow when $C_{AH}/C_{ML} = 1$ or 2 and cannot kinetically compete with the reduction of the complexes by e_{sol}^-. Therefore the lower yields must be interpreted in terms of the formation of products with small extinction coefficients in the reaction of e_{sol}^- with the azacyclophanes. Changes of the optical density recorded at various wavelengths, $\lambda_{obs} \geqslant 350$ nm, with a delay shorter than 2 μs suggest that reactions with the solvated electron produce Cu^I(hexaazacyclophaneH) and Co^{III}(hexaazacyclophane)(H), respectively, with appreciable yields, Eqs. (11) and (12).

$$\mathrm{Cu^{II}(hexaazacyclophaneH)^+} + e_{sol}^- \longrightarrow \mathrm{Cu^{I}(hexaazacyclophaneH)} \quad (11)$$

$$\mathrm{Co(hexaazacyclophaneH)^+} + e_{sol}^- \longrightarrow \mathrm{Co^{III}(hexaazacyclophane)(H)} \quad (12)$$

Because these processes, Eqs. (11) and (12), had to be investigated over the spectral changes caused by the reactions of $^\bullet CH_2OH$, Eq. (4), their rates could not be measured with sufficient accuracy. In a longer time scale, spectral changes recorded at 200 μs ($C_{AH}/C_{ML} = 1$) or at 25 μs ($C_{AH}/C_{ML} = 2$) suggest conversion of the Cu(I) product into the same products as Eq. (4). The disproportionation of the Cu(I) products must result, therefore, in reduction of the macrocycle and the process can probably be represented by Eq. (13).

$$2Cu^{I}(hexaazacyclophaneH) \xrightarrow{H^+} Cu(hexaazacyclophaneH_2) + Cu^{II}(hexaazacyclophaneH)^+ \quad (13)$$

3.4. Interception of the reduction products with CO_2

Pulse radiolysis experiments were also carried out with solutions of the Co and Cu hexaazacyclophane complexes in methanol saturated with CO_2 under 1 atm., i.e. almost 10^{-1} M in CO_2. While conductance and UV spectra of the solutions are in accordance with a quantitative protonation of the complexes, Fig. 1 and Table 1, the concentration of proton, i.e. from excess CO_2, is too low to trap the e_{sol}^-. The spectral changes observed over 20 μs after the irradiation of the solutions are those expected for the deprotonation of the complexes, Eq. (1) and Figs. 1 and 4. This acid–base effect can be of consequence in annihilation of the $CO_2^{\cdot -}$ and $^{\cdot}CH_2OH$ radicals according to Eqs. (14) and (15).

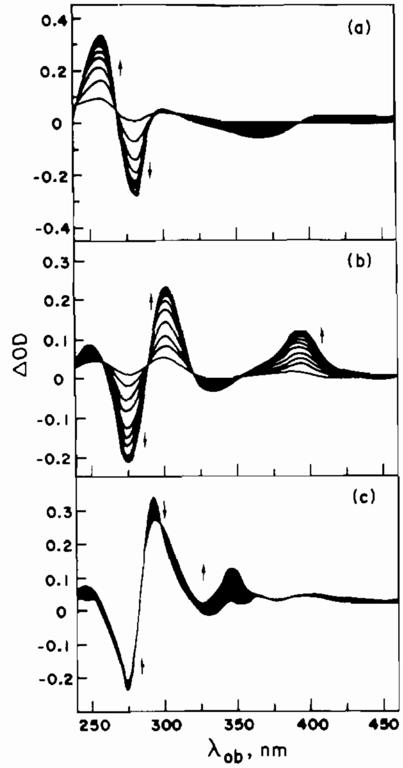


Fig. 4. Transient difference spectra recorded for the interception of reaction intermediates with CO_2. The arrows give the sense of increasing sampling intervals. In (a) the spectra were recorded (0.6 μs after the pulse irradiation at 0.6 μs intervals) in the irradiation of 1.8×10^{-5} M Cu(hexaazacyclophane) in CH_3OH equilibrated under 0.5 atm. CO_2 and 0.5 atm. N_2. Spectra in (b) were recorded with the same time delays of (a) after irradiation of 1.8×10^{-5} M Cu(hexaazacyclophane) in CH_3OH equilibrated under a 0.33 atm. CO_2 and 0.67 atm. N_2O gas mixture. Spectral changes recorded in (c) for the reaction of the Co(hexaazacyclophane) reduction products (see also Fig. 2) with CO_2. Spectra were recorded (36 μs after the pulse irradiation at 6 μs intervals) in the irradiation of 1.8×10^{-5} M Co(hexaazacyclophane) in CH_3OH equilibrated under 0.33 atm. CO_2 and 0.64 atm. N_2O.

$$CO_2 + e_{sol}^- \longrightarrow CO_2^{\cdot -} \quad (14)$$

$$CO_2^{\cdot -} + {}^{\cdot}CH_2OH \longrightarrow CH_3O^- + CO_2 \quad (15)$$

In order to prevent such reactions, solutions of the complexes in CH_3OH were deaerated with and equilibrated under a 3:1 mixture of N_2O and CO_2, i.e. 3.5×10^{-2} M CO_2 and 9.7×10^{-2} M N_2O, before their pulsed irradiations. A fraction 24% or less of all the radiolytically generated e_{sol}^- reacts with CO_2 to give $CO_2^{\cdot -}$ with such concentrations of N_2O and CO_2. The small concentration of $CO_2^{\cdot -}$ produced in such experimental conditions does not interfere with the observation of the $^{\cdot}CH_2OH$ reactions. Indeed, the spectral changes observed between 240 and 450 nm in pulse radiolyses of 2.0×10^{-5} M Co or Cu complexes were the same recorded in less than 1 μs with HTFSM-acidified and N_2O-saturated solutions (above). They correspond to the generation of the metal–ligand radical species in Eqs. (3) and (4). New species, e.g. $\lambda_{max}\approx 340$ nm, appear after the growth of the radical products with nearly the same lifetime, $\tau = (3.6\pm0.5)$ μs for Cu and $\tau \approx (70.0\pm0.4)$ μs for Co, Fig. 4. Since these species are only observed in the presence of CO_2 and have similar spectra with different metal ions, they could be adducts between CO_2 and the hexaazacyclophane radicals. A number of adducts between CO_2 and transition metal complexes has been reported in the literature [21]. Some of the molecular structures assigned to them can explain the observed reactions. Experimental observations in a longer time scale revealed the decay of these reaction intermediates with $t_{1/2} > 300$ μs. The participation of these adducts in the activation of CO_2 remains to be demonstrated.

3.5. Concluding remarks

In terms of the reactions discussed above, the hexaazacyclophane complexes appear related to the phthalocyanines and some porphyrins. For example, the reduction of the ligand followed later by a charge transfer from the macrocycle to the metal center has been previously observed with phthalocyanines of Co(II). If this correlation between Co(hexaazacyclophane) complexes and porphyrins can be carried a step further, homologues of B_{12} should be accessible products. The generation of reaction intermediates with carbon–cobalt and carbon–copper bonds was not observed but remains an open possibility for reactions between these complexes and various carbon-centered radicals.

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