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Photochemically Produced Cobalt(II) Complexes with Coordinated Free Radicals: Intramolecular Oxidation of the Metal Center by the Coordinated Alkyl Radical

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Cobalt(III) complexes of the type [Co(bpy)(Am)(AA)]$^{2+}$, where bpy is 2,2′-bipyridine, Am is ethylenediamine or propylenediamine, and AA is an amino acid, on photolysis in aqueous solution show the formation of cobalt(III)–alkyl complexes. In all the cases investigated, the flash photolysis technique is used to study the kinetics of the formation of the cobalt(III)–alkyl complex and subsequent reactions. In the case of the [Co(bpy)$_2$(gly)]$^{2+}$ ion, a stable cobalt(III)–alkyl complex is formed on photolysis, while in all the other cases the cobalt(III)–alkyl compound formed decomposes. The kinetics of the decomposition of the complexes has been investigated. It is observed that when two polypyridyl ligands are present in the coordination sphere, the cobalt(III)–alkyl complex formed is stabilized, while when only one bpy and an amine are present, the cobalt(III)–alkyl complex undergoes decomposition. Quantum yields for cobalt(II) formation have been determined in all the cases. The presence of dissolved oxygen does not seem to affect the photochemistry in aqueous solution.

Introduction

Cobalt(III)–amine complexes are known to undergo photoredox reactions on excitation in the charge-transfer bands which lead to the formation of cobalt(II) species in aqueous solution.[1] In some cases the photoproduced oxidized ligand radicals have been observed[2] as transient species and the nature of the excited states involved in the reaction has been understood by studying the characteristics of the transients. More recently[3] transient species which are identified to be cobalt(II) complexes with coordinated free radicals have been observed in the photoredox reactions of cobalt(III)–amine complexes. Macrocyclic complexes of cobalt(II) are known[4–6] to react with alkyl radicals to produce corresponding alkyl complexes. In the case of amino acid complexes of cobalt(III) with bipyridyl ligands, photolysis in the charge-transfer bands leads to the formation of cobalt(III)–alkyl complexes which have been isolated and characterized[7]. We have reported[8] on the direct observation of the intramolecular oxidation of the cobalt(II) complex by the coordinated alkyl free radical to produce a cobalt(III)–alkyl complex. In the present study we have investigated a series of cobalt(III)–amino acid chelates with different ligands in order to obtain information on the formation of the cobalt(III)–alkyl complex and its stability under different conditions in aqueous solutions.

Experimental Section

The chemicals and solvents used in this investigation were of AnalaR, GR, or other high-purity grade. The complexes [Co(bpy)$_2$(gly)](ClO$_4$)$_2$·H$_2$O (**1**), [Co(pn)(gly)(NO$_2$)$_2$], [Co(pn)(ala)(NO$_2$)$_2$], and [Co(en)(ala)(NO$_2$)$_2$] (where en = ethylenediamine, pn = propylenediamine, bpy = 2,2′-bipyridine, gly = glycine, and ala = alanine) were prepared as described earlier.[9] The complexes [Co(bpy)(en)(ala)](ClO$_4$)$_2$ (**3**), [Co(bpy)(pn)(gly)(ClO$_4$)$_2$ (**4**), and [Co(bpy)(pn)(ala)](ClO$_4$)$_2$ (**5**) were prepared by following the procedure adopted for the synthesis of [Co(en)(bpy)(gly)](ClO$_4$)$_2$ (**2**). A typical procedure for the synthesis of the complexes investigated is given below. A suspension of 1.5 g of [Co(en)(ala)(NO$_2$)$_2$] and 3.8 mL of concentrated hydrochloric acid was warmed on a water bath, when the yellowish suspension began to dissolve with the evolution of nitrogen dioxide with the color of the mixture turning violet. The pH of the violet solution was adjusted to 5–6 using 1 N aqueous lithium hydroxide. A solution of 2,2′-bipyridine (0.77 g) in a small quantity of acetone and activated carbon (1.5 g) was added to the solution. This mixture was refluxed for about 30 min on a water bath. The violet color changed to orange when the activated charcoal was filtered off, and lithium perchlorate (2.5 g) was added to the filtrate. Orange crystals separated as the perchlorate salt were filtered and washed with cold water, ethanol, and then ether. The complex was recrystallized in hot water by adding lithium perchlorate. The purity of the complexes was checked by comparing the UV–visible, infrared, and PMR spectra reported earlier[9] for analogous complexes and by determining the elemental analysis. Anal. Calcd for [Co(bpy)$_2$(gly)](ClO$_4$)$_2$·H$_2$O, $C_{22}H_{22}CoCl_2N_5O_{11}$: C, 39.9; H, 3.3; N, 10.6; Co, 8.9. Found: C, 39.9; H, 3.4; N, 10.5; Co, 8.8. Calcd for [Co(bpy)(en)(gly)](ClO$_4$)$_2$, $C_{14}H_{17}CoCl_2N_5O_{10}$: C, 30.6; H, 3.6; N, 12.8; Co, 10.8. Found: C, 31.2; H, 3.7; N, 12.7; Co, 10.6. Calcd for [Co(bpy)(en)(ala)](ClO$_4$)$_2$, $C_{15}H_{19}CoCl_2N_5O_{10}$: C, 32.0; H, 3.9; N, 12.5; Co, 10.5. Found: C, 31.5; H, 3.9; N, 12.3; Co, 10.3. Calcd for [Co(bpy)(pn)(gly)](ClO$_4$)$_2$, $C_{15}H_{19}CoCl_2N_5O_{10}$: C, 32.0; H, 3.9; N, 12.5; Co, 10.5. Found: C, 31.5; H, 4.1; N, 12.3; Co, 10.3. Calcd for [Co(bpy)(pn)(ala)](ClO$_4$)$_2$, $C_{16}H_{21}CoCl_2N_5O_{10}$: C, 33.3; H, 4.2; N, 12.2; Co, 10.2. Found: C, 32.9; H, 4.2; N, 12.3; Co, 10.2.

