Photoredox Decomposition of [Cobalamin-μ-NC-FeII(CN)5]3- Induced by Metal-to-Metal Charge Transfer Excitation

H. Kunkely, A. Vogler*

Institut für Anorganische Chemie, Universität Regensburg, D-93040 Regensburg, Germany

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In the presence of oxygen aqueous solutions of the binuclear complex [cobalamin-μ-NC-Fe(CN)₅]³⁺ undergo a redox photolysis (φ ~ 2 x 10⁻³ at λᵣ = 405 nm) which yields aquocobalamin and [Fe(CN)₆]³⁻. It is suggested that this photoreaction is induced by direct metal-to-metal charge transfer (MMCT) excitation. On the contrary, [cobalamin-μ-NC-Ru(CN)₅]³⁻ is photo-inert because a reactive MMCT state is not accessible.

Introduction

The interaction of aquocobalamin (vitamin B₁₂) with cyanoferate complexes has been studied by several groups [1–5]. Initially these investigations were stimulated by the intention to use vitamin B₁₂ as an antidote for cyanide poisoning induced by the hypotensive compound nitroprusside [6]. Another interesting feature of such binuclear complexes should be the charge transfer (CT) interaction of Co(III) and Fe(II). Optical metal-to-metal charge transfer (MMCT) of simple binuclear complexes which contain a reducing and an oxidizing metal center has been investigated extensively [7–9]. Photoredox reactions induced by MMCT excitation were also observed for binuclear complexes which contain Co(III) as acceptor and Fe(II) as [Fe(CN)₆]³⁻ or Ru(II) as [Ru(CN)₆]⁴⁻ as donor [7–11]. Although photoredox processes of porphyrin [12–14] and corrin [15] complexes are of considerable importance, they have not yet been reported to occur upon direct MMCT excitation. This is, however, not surprising since the detection of optical MMCT is hampered by the presence of intense porphyrin or corrin intraligand (IL) absorptions which extend from the UV to the red spectral region. Any other bands of different origin are then difficult to identify. As a suitable candidate for the detection of a photoactive MMCT transition in binuclear complexes containing porphyrin or corrin ligands we selected the anion [cobalamin-μ-NC-Fe(CN)₅]³⁻ [5] (abbreviation: [B₁₂-Fe(II)(CN)₆]³⁻). For comparison the corresponding ruthenium complex [B₁₂-Ru(II)(CN)₆]³⁻ was investigated, too.

Experimental Section

Materials

An aqueous solution of K₃[cobalamin-μ-NC-Fe(CN)₅] was prepared in situ by the reaction of aquocobalamin chloride (hydroxocobalamin hydrochloride from Sigma) with equimolar amounts of K₄[Fe(CN)₆] in water [5]. Solutions of K₃[cobalamin-μ-NC-Ru(CN)₅] were obtained by the same procedure using K₄[Ru(CN)₆] instead of K₄[Fe(CN)₆].

Photolyses

The light source was an Osram HBO 100 W/2 or a Hanovia Xe/Hg 977 B-1 (1 kW) lamp. Monochromatic light was obtained by means of the Schott PIL/IL interference filters 366, 405, 436 and 546 nm or by a Schoeffel GM 250/1 high-intensity monochromator. The photolyses were carried out in aqueous solutions in 1 cm spectrophotometer cells at room temperature. Progress of the photolyses was monitored by UV-visible spectrophotometry for quantum yield determinations the concentrations of the complexes were such as to have essentially complete light absorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproduct. Absorbed light intensities were determined by a Polytec pyroelectric radiometer which was calibrated and equipped with a RkP-345 detector.

* Reprint requests to Prof. Dr. A. Vogler.
Instrumentation

Absorption spectra were measured with a Hewlett Packard 8452A diode array spectrometer.

