

Studies on photochemically produced metal complexes with coordinated free radicals

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Abstract. In cobalt(III) amine complexes containing amino acids, photolysis in the charge-transfer bands leads to the formation of alkyl cobalt(III) complexes. Steady and flash photolysis of complexes $[\text{Co}(\text{LL})_2\text{X}]^{2+}$ and $[\text{Co}(\text{LL})_2\text{Y}_2]^+$ (LL = ethylene diamine, polypyridyl or propylenediamine, X = amino acid and Y = nitro ligand) were carried out. Steady irradiation of $[\text{Co}(\text{bpy})_2(\text{gly})]^{2+}$ ion (bpy = bipyridine, gly = glycine) in aqueous medium (pH 1–7) produces the six-coordinated complex $[\text{Co}(\text{bpy})_2(\text{CH}_2\text{NH}_2)]^{2+}$. Flash photolysis of the complex under identical conditions gives an alkyl complex. The alkyl complex formed in the case of $[\text{Co}(\text{bpy})_2(\text{gly})]^{2+}$ ion is stable and could be isolated; the corresponding alkyl complex formed from $[\text{Co}(\text{bpy})(\text{en})(\text{gly})]^{2+}$ ion leads to the labilisation of the ethylenediamine ligand in acidic solutions. Photolysis of the nitro complexes of the type $[\text{Co}(\text{en})_2(\text{NO}_2)_2]^+$ ion in acetonitrile, methanol and ethanol produces a π -bonded transient nitro complex which reacts with molecular oxygen to give the mononuclear superoxo, dinuclear superoxo and dinuclear peroxo complexes in sequence. The formation of these products from the free radical coordinated cobalt(II) complex has been followed by the flash photolysis method and the rate constants have been determined. The details of the mechanisms are discussed.

Keywords. Coordination compounds; metal-alkyl complexes; photochemistry.

1. Introduction

Coordination compounds undergo a wide range of electron-transfer reactions with organic compounds and in a number of these reactions, free-radical-coordinated metal ions are proposed as intermediates (Balzani and Carassiti 1970; Wilkinson 1987). Since these species are highly reactive, isolation of these species has not been possible in most cases (Poznyak and Pavlovski 1988). The structure and detailed mechanisms of reactions of these species have not been understood in detail. More recently (Meyerstein and Schwarz 1988) free radicals and free radical-coordinated metal complexes have been generated by photolysis and radiolysis techniques and the spectroscopy, reactivity and even photochemistry of the transient species have been investigated (Natarajan and Fessenden 1989).

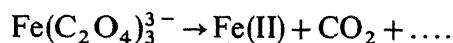
Metal-carbon bonded coordination compounds have been of interest for quite sometime and a large number of metal-alkyls have been synthesized (Roche and Endicott 1974; Poznyak and Pawlowski 1982). One of the well-known naturally occurring metal-alkyls, cobalamin, has been of great interest and several studies have

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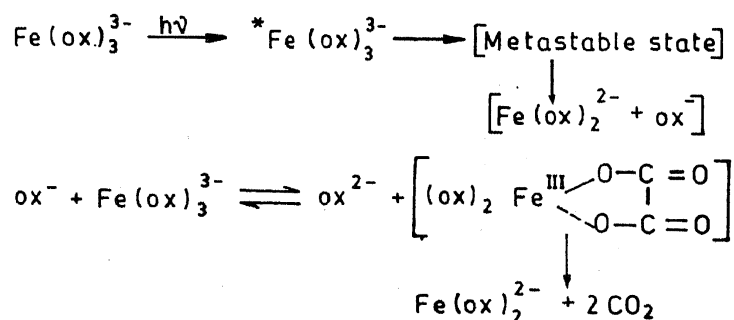
been carried out to understand the formation and reactions of these metal-alkyl systems (Pratt and Craig 1973; Kemmitt and Russell 1982). In this account we have outlined studies on some of the metal-alkyl species generated as a result of photolysis and also report on the isolation of a few stable metal-carbon bonded and metal-dioxygen species and studies on these systems.

2. Photoredox reactions of labile coordination compounds with carboxylate and amino acid ligands

Coordination compounds with carboxylic acids or carboxylates and their derivatives as ligands undergo photoredox reactions (Endicott 1975). One of the earliest examples and perhaps the best known is the photoreaction of *tris*(oxalato)ferrate(III) which produces iron(II) and oxidised carboxylate radicals among other products. The carboxylate radical loses carbon dioxide readily.



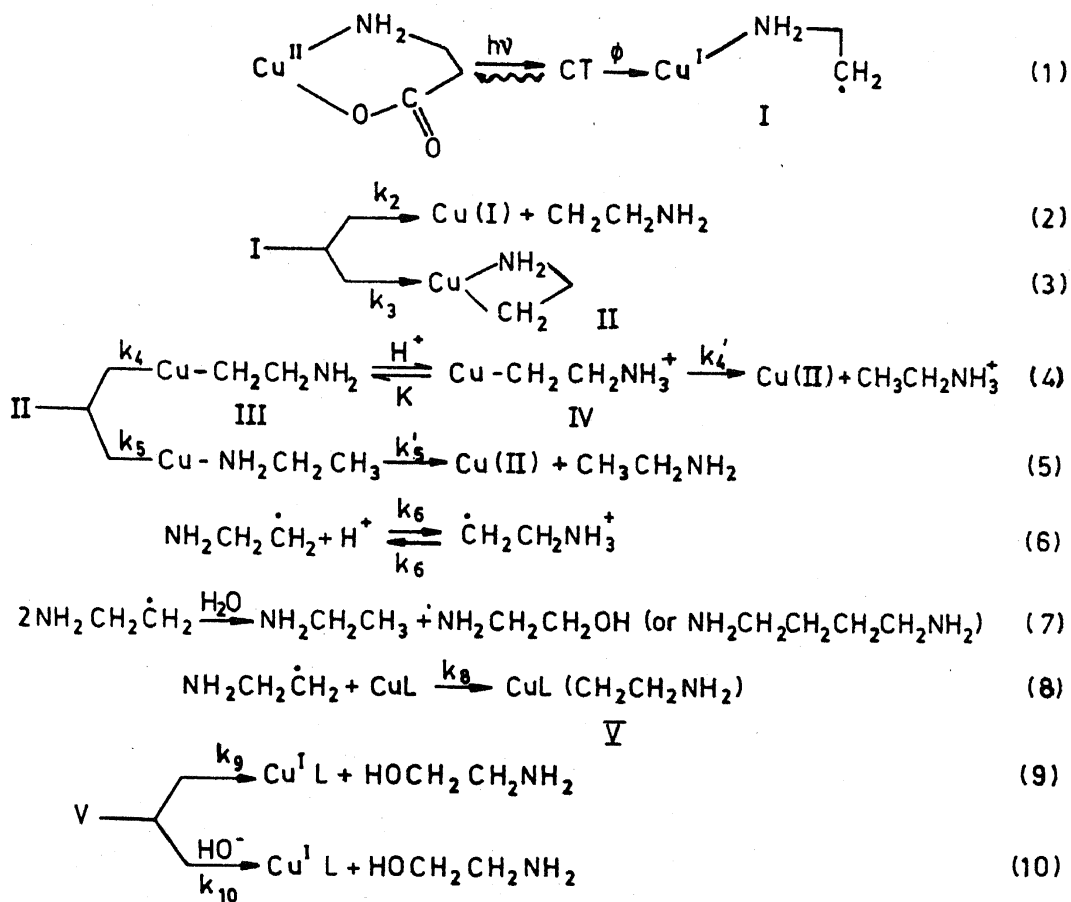
This system is used as an actinometer for UV and visible light. Detailed examination (Parker and Hatchard 1959) of the system on flash photolysis indicates the formation of the transient species corresponding to the coordinated oxalate free radicals. Since the metal ion is labile, a number of coordinated radical species have been detected as shown in scheme 1.



Scheme 1.

Another series of complexes involving carboxylate and amine coordination by chelation are the amino acid complexes of copper(II) whose photochemistry has been studied quite extensively (Natarajan and Ferraudi 1981; Ferraudi and Murdharan 1981; Namasivayam and Natarajan 1983). In this labile system, photolysis of different amino acid-coordinated copper(II) complexes on excitation in the charge-transfer band produces copper(I) coordinated to the free radical. The reactions of the coordinated free radicals have been investigated using flash kinetic spectroscopy and the reactions of the coordinated free radicals are summarised in scheme 2.

Loss of carbon dioxide from the radical leads to an alkyl-free radical coordinated copper(I) and in the subsequent steps the coordinated alkyl radical oxidises copper(I) to form a copper(II) alkyl complex. Detailed flash photolysis studies show further decomposition of the alkyl copper(II) complex to other products. Studies involving a number of amino acid-copper(II) complexes show similar results, namely that photoreduction of the complexes results in the formation of metal-alkyl complexes. The transient spectra obtained on flash photolysis of the copper(II) amino acid



Scheme 2.

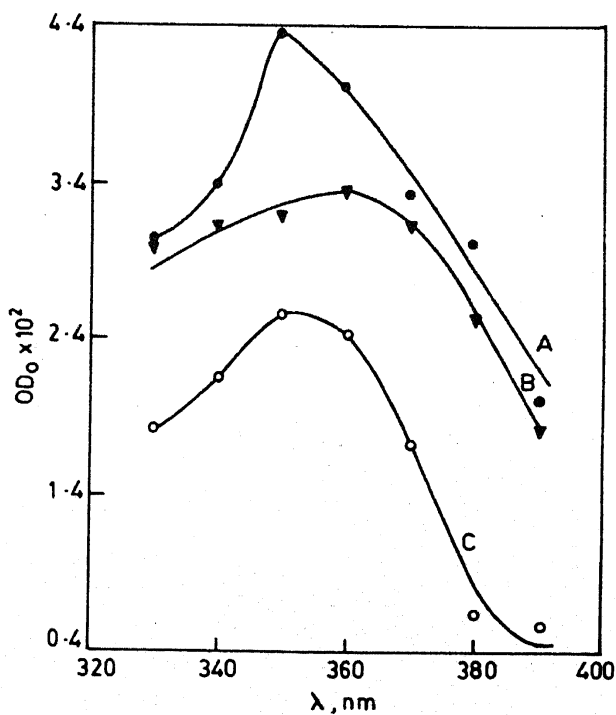
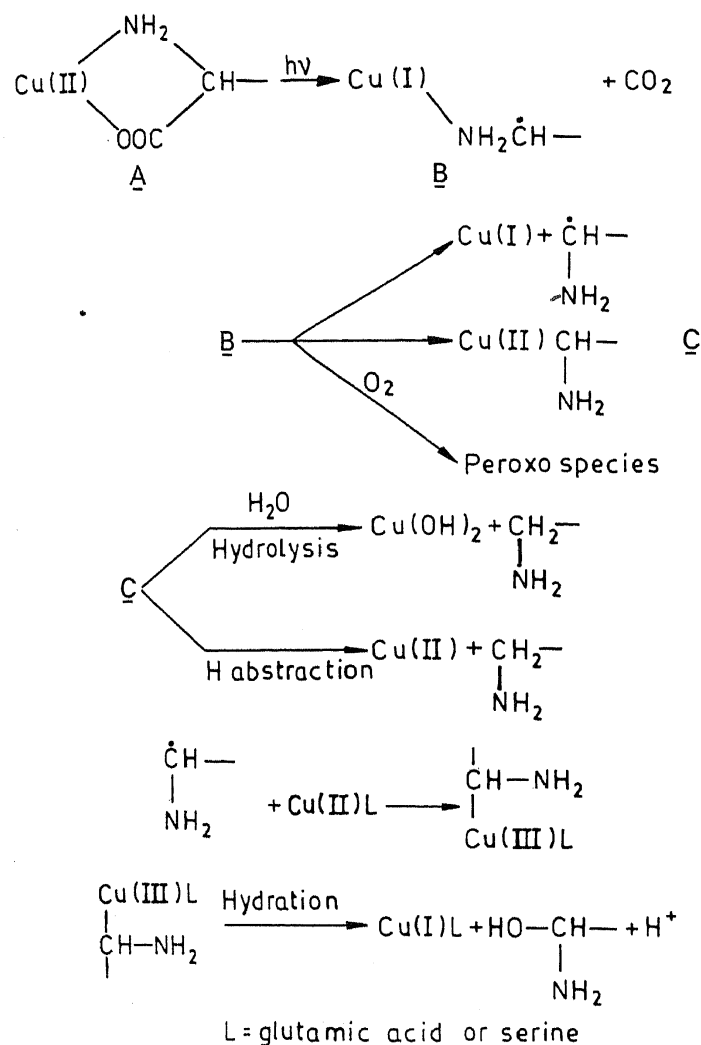


Figure 1. Spectra of transients for the flash photolysis of $\text{Cu}(\text{glu})_2$ at $\text{pH} = 5$, (A) deaerated, (B) aerated, (C) oxygenated.

complexes are shown in figure 1. It has also been observed that photopolymerisation reactions are initiated by the copper(I) amino alkyl radical and study of the kinetics of polymerisation reactions has thrown light on the nature of the initiating species. The copper(II) alkyl complexes have absorption maximum around 350 nm in the case of glutamic acid, serine and valine-coordinated complexes. The reactions of these alkyl copper(II) complexes are summarized in scheme 3.

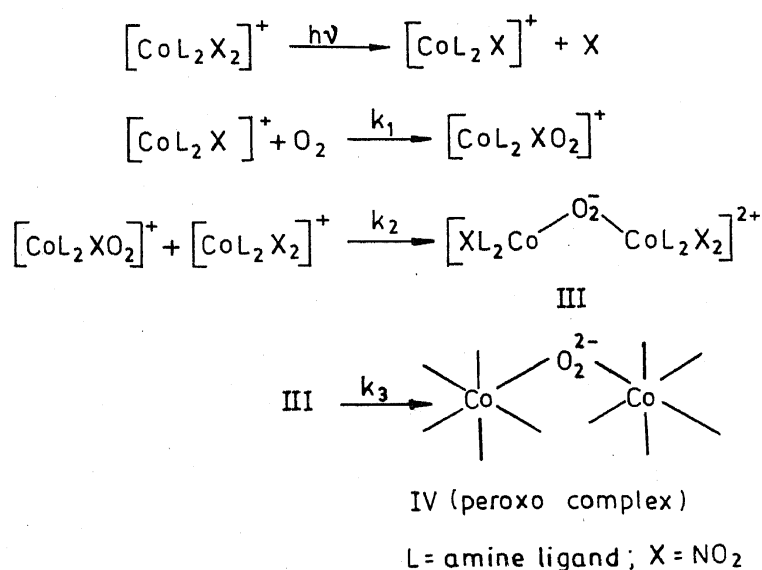


Scheme 3.

3. Photoredox reactions of inert coordination compounds with amino acid ligands

Photoredox reactions are known to originate from the charge-transfer-to-metal excited states. Photoredox reactions of cobalt(III) and ruthenium(II) have been extensively studied (Wilkinson 1987). Excited state redox reactions are observed in Rh(III), Ir(III), Pt(IV) and other metal complexes which are inert. Cobalt(III) amine complexes undergo redox break-down to give a labile cobalt(II) complex which aquates rapidly in aqueous solution. While Co(II) ammine complexes aquate much faster, the first three ammonia moieties in $\text{Co}(\text{NH}_3)_5^{2+}$ ion are aquated in less than a few microseconds; the chelated amines are labilised much more slowly (Lilie and Simic

1974; Lilie *et al* 1976). Photo-produced cobalt(II) amines undergo intramolecular and intermolecular redox reactions, in the presence of molecular oxygen. In non-aqueous solvents molecular oxygen oxidises the cobalt(II) amines to form mononuclear superoxo complexes (Natarajan 1980) which undergo further reactions to form dinuclear superoxo complexes (Ramamurthy and Natarajan 1985) and eventually produce dinuclear peroxo complexes (Natarajan and Radhakrishnan 1982) which can be isolated and characterised. The details of these reactions have been investigated by the flash photolysis method (Ramamurthy and Natarajan 1986) and the reaction scheme is summarized in scheme 4.



Scheme 4.

Rate constants observed for the reactions in different solvents are given in table 1.

The μ -peroxo dicobalt(III) amines have been prepared by a general method in which oxygen is bubbled through a solution containing cobaltous salt and amine in a slightly alkaline solution. More recently, μ -peroxo complexes have also been isolated by photochemical methods where oxygen is allowed to react with the cobalt(II) intermediate generated by the photolysis of the cobalt(III) complexes. The photochemical route offers the advantage of almost quantitative yield and also the facility to prepare mixed ligand μ -peroxo complexes.

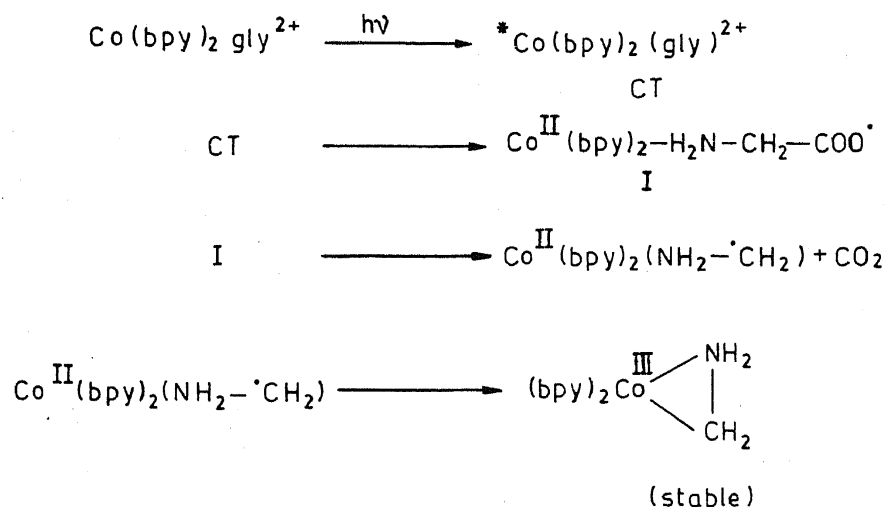
The amino acid coordinated amine complexes of cobalt(III) ion show a different type of photoredox behaviour. Photolysis of $\text{Co}(\text{bpy})_2\text{gly}^{2+}$ ion in aqueous solution by irradiating in the CTTM band leads to the formation of octahedral $\text{Co}(\text{bpy})_2(\text{CH}_2\text{-NH}_2)^{2+}$, a cobalt-alkyl complex which has been characterized and the structure determined (Poznyak *et al* 1982). The complex on flash photolysis shows the formation of the cobalt(III)-alkyl complex by the intramolecular oxidation of the cobalt(II) centre by the coordinated alkyl radical (Natarajan and Natarajan 1989). Since the cobalt(III)-amine complexes do not show emission in the excited states, the nature of the reactive state has not been understood. However, the reactions of the coordinated free radicals have been monitored and are shown below.

A number of cobalt(III) complexes of the type $\text{Co}(\text{bpy})(\text{Am})(\text{AA})^{2+}$, (Am = amine, AA = amino acid) have been investigated (Natarajan and Natarajan 1990) by flash photolysis methods in aqueous solution and the reactions observed are summarized in

Table 1. Flash photolysis of cobalt(III)-amines in CH₃CN and CH₃OH.
Monitoring wavelength = 400 and 700 nm