Steady photolysis experiments were carried out by using a low-pressure mercury pen-ray quartz lamp (254 nm) of Ultra violet Products Inc. Conventional flash photolysis experiments were carried out using an Applied Photo Physics flash system (KN02), which was described elsewhere.[10] Laser flash photolysis experiments were carried out using an Applied Photo Physics excimer laser operated with Kr/F$_2$ mixtures (249 nm, with an energy of 200 mJ/pulse and a width of 30 ns). All the laser flash photolysis experiments were carried out at room temperature using a flow system. The stock solution under study was taken in a container bubbled with nitrogen, and the solution was allowed to flow due to gravity with a flow rate of ca. 1 mL/min. The transient signals initially captured by a Biomation Gould-4500 instrument were transferred to a PDP 11/23 computer, which controls the experiments and provides suitable processing, storage, and hard copy facilities. Absorption spectral measurements, kinetics at a slower time scale, and the spectral analysis of the photoproducts were carried out using a Hitachi-320 UV-visible double-beam spectrophotometer. The first-order plots of log $(A_t - A_\infty)$ versus time were fitted to a linear least-squares program, and the correlation coefficient obtained was >0.99. Quantum yields for cobalt(II) formed in steady photolysis reactions were determined by Kitson's method.[11] The pH of the solution was measured using a Philips Model pp9046 digital pH meter accurate to 0.01 pH units. The aqueous solutions were deaerated by bubbling oxygen-free nitrogen through the solution for not less than 30 min. In the case of pH dependence studies, solutions of pH 4–6 were made with the use of acetate buffering with total acetate concentration of about 0.2 M. The pH of the buffer solutions was checked

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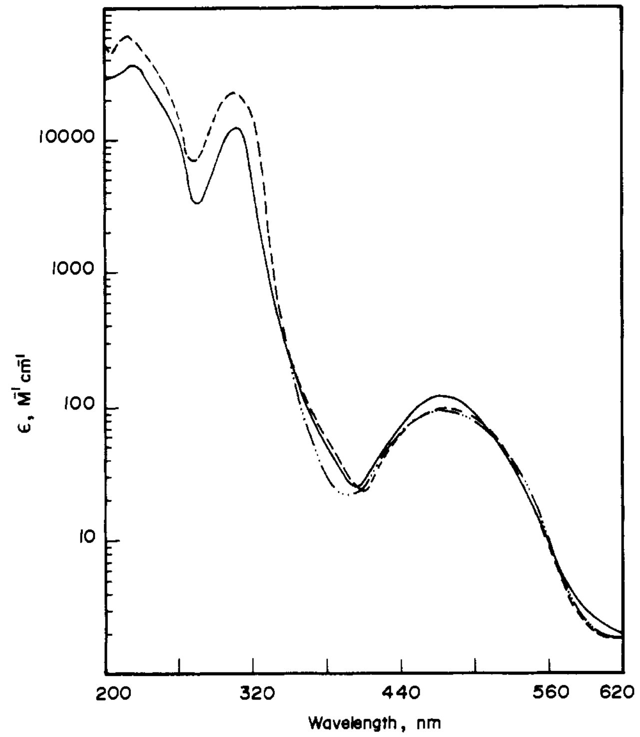

Figure 1. Visible and ultraviolet spectra of $[Co(bpy)_2(gly)](ClO_4)_2{\cdot}H_2O$ (---), $[Co(bpy)(en)(gly)](ClO_4)_2$ (-···-), and $[Co(bpy)(en)ala)](ClO_4)_2$ (—) in water.

before each use by means of the digital pH meter.

Table I. Co^{2+}(aq) Quantum Yields from the Photolysis of Cobalt(III)–Amino Acid Complexes

complex	pH	$\phi_{Co^{2+}}$ 254 nm[a]	350 nm[a]
$[Co(bpy)_2(gly)](ClO_4)_2{\cdot}H_2O$	6.2	$<10^{-3}$	$<10^{-3}$
	1.0	$<10^{-3}$	$<10^{-3}$
$[Co(bpy)(en)(gly)](ClO_4)_2$	6.2	0.04	$<10^{-3}$
	5.0	0.04	$<10^{-3}$
	4.0	0.04	$<10^{-3}$
	3.0	0.05	$<10^{-3}$
	2.0	0.05	$<10^{-3}$
	1.0	0.05	$<10^{-3}$
$[Co(bpy)(pn)(gly)](ClO_4)_2$	6.2	0.04	$<10^{-3}$
	5.0	0.04	$<10^{-3}$
	4.0	0.04	$<10^{-3}$
	3.0	0.05	$<10^{-3}$
	2.0	0.05	$<10^{-3}$
	1.0	0.05	$<10^{-3}$
$[Co(bpy)(en)(ala)](ClO_4)_2$	6.2	0.03	$<10^{-3}$
	5.0	0.03	$<10^{-3}$
	4.0	0.04	$<10^{-3}$
	3.0	0.06	$<10^{-3}$
	2.0	0.07	$<10^{-3}$
	1.0	0.08	$<10^{-3}$
$[Co(bpy)(pn)(ala)](ClO_4)_2$	6.2	0.03	$<10^{-3}$
	5.0	0.03	$<10^{-3}$
	4.0	0.04	$<10^{-3}$
	3.0	0.05	$<10^{-3}$
	2.0	0.07	$<10^{-3}$
	1.0	0.08	$<10^{-3}$

[a] Wavelength of irradiation.

Results

The electronic spectral details of the complexes investigated are shown in Figure 1. Photolysis of the cobalt(III)–amino acid chelates leads to spectral changes as shown in Figure 2 in a typical case of **2**. The isosbestic points are observed when the photolysis of the complexes is restricted to 5–10% decomposition of the concentration of the complex taken initially. Prolonged irradiation of the solution leads to secondary photolysis of the products formed as seen from the spectral changes observed. Analysis of the photolyzed solution shows the presence of cobalt(II), as determined colorimetrically, and dissolved carbon dioxide, which was confirmed by bubbling the photolyzed solution with nitrogen and passing the effluent nitrogen through a barium hydroxide solution, which gave rise to a white precipitate. Quantum yields were determined for cobalt(II) on irradiation of the amino acid chelates, and the results are given in Table I. In the case of complex **1**, the quantum yield for cobalt(II) measured is the total quantum yield for cobalt(II) formation, since the photoproduct, a three-membered aminomethyl complex which is stable in water, decomposes in acetone as well as in presence of ammonium thiocyanate during estimation to give the cobaltous ion quantitatively. Flash photolysis of the complexes in air equilibrated and in deaerated aqueous media produces identical transient species, and the growth and the decay of the transient species are given in Figure 3 for complex **3** as a typical case. The spectra of the transients monitored in the flash photolysis system for the com-

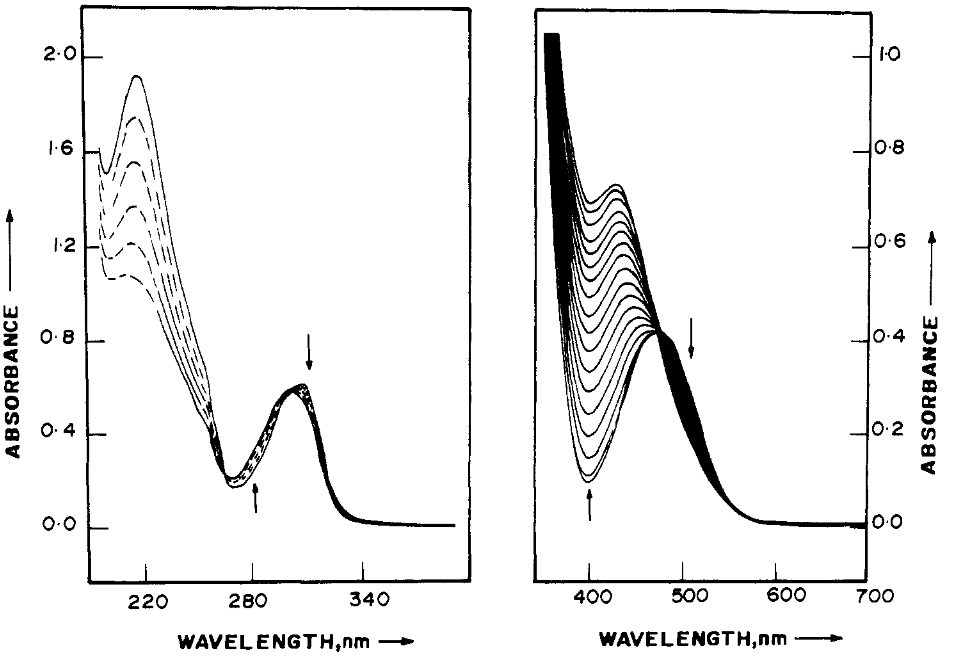

Figure 2. Absorption spectra of the unirradiated solution and successive irradiated solution of the complex $[Co(bpy)(en)(gly)](ClO_4)_2$ at pH = 1.

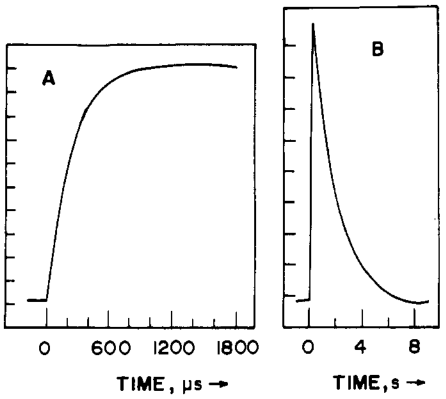

Figure 3. Transient absorption growth at (A) 410 nm and transient decay at (B) 410 nm of $[Co(bpy)(en)(ala)](ClO_4)_2$ at pH = 1.

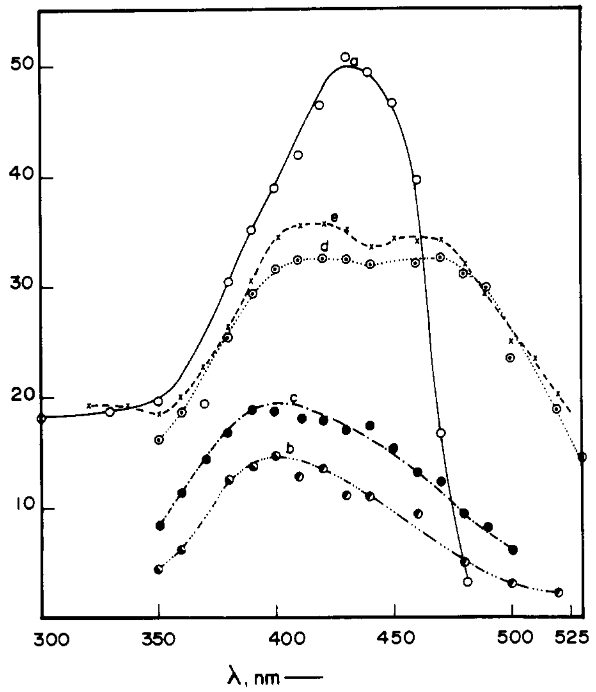

Figure 4. Transient absorbance spectrum recorded in 10 ms after flash photolysis in water for the complexes (a) $[Co(bpy)_2(gly)](ClO_4)_2 \cdot H_2O$, (b) $[Co(bpy)(en)(gly)](ClO_4)_2$, (c) $[Co(bpy)(pn)(gly)](ClO_4)_2$, (d) $[Co(bpy)(en)(ala)](ClO_4)_2$, and (e) $[Co(bpy)(pn)(ala)](ClO_4)_2$.

plexes investigated are shown in Figure 4. The rate constants for the growth and decay of the transients were determined by the log (Δ absorbance) versus time plots, and the results are summarized in Table II. The rate constants for the decay of the transients were found to change with the pH of the solution. The product formed in the photolyzed solution decomposed at a slower time scale, and the rate constants for this decomposition observed are given in Table II. The rate constants for the decay were found to be pH dependent, and the results are shown in Figure 5. Complex **1** was photolyzed using light of wavelength 254 nm, and the product of photolysis was separated using CM-Sephadex C25 cation-exchange resin; the spectrum of the separated photoproduct was found to be identical to that reported[7] for the product $Co(bpy)_2(CH_2NH_2)^{2+}$ ion.

Discussion

Cobalt(III)-amine complexes with carboxylate ligands in general show[12] two ligand field bands around 500 and 350 nm and one intense charge-transfer band in the ultraviolet region. In

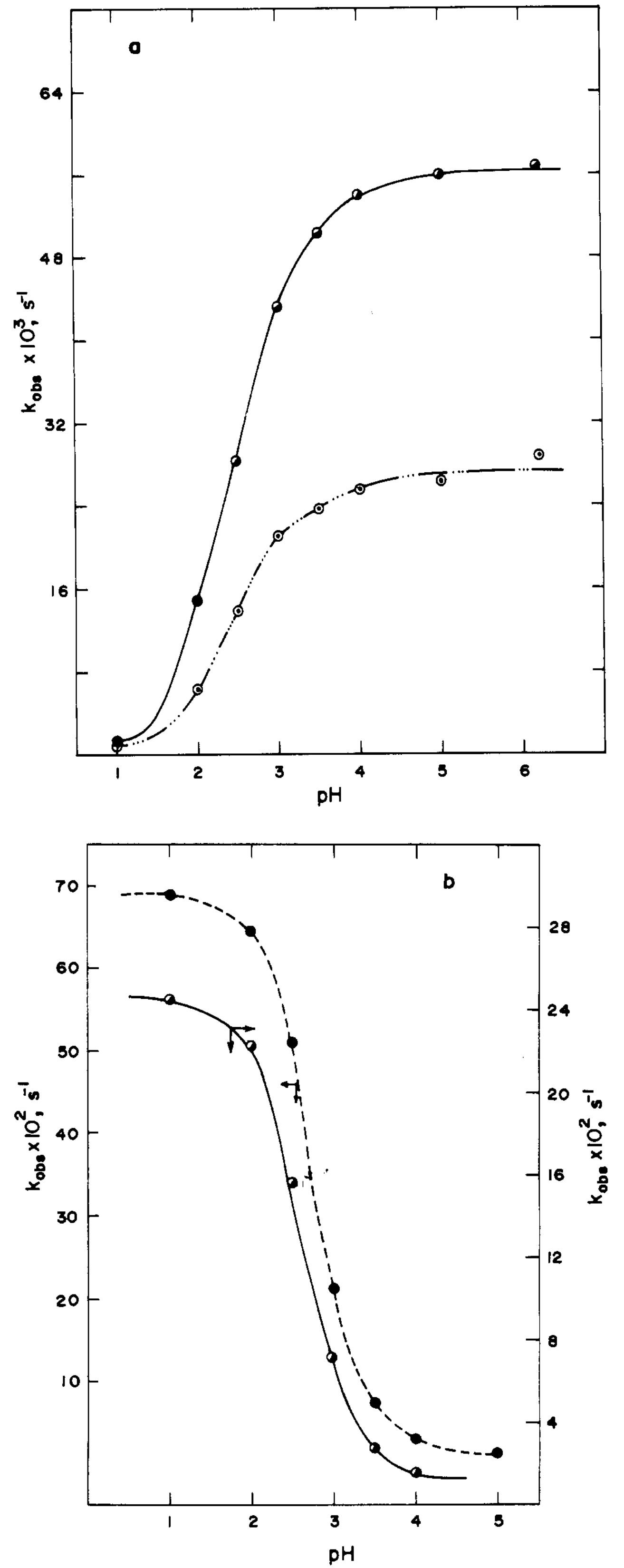

Figure 5. (a) Plot of k_{obs} versus pH for the complexes $[Co(bpy)(en)(gly)](ClO_4)_2$ (—) and $[Co(bpy)(pn)(gly)](ClO_4)_2$ (-···-) in spectrometric kinetics. (b) Plot of k_{obs} versus pH for the complexes $[Co(bpy)(en)(ala)](ClO_4)_2$ (---) and $[Co(bpy)(pn)(ala)](ClO_4)_2$ (—) in flash photolysis.

the case of the carboxylate complexes containing bipyridine, the second high-energy d–d band was masked by the intraligand transition seen for coordinated bipyridine ligands. When only one bipyridyl ligand is coordinated to the metal ion, the molar extinction coefficient for **2–5** is 12 000 M^{-1} cm^{-1} at 310 nm whereas

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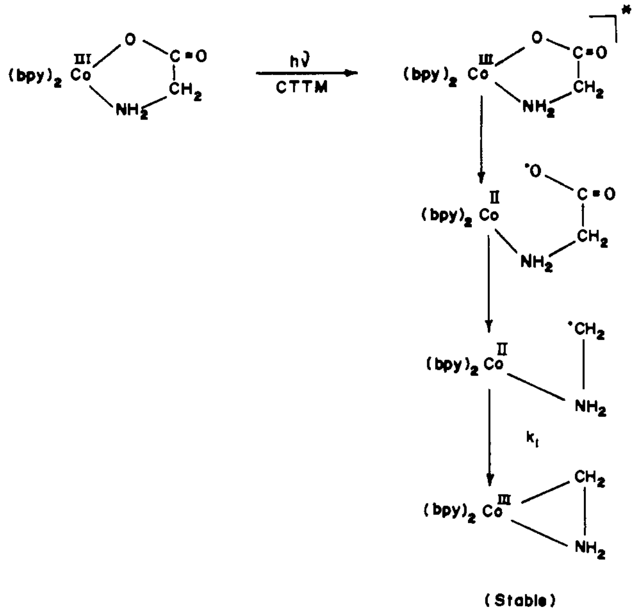
Table II. First-Order Rate Constants for the Formation and Decay of the Organocobalt Complexes in Aqueous Medium

complex	k	rate constant value, s^{-1} pH = 1	pH = 2	pH = 3	pH = 4	pH = 5	pH = 6.2
$[Co(bpy)_2gly](ClO_4)_2 \cdot H_2O$	$10^{-3}k_1$	3.88	4.08	4.16	3.90	3.98	3.99
	k_2	*a*	*a*	*a*	*a*	*a*	*a*
$[Co(bpy)(en)(gly)](ClO_4)_2$	$10^{-3}k_1$	3.95	4.09	4.12	4.84	3.82	4.14
	10^3k_2	1.29	14.77	43.74	54.15	56.05	56.83
$[Co(bpy)(pn)(gly)](ClO_4)_2$	$10^{-3}k_1$	3.86	3.89	3.80	4.04	3.81	3.57
	10^3k_2	1.29	6.45	21.27	25.57	27.27	28.72
$[Co(bpy)(en)(ala)](ClO_4)_2$	$10^{-3}k_1$	4.12	4.05	4.37	4.14	3.98	3.94
	10^2k_2	69.11	64.65	20.13	3.24	1.14	*a*
$[Co(bpy)(pn)(ala)](ClO_4)_2$	$10^{-3}k_1$	4.08	4.40	4.08	4.05	3.70	4.17
	10^2k_2	24.49	22.29	7.25	1.74	*a*	*a*

[a] No decay is observed.

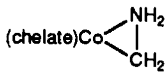
for **1** it is found to be 24 000 $M^{-1}\ cm^{-1}$ at the same wavelength. The electronic spectra of all the five complexes do not change in solution when the pH was varied from 0 to 6.

Scheme I



Formation of Cobalt(III)-Alkyl Complexes by Intramolecular Oxidation of the Cobalt(II) Center. On irradiation in the charge-transfer region, the cobalt(III)-amino acid complexes investigated at present undergo intramolecular electron transfer from ligand to metal to give an aminoalkanecarboxylato free radical coordinated to the cobalt(II) ion. The removal of an electron from the aminoalkanecarboxylate group leads to the loss of carbon dioxide with simultaneous delocalization of the unpaired electron in the remaining ligand part to give an aminoalkyl radical. The analysis of the kinetics of the transient produced on laser flash photolysis shows a clean first-order reaction. In addition to this, the product formed is the cobalt(III)-alkyl complex, as determined from the absorption spectra of the transients and from the steady photolysis results.[13] The rate constants observed for the formation of the cobalt(III)-alkyl complexes are independent of hydrogen ion concentration. The reaction between the coordinated oxidized ligand radical and the cobalt(II) complexes has not been observed prior to this study. In many biological reactions involving vitamin B_{12}, the occurrence of such a reaction is proposed. Formation of a cobalt(III)-carbon bond has been proposed[2,14,15] for the redox photolysis of $[Co(NH_3)_4C_2O_4]^+$, $[Co(en)_2C_2O_4]^+$, $[Co(NH_3)_5O_2CH]^{2+}$, and $[Co(en)_2(gly)]^{2+}$ by an intramolecular pathway. The reaction between a cobalt(II) complex and an alkyl free radical has negligibly small activation enthalpy, and it is known that the rate constants for a number of reactions between alkyl radicals and cobalt(II) complexes are in the order of 10^7 $M^{-1}\ s^{-1}$. Meyerstein et al.[16,17] have studied the intermolecular reactions of various cobalt(II) complexes with free radicals produced pulse radiolytically which lead to the formation of organocobalt complexes. Espenson et al.[5,18] have reported some novel synthetic methods for preparing cobalt(III)-alkyl complexes by intermolecular reactions between photochemically generated alkyl radicals and cobalt(II) macrocyclic complexes. The formation of an organocobalt complex either as a stable product or as an intermediate with the result of the reaction of carbon-centered radicals with cobalt(II) species seems to be a typical reaction. It may be mentioned that the aminomethyl ligand is found to react with cobalt(II) complexes similar to the way molecular oxygen reacts to give three-membered-ring complexes.[10]


mononuclear superoxo dioxygen adduct


organocobalt complex

A crystal structure study[13] of the complexes shows the structural analogy between the molecular oxygen adduct and the (aminomethyl)cobalt compound. Furthermore, O_2^- is isoelectronic with CH_2NH_2, which explains the apparent similarity in the reactivity and structure of the products formed. Reactions of this kind have also been reported in the photolysis of malonato complexes[19] of Mn(III) and complexes of Cu(II) with carboxylic acids or amino acids.[20]

In the case of the bis(bipyridine)cobalt(III) complex, the alkyl complex formed on photolysis is stable, which is due to the nature of the bipyridyl ligands, which are known to facilitate stabilization of the cobalt-carbon σ-bonds.[21] The resulting organocobalt complex possesses one aminomethyl and two bipyridine ligands,

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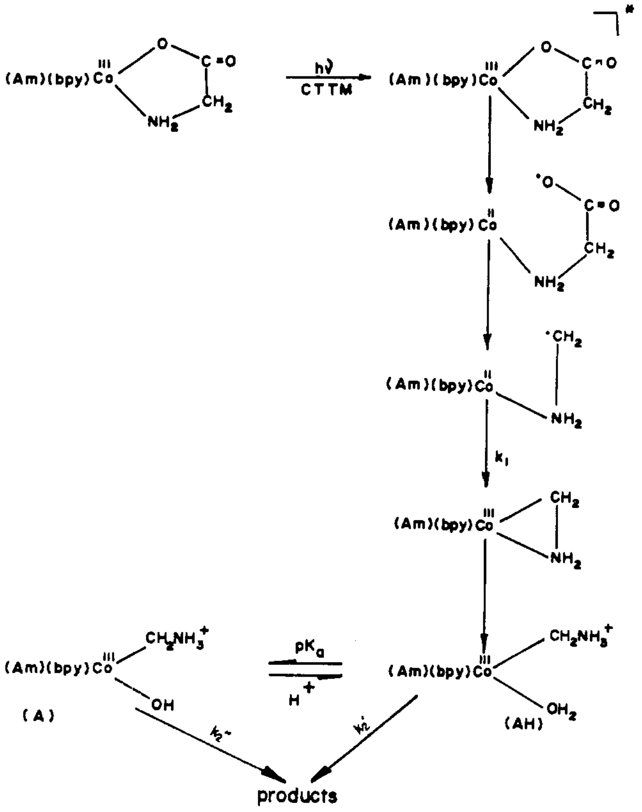
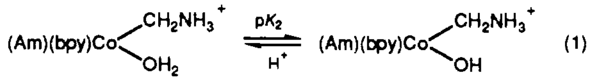
forming a three-membered ring and two five-membered rings, respectively, with the cobalt center. It may be mentioned that among the metal chelates the size of the rings containing a metal is in general five or six membered. The three-membered-ring structure observed in the present case is not common for cobalt(III) complexes. Compounds of other metals with similar group have been prepared,[22,23] which are regarded as π-complexes with the methyliminium ion, $CH_2{=}NH_2^+$, or its derivatives. Organocobalt compounds with a three-membered ring have recently been isolated[24,25] as crystalline solids by the photodecarboxylation of complexes containing ligands such as 1,10-phenanthroline, ethylenediaminetetraacetic acid, *N,N*-bis(2-aminoethyl)glycinate, and diethylenetriamine-1-acetate. The mechanism of photoredox reaction of the (glycinato) bis(bipyridine)cobalt(III) complex is represented by Scheme I. This scheme does not include the deactivation of the excited states back to the ground state, which must be an important process as demonstrated by less than unity quantum yields observed for cobaltous ion formation.

When the bipyridine ligands are replaced by ethylenediamine, the organocobalt complex formed photochemically is unstable and undergoes ligand labilization reactions. It is not possible to isolate the complex even at low temperature. Since the photoredox reaction of complex **1** is well understood with the isolation of the product and the spectrum of the transient obtained in the flash photolysis experiment is consistent with the stable product formed, the interpretation of the photochemical behavior of the amino acid complexes **2–5** is provided with reference to **1**. In the case of the complexes **2–5**, when one of the bipyridine ligands is replaced by a diamine, flash photolysis in aqueous solution leads to the formation of a species which is also not stable and undergoes further reaction. Stable alkyl complexes of the type $Co(bpy)_2R_2^+$ (where R = C_2H_5, CH_3, benzyl) are known, which again confirms[26] that the stability of the cobalt(III)–alkyl complexes is enhanced by the presence of bipyridine ligand compared to the diamine ligands. The spectra of the transients produced on flash photolysis of the complexes at 1 ms show a maximum around 420 nm, which is known to be a characteristic feature[2,25] for the cobalt(III)–alkyl complexes and is assigned as a metal to ligand charge-transfer band (Co–C MLCT).[27]

Reactions of Cobalt(III)–Alkyl Complexes in Aqueous Medium. Except in the case of $[Co(bpy)_2(gly)]^{2+}$, the organocobalt complexes produced photochemically undergo decomposition in the range 1 < pH < 6.2, which could be monitored by a flash kinetic spectrometer or by a UV–visible spectrophotometer. In acidic solutions at pH < 2, three consecutive reactions are observed in the case of complexes containing glycine. Decomposition of the organocobalt complexes obeys first-order kinetics, and the rate constants depend upon the pH of the medium. A plot of k_{obs} versus pH shows an abrupt increase in the rate constant between pH 3 and 4, which represents the pK_a for the water coordinated to the metal center.

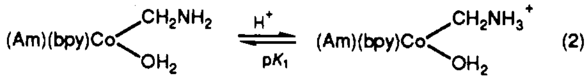
Scheme II





$$(\mathrm{Am})(\mathrm{bpy})\mathrm{Co}\begin{matrix}\mathrm{CH_2NH_3}^+\\ \mathrm{OH_2}\end{matrix} \underset{\mathrm{H^+}}{\overset{\mathrm{p}K_2}{\rightleftharpoons}} (\mathrm{Am})(\mathrm{bpy})\mathrm{Co}\begin{matrix}\mathrm{CH_2NH_3}^+\\ \mathrm{OH}\end{matrix} \qquad (1)$$

The observed rate constants for the decomposition of cobalt(III)–alkyl complexes are related to the fraction of alkyl complexes f_A and f_{AH} present in the solution as $k_{obs} = f_{AH}k_{AH} + f_Ak_A$, as shown in Figure 5. The protonation reactions of organocobalt(III) complexes are in general complicated and could occur either at the metal center, at the alkyl ligand, at the equatorial ligands, or at the axial base ligand. The pK_a values of the ligands coordinated through various atoms decrease[14,28–30] when they are coordinated to a cobalt(III) center. The pK_a value observed in the present study cannot be assigned to the protonation of the coordinated alkylamines represented by reaction 2, since the pK_a value for the C-coordinated alkylamines should be greater than that of the uncoordinated alkylamines (pK_a = 10.66).[28] It is surprising that the pK_a of the water molecule coordinated to a cobalt(III) complex is smaller by 3 orders of magnitude as compared to the aquo amine complexes of cobalt(III). It appears likely that a concerted ionization process producing a five-membered chelate ring in which $CH_2NH_3^+$ is hydrogen bonded to the adjacent OH^- ion occurs in the reaction.



$$(\mathrm{Am})(\mathrm{bpy})\mathrm{Co}\begin{matrix}\mathrm{CH_2NH_2}\\ \mathrm{OH_2}\end{matrix} \underset{\mathrm{p}K_1}{\overset{\mathrm{H^+}}{\rightleftharpoons}} (\mathrm{Am})(\mathrm{bpy})\mathrm{Co}\begin{matrix}\mathrm{CH_2NH_3}^+\\ \mathrm{OH_2}\end{matrix} \qquad (2)$$

On the basis of the above arguments, a general mechanism is proposed as shown in Scheme II for the formation and decay of the organocobalt complexes on the flash and steady photolysis of mono(bipyridine)cobalt(III) complexes containing glycine.

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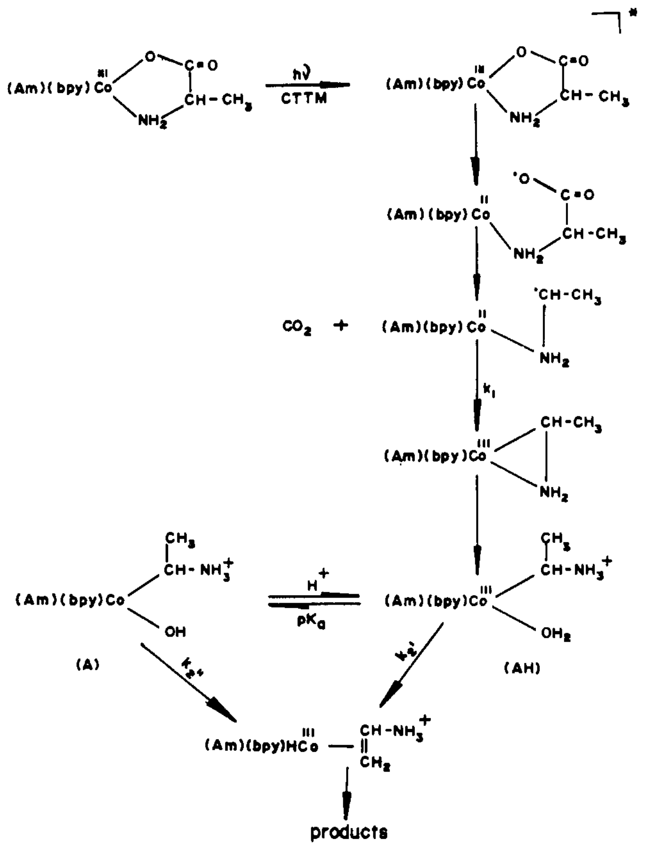
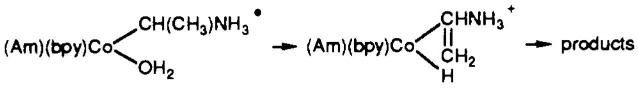
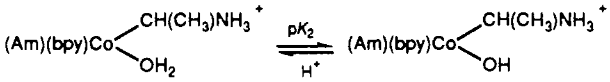
Scheme III



In the case of alanine-coordinated complex ions **3** and **5** the decomposition of the alkyl complex (bpy)(Am)Co–CH(CH$_3$)NH$_3^+$ produced photochemically obeys first-order kinetics and the presence of methyl group on the α-carbon atom of the amino acid alters the nature of the decomposition, which differs from that for the glycine complex (bpy)(Am)CoCH$_2$NH$_3^+$:



Hydride transfer from a β-carbon to a metal is well-known in aqueous medium.[31] The rate constant for the decomposition of (bpy)(Am)Co–CH(CH$_3$)NH$_3^+$ as a function of pH (Figure 5b) indicates a pK_a around 2.6, which is assigned to the dissociation of coordinated water (reaction 3). A general mechanism (Scheme III) is proposed for the formation and decay of the organocobalt complexes formed from cobalt(III)–bipyridine complexes containing α-alanine.

 (3)

Cobalt–carbon bond stability has been studied[4,16,32] by generating the cobalt(III)–alkyl complexes, by the reaction of the pulse radiolytically produced free radicals such as $^\bullet$CH$_2$OH, $^\bullet$CH$_2$CHO, $^\bullet$CH(CH$_3$)OH, $^\bullet$CH(OH)CH$_2$OH, and $^\bullet$CH$_2$COCH$_3$, and looking at their decomposition. In the present study the stability of the cobalt–carbon bond is studied by producing aminoalkyl radicals photochemically, which is more difficult to generate in pulse radiolysis experiments. The present study illustrates the possibilities for further investigation of the products formed and the mechanistic details of the reactions of unstable organocobalt complexes using different amino acids and related biologically important ligands which could provide clues to vitamin B$_{12}$ metabolism.

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Predictions and Methods of Separation of Racemic Bidentate Ligands via Stereoselective Ligand Exchange Reactions

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The technique of molecular mechanics has been applied to the prediction of isomer distributions of several complexes of chiral quadridentate amine ligands in conjunction with some optically active bidentate substrates. Specifically, the systems reported comprise the cobalt(III) and nickel(II) complexes of *N,N'*-bis[2(*S*)-2-pyrrolidinylmethyl]ethane-1,2-diamine (*S,S*-epm) and *N,N'*-bis[2(*S*)-2-pyrrolidinylmethyl]propane-1,3-diamine (*S,S*-ppm) in combination with the chiral bidentate ligands propane-1,2-diamine, (pn) 2-pyrrolidinylmethanamine (pam), and alanine (ala). Agreement between all predicted and observed isomer ratios was within 5%. The experimentally determined enantiomer ratios were as follows: [Co(*S,S*-ppm)(pn)]$^{3+}$, 49/51 *R*-pn/*S*-pn; [Ni(*S,S*-ppm)(pn)]$^{2+}$, 57/43 *R*-pn/*S*-pn; [Ni(*S,S*-ppm)(pam)]$^{2+}$, 44/56 *R*-pam/*S*-pam; [Ni(*S,S*-epm)(pn)]$^{2+}$, 43/57 *R*-pn/*S*-pn; [Ni(*S,S*-epm)(pam)]$^{2+}$, 70/30 *R*-pam/*S*-pam. Various experimental methods are reported for the determination of chiral separation.

Introduction

Many different approaches may be adopted in the pursuit of optically pure reagents. If direct synthetic methods such as asymmetric syntheses cannot be performed, then enantiomeric separation of racemic mixtures must be undertaken. This approach may take several forms, including fractional crystallization of diastereomers (with optically pure counterions),[1] conglomerate crystallization,[2] and various forms of chromatographic separation incorporating both chiral mobile and stationary phases.[3]

Separation of racemic mixtures based on stereoselective ligand exchange reactions specifically involves coordination of chiral substrate molecules to a chiral matrix host.[4] The relative sta-

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