Results and Discussion

The electronic absorption spectra of [B12-Fe(CN)6]3- (λmax = 537 nm, ε = 10 400; λmax = 508 nm, ε = 10 100; λmax = 410 nm, ε = 4 700; λmax = 356 nm, ε = 31 350 M cm⁻¹) and [B12-Ru(CN)6]3- (Fig. 1) are nearly identical. The ruthenium complex displays band maxima at λ = 536 (10 200), 506 (10 100), 410 (4 700), and 355 nm (30 700). In analogy to many other cyanide-bridged complexes [7–9] the anions [B12-M(CN)6]3- are expected to show absorptions which separately can be attributed to the mononuclear components B12-NC and [M(CN)6]4-. Both species constitute the binuclear complexes. In addition, MMCT bands should appear. Compared to [B12-Fe(CN)6]3- the MMCT transition of [B12-Ru(CN)6]3- requires a higher energy since [Ru(CN)6]4- is less reducing than [Fe(CN)6]4- (ΔE = 0.5 V or 4033 cm⁻¹) [7]. Since both [M(CN)6]4- complexes do not absorb above 340 nm [11], the bands at longer wavelength must be assigned to transitions within the B12 moiety and possibly to MMCT transitions from M(II) to Co(III). However, the close similarity of the absorption spectra of [B12-Fe(CN)6]3- and [B12-Ru(CN)6]3- is only consistent with the assumption that all long-wavelength bands of both complexes can be attributed to the B12 moiety. From the comparison with other B12 complexes [15] such as cyano and aquocobalamin it follows that these absorptions of [B12-M(CN)6]3- are exclusively of the IL (corrin) type. Most prominent are the α, β, and γ (Soret) bands (Fig. 1). MMCT absorptions of [B12-M(CN)6]3- are expected to occur in the same spectral region. Such bands were identified for [(NC)5CoII-μ-CN-MIII(CN)5]6+ at λmax = 385 nm (ε = 630) with M = Fe and λmax = 312 nm (ε = 460) with M = Ru [11], and for [(NH3)5CoII-μ-CN-RuII-(CN)5]6+ at λmax = 375 nm (ε = 690) [10]. However, in the case of [B12-M(CN)6]3- these MMCT bands which should show up at different energies are apparently hidden under the intense corrin IL absorptions.

Generally, mononuclear B12 complexes are light sensitive [15,16–20]. The photoreactivity depends on the nature of the reactive excited state. For example, in the case of B12-CN (cyanocobalamin) corrin IL excitation is followed by the population of a ligand field LF excited state which is substitutionally labile and undergoes an aquation of the cyanide ligand [21]. Organocobalamins such as methylcobalamin have available redox active CT states [22]. CT excitation leads to a homolytic splitting of the cobalt(III)-carbon bond yielding B12r (CoII) and methyl radicals in the primary photochemical step [23].

Although [B12-M(CN)6]3- might also be expected to undergo a photosubstitution with the formation of B12a (B12-H2O+ or aquocobalamin) and [M(CN)6]4-, such a photolysis was not observed. This is, however, not surprising since B12a and [M(CN)6]4- would rapidly regenerate the binuclear complexes [5]. This reaction, which is also used to synthesize [B12-M(CN)6]3- (see above), is certainly facilitated by ion pairing of the aquocobalamin cation and the highly charged [M(CN)6]4- anion.

While [B12-Ru(CN)6]3- was not light sensitive at all, aqueous [B12-Fe(CN)6]3- underwent a photoredox photolysis with φ ~ 2 x 10⁻³ if the irradiation was performed in the presence of oxygen with an excitation wavelength of λ = 405 nm. Irradiations at other wavelengths were not effective. The slight spectral changes which accompanied the photolysis were compatible with the formation of B12- H2O⁺ [21]. In addition [Fe(CN)6]3- was formed. Its presence in the irradiated solution was confirmed by its reaction with Fe2+ which yielded Prussian blue.
It is concluded that the photolysis proceeds according to the equations:

\[ \text{[B}_{12}\text{-Fe(CN)}_6]^{3-} \xrightarrow{h\nu} \text{B}_{12r} + [\text{Fe}^{III}(\text{CN})_6]^{3-} \]  