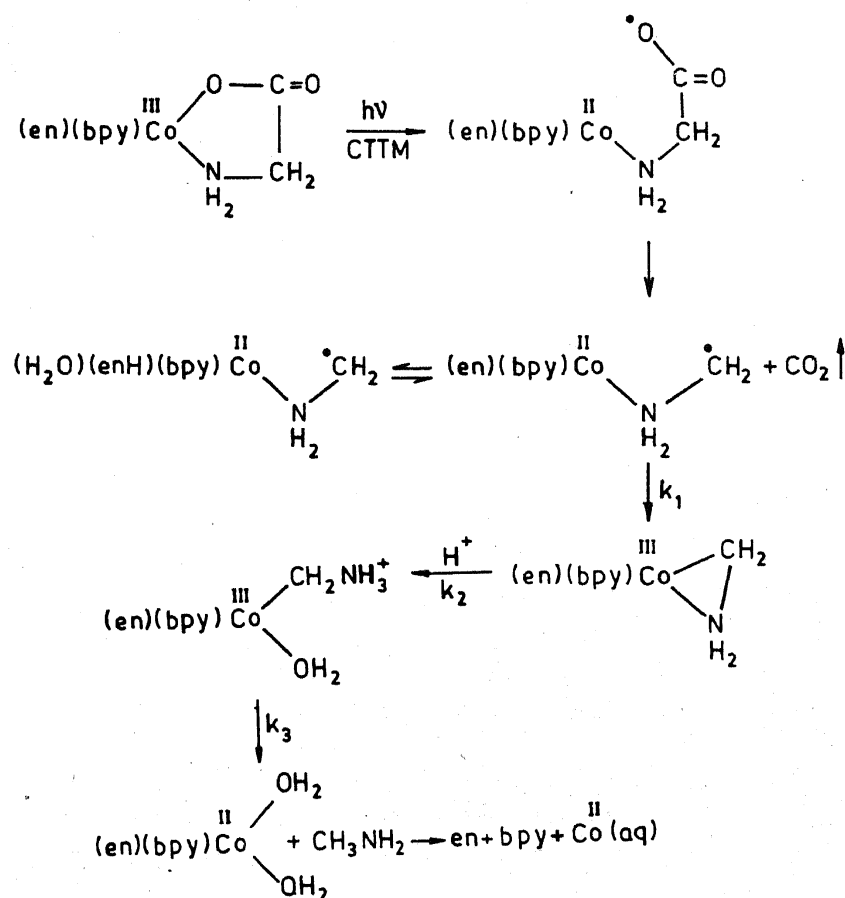
| Complex | CH ₃ CN | | CH ₃ OH | |
|--|--|---|--|--------------------------------------|
| | 400 nm growth $k_{\text{obs}}(\text{s}^{-1})$ | 700 nm decay $k_3(\text{s}^{-1})$ | 400 nm growth $k_{\text{obs}}(\text{s}^{-1})$ | 700 nm decay $k_3(\text{s}^{-1})$ |
| <i>cis</i> -[Co(pn) ₂ (NO ₂) ₂]ClO ₄ | 480 ± 35 595 ± 20 ^a 0.5 ± 0.02 ^b | 2.05 ± 0.10 6.10 ± 0.30 ^c | 42.6 ± 5.0 | 0.56 ± 0.08 |
| <i>trans</i> -[Co(pn) ₂ (NO ₂) ₂]ClO ₄ | 300 ± 20 | 0.11 ± 0.01 | 30.1 ± 2.0 | 0.39 ± 0.09 |
| <i>trans</i> -[Co(pn) ₂ Cl ₂]ClO ₄ | 408 ± 20 | 0.38 ± 0.02 | — | — |
| <i>trans</i> -[Co(tn) ₂ (NO ₂) ₂]ClO ₄ | 72 ± 10 | 1.41 ± 0.10 | 8.4 ± 1.5 | 0.39 ± 0.10 |
| <i>trans</i> -[Co(tn) ₂ (NO ₂)Cl]ClO ₄ | 146 ± 10 | 0.90 ± 0.12 | 0.3 ± 0.05 | 0.99 ± 0.05 |
| <i>trans</i> -[Co(tn) ₂ Cl ₂]ClO ₄ | 488 ± 30 | 0.35 ± 0.10 | — | — |
| [Co(dien)(NO ₂) ₃] | 50 ± 5 ($k_1 = 1.2 \times 10^3, \text{M}^{-1}\text{s}^{-1}$) ^d ($k_1 = 3.1 \times 10^4, \text{M}^{-1}\text{s}^{-1}$) ^e | 0.36 ± 0.05 | 0.5 ± 0.1 | 0.98 ± 0.10 |
| [Co(dien)(en)NO ₂](ClO ₄) ₂ | 588 ± 10 | 0.15 ± 0.02 | 66.2 ± 8.0 | 0.23 ± 0.05 |
| [Co(dien)(pn)NO ₂](ClO ₄) ₂ | 134 ± 5 | 1.47 ± 0.10 | 289 ± 10 | 0.52 ± 0.08 |

^a In oxygen saturated solution; ^b in presence of 3.26×10^{-4} M cobalt(II) perchlorate; ^c in presence of 1×10^{-4} M sodium nitrite; ^d Wilkinson (1987) reported value for [Co(dien)₂]²⁺; ^e rate constant calculated using the dissolved oxygen concentration (1.6×10^{-3} M).



the scheme 5. The rate constants observed for different reactions are given in table 2. In the case of cobalt(III) ion the alkyl complex formed is stabilised by two bipyridyl ligands coordinated to the metal ion. Even when one of the bipyridyl ligands is replaced by an amine the alkyl compound formed is unstable and decomposes.

Investigation of the protoredox behaviour of the (Am)₂ cobalt(III) amino acid chelates in non-aqueous medium shows that the charge-transfer excited states lead to



Scheme 5.

Table 2. Flash photolysis studies on cobalt(III)-amine complexes containing amino acid.

| Name of the complex | pH | Monitoring wavelength | | |
|--|-----|-------------------------|------------------------|------------------------|
| | | 410 nm growth (k_1) | 410 nm decay (k_2) | 220 nm decay (k_3) |
| [Co(bpy) ₂ (gly)] ²⁺ | 1.0 | 3.99E3 | * | * |
| [Co(bpy)(en)(gly)] ²⁺ | 1.0 | 3.95E3 | 1.34E3 | 1.29E-5 |
| | 2.0 | 4.09E3 | ** | 1.48E-4 |
| | 3.0 | 4.12E3 | ** | 3.37E-4 |
| | 4.0 | 3.84E3 | * | 1.23E-4 |
| | 5.0 | 3.82E3 | * | 2.20E-4 |
| | 6.2 | 4.14E3 | * | 1.66E-5 |
| [Co(bpy)(en)(ala)] ²⁺ | 1.0 | 4.12E3 | 0.59 | 3.58E-3 |
| | 2.0 | 4.05E3 | 0.72 | 8.12E-3 |
| | 3.0 | 4.37E3 | ** | 1.01E-2 |
| | 4.0 | 4.14E3 | * | 2.74E-2 |
| | 5.0 | 3.49E3 | * | 2.27E-2 |
| | 6.2 | 3.49E3 | * | 1.51E-2 |
| [Co(bpy)(pn)(gly)] ²⁺ | 1.0 | — | 1.03E3 | 1.13E-5 |
| | 3.0 | — | * | 6.31E-3 |
| | 6.2 | — | * | 5.18E-6 |
| [Co(bpy)(pn)(ala)] ²⁺ | 1.0 | 4.08E3 | 0.37 | * |
| | 3.0 | 4.08E3 | 0.09 | 5.96E-2 |
| | 6.2 | — | * | 1.10E-4 |

* no decay is observed

**small decay is observed

the formation of the cobalt(III)-alkyl complexes as transients which further react with dissolved oxygen to give dioxygen insertion products (Kolochoi 1987).

4. Photoredox reactions of chromium(III) complexes and the formation of chromium(III)-alkyl complexes

Chromium(III) - amine complexes are known to undergo predominantly photoaquation reactions on irradiation in the *d-d* bands and in the charge transfer bands. Although there were claims (Porter and Van Hovten 1979, 1980) that redox reactions occur on excitation in the charge-transfer bands, such reactions are not observed for many systems. In the case of polypyridyl-chromium(III) complexes, electronic excitation of the complexes leads to aquation of the ligands and the reactions observed are similar to thermal reactions. More recently (Anbalagan and Natarajan 1990) we have synthesised polypyridyl complexes of chromium(III) coordinated to poly (acrylic acid) and poly (methacrylic acid). These macromolecular chromium(III) complexes undergo aquation reactions labilising the polypyridyl ligand on excitation in the *d-d* bands. However on excitation in the higher energy bands these polymer bound complexes show a transient which has a spectrum as shown in figure 2. The transient decays with a rate constant of 90 s^{-1} . One of the products of photolysis is found to be carbon dioxide and the photochemical reaction proposed is shown in scheme 6.

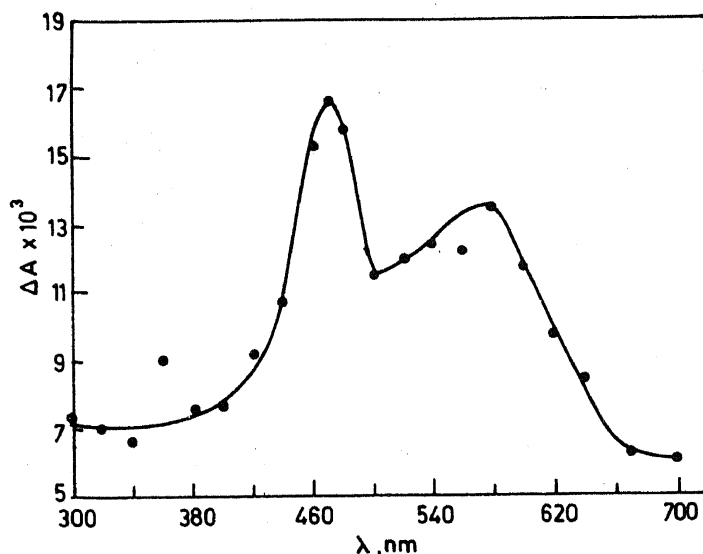
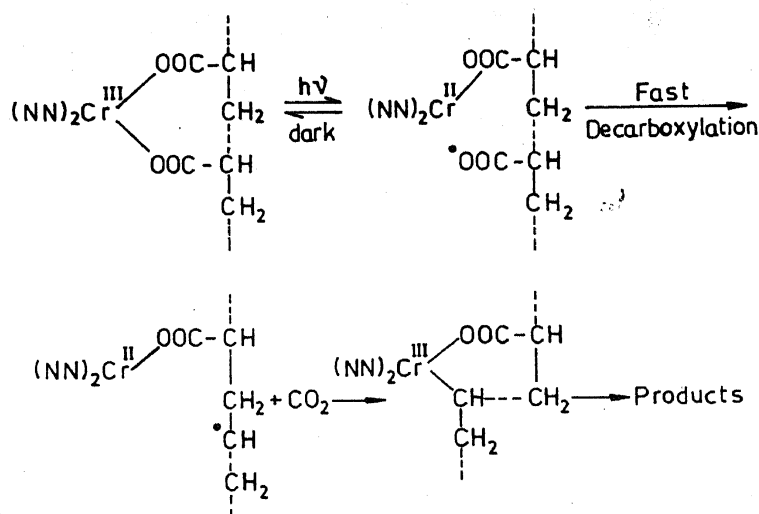


Figure 2. Transient absorption spectrum of 1 mM $[\text{Cr}(\text{phen})_2(\text{PAA})_2]^+$ (PAA: Cr = 8:1) in air-equilibrated aqueous solution at 26°C, pH = 7.2 and 0.02 M ionic strength (NaNO_3). Absorbance recorded 1 ms after flash.



Scheme 6.

In the case of monomeric complexes of the type $\text{Cr}(\text{bpy})_2(\text{C}_2\text{O}_4)^+$ no transient however was observed indicating that the macromolecular environment facilitates separation of the primary photoredox products. Eventually the coordinated carboxylato radical loses carbon dioxide to give the alkyl coordinated radical. The latter reoxidises chromium(II) to give chromium(III)-alkyl complex. There have been a number of studies (Bakac *et al* 1982) involving redox reactions of chromium(II) and organic compounds to form chromium(III)-alkyl intermediates. Not many chromium(III)-alkyl compounds have been isolated as in the case of cobalt-alkyl complexes.

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