(1)

\[ \text{B}_{12r} + [\text{Fe}^{III}(\text{CN})_6]^{3-} \rightarrow \text{[B}_{12}\text{-Fe(CN)}_5(\text{CN})]^{2-} \]  

(2)

\[ \text{B}_{12r} \xrightarrow{\text{oxygen}} \text{[B}_{12}\text{-H}_2\text{O}]^{+} \]  

(3)

The primary photochemical step (1) is indicative of MMCT excitation which involves an electron transfer from Fe(II) to Co(III). As a consequence, the binuclear complex collapses to the radical pair \([\text{B}_{12r} \cdot \text{Fe(CN)}_6]^{3-}\), which can undergo a cage escape. In the absence of oxygen \([\text{B}_{12}\text{-Fe(CN)}_6]^{3-}\) is effectively regenerated by an inner-sphere electron back transfer (2). In air-saturated solutions Co(II) \([\text{B}_{12r}]\) is intercepted by oxygen yielding finally \(\text{B}_{12a}\) (3). The low overall efficiency of the photolysis seems to reflect the relatively slow reaction of \(\text{B}_{12r}\) with oxygen [15].

According to this reaction scheme the photolysis of \([\text{B}_{12}\text{-Fe(CN)}_6]^{3-}\) proceeds in analogy to that of \([\text{NC})_3\text{Co}^{III}\cdot\text{CN-Fe}^{II}(\text{CN})_6]^{6-}\) which is also induced by Fe(II) to Co(III) MMCT \((\lambda_{\text{max}} = 385 \text{ nm}, \varepsilon = 630)\) [11] excitation. Although in distinction to \([\text{NC})_3\text{Co}^{III}\cdot\text{CN-Fe}^{II}(\text{CN})_6]^{6-}\) a MMCT band was not detected for \([\text{B}_{12}\text{-Fe(CN)}_6]^{3-}\), it is assumed that a MMCT band of the latter complex is present at the irradiation wavelength (~405 nm), but is hidden under the more intense corrin IL band \((\varepsilon = 4600)\) at this wavelength. Nevertheless, a considerable fraction of the exciting light can still be absorbed by the MMCT band. Irradiation with light of other wavelengths apparently does not initiate the redox photolysis since in agreement with previous observations [7–11] only direct MMCT excitation can induce this redox photolysis. In comparison to \([\text{B}_{12}\text{-Fe(CN)}_6]^{3-}\) the MMCT absorption of \([\text{B}_{12}\text{-Ru(CN)}_6]^{3-}\) must be shifted to higher energies by approximately 4033 cm\(^{-1}\) (see above). The MMCT band of the ruthenium complex would then coincide with the Soret absorption which has a very high intensity \((\varepsilon = 30\,700)\). Accordingly, upon irradiation in this spectral region the fraction of light absorbed by the MMCT band of \([\text{B}_{12}\text{-Fe(CN)}_6]^{3-}\) is negligible and a redox photolysis does not occur.

In summary, \([\text{B}_{12}\text{-Fe(CN)}_6]^{3-}\) is an interesting example of a binuclear complex of biological importance which undergoes a photoredox process upon direct MMCT excitation. There are indications that this type of CT interaction may also apply to other polynuclear metalloenzymes [24]. In this context it is of considerable interest that our results supplement a large number of observations on photoinduced electron transfer between porphyrins and various donors and acceptors (e.g. diads, triads) [25,26]. However, in these cases intramolecular electron transfer generally was not achieved by direct CT interaction, but by excited state electron transfer. For the majority of metalloporphyrins this process is not feasible since the excited states of the porphyrin ligands are rapidly deactivated by the intervention of lower-energy excited states of different origin such as LF states [12–14].

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References:


