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Cobalt(III) complexes of unsaturated carboxylic acids: synthesis, characterization, and photochemical studies in aqueous medium

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Abstract Cobalt(III) ammine complexes coordinated to carboxylic acids are classic examples showing photoredox reactions originating from the ligand to metal charge transfer excited states. Cobalt(III) pentaammine complexes coordinated to unsaturated carboxylic acids as ligands were synthesized and characterized by spectroscopic methods. The photolysis of these complexes produces a carboxylate free radical. This free radical undergoes further transformation to form organic photoproducts. The organic photoproducts were characterized by spectroscopic methods. The nature of the decomposition products from the organic photoproduct was examined in detail. The quantum yields were also determined. The photochemical reactions have the potential to produce novel compounds from the decarboxylation of unsaturated acids, which shows interesting reaction pathways.

Keywords Photolysis · Carboxylatopentaamminecobalt(III) complex · Ligand to metal charge transfer · Carboxylic acid

Introduction

Cobalt(III) complexes undergo redox reactions from the charge transfer to metal (LMCT) excited states, leading to the reduction of the metal center and the

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$$RCOOCo^{III}L_5 \xrightarrow[254\text{nm};\ H_3O^+]{h\nu} RCOO^{\bullet}\ CoL_5$$

$$RCOO^{\bullet}\ CoL_5 \xrightarrow{\text{solvent}} RCOO^{\bullet} + SCo^{II}L_5$$

$$RCOO^{\bullet} \longrightarrow R^{\bullet} + CO_2$$

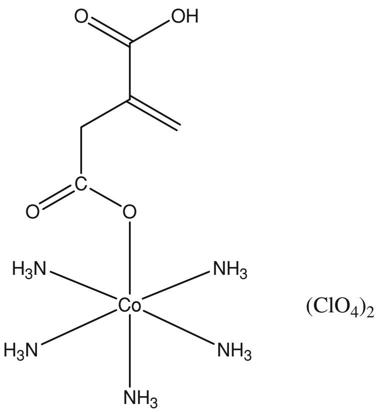
$$R^{\bullet} \longrightarrow \text{Products}$$

Scheme 1 Mechanism for the photoredox reaction of carboxylatopentaamminecobalt(III) complex

corresponding oxidation of ligands on excitation with ultraviolet and visible light [1–4]. The general reaction mechanism for the photochemistry of carboxylatopentaamminecobalt(III) is shown in Scheme 1 [5–8].

Earlier studies have concentrated on these photochemical reactions for exploring the nature of products formed using amino acids and carboxylic acids as ligands [4, 9–14]. In the present investigation, the photoredox chemistry of cobalt(III) ammine complexes coordinated with unsaturated carboxylic acids such as itaconic acid and sorbic acid as ligands has been carried out with a view to elucidate the photoproducts from the photo-oxidized ligands, which may lead to the synthesis of value-added products.

The structure of the carboxylatopentaamminecobalt(III) complexes **1** and **2** is shown below:



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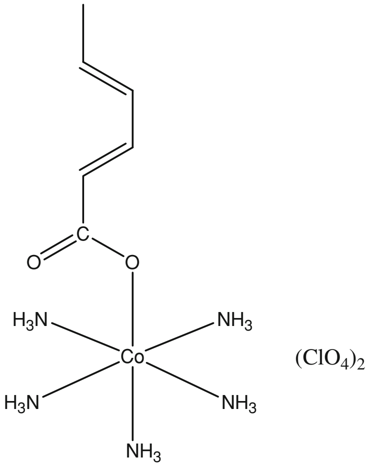

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Detailed investigations on the continuous photolysis of complexes **1** and **2** were systematically carried out. The nature of the photochemically formed $R^{\bullet}$ radical of the complex is of particular interest [where $R^{\bullet}$ for complex **1**; HOOC–C(=CH_2)–

$CH_2^{\bullet}$ and for complex **2**; CH_3–CH=CH–CH=$CH^{\bullet}$]. The effect of the substituent R in the carboxylic acid ligand, the quantum yield of product formation, the identification of the $R^{\bullet}$ radical, and its subsequent behavior are important in order to be able to understand the nature of the primary processes occurring in the photochemistry of the cobalt(III) carboxylato complexes.

Experimental

Materials and methods

Cobaltous nitrate hexahydrate, acetone, diethyl ether, perchloric acid (70 %), and liquid ammonia were purchased from Merck Chemicals. Itaconic acid and sorbic acid used in this investigation were obtained from Aldrich Chemicals. Dowex 50W-X4 cation exchange resin (200–400 mesh) was purchased from Sigma Chemicals. All other reagents used in this investigation were of laboratory grade.

The absorption spectra were recorded using a Hewlett-Packard Model-8452A UV–Visible diode-array spectrophotometer. The fluorescence spectra were recorded using a Perkin-Elmer LS-5B luminescence spectrometer interfaced with a PC via an RS-232C interface. The infrared spectra were recorded in a Perkin Elmer Model-783 spectrophotometer in the spectral range 4,000–400 cm^{-1}, using KBr pellets. NMR spectra were recorded using JEOL GSX400 and Bruker 300-MHz spectrometers. Gas chromatography/mass spectrometry (GC-Mass) spectra of photoproducts were recorded in a Shimadzu QP-5000 GC/MS instrument using a DB-1 non-polar column, and a Perkin-Elmer AutoSystem XL Gas TurboMass mass spectrometer (EI, 70 eV), with helium as the carrier gas at a flow rate of 1 ml/min. The elemental analyses were carried out by using a Carlo Erba Model 1106 elemental analyzer performed at the catalysis division, IIT, Chennai.

Fluorescence lifetime measurements were carried out in a picosecond laser-excited, time-correlated, single-photon counting (TCSPC) spectrometer. The excitation source is the tunable Ti-sapphire laser (Tsunami, Spectra Physics, USA). The laser pulse (pulse width of <2 ps and repetition rate of 82 MHz) was derived from the frequency-doubled output (532 nm) of the locked mode, which is based upon the regeneratively initiated technique (Spectra Physics, USA). The Ti-sapphire rod is refringent, and uninterrupted tuning is achieved when the rod is aligned coplanar with the polarization of the electric field within the cavity. The tuning range is 840–1,000 nm. A polarized picosecond laser pulse at 295 nm excites the sample. The fluorescence emission was monitored at right angles to the excitation path and the first photon was detected by an MCP-PMT detector (Hamamatsu-R 3809U). When the first excitation pulse occurs, a synchronization pulse triggers the charging of the capacitor in the TAC through the discriminator. The voltage on the capacitor increases linearly until a stop timing pulse is detected on repeating the start–stop cycle. A histogram representative of the fluorescence decay is obtained, which is further analyzed using the IBH software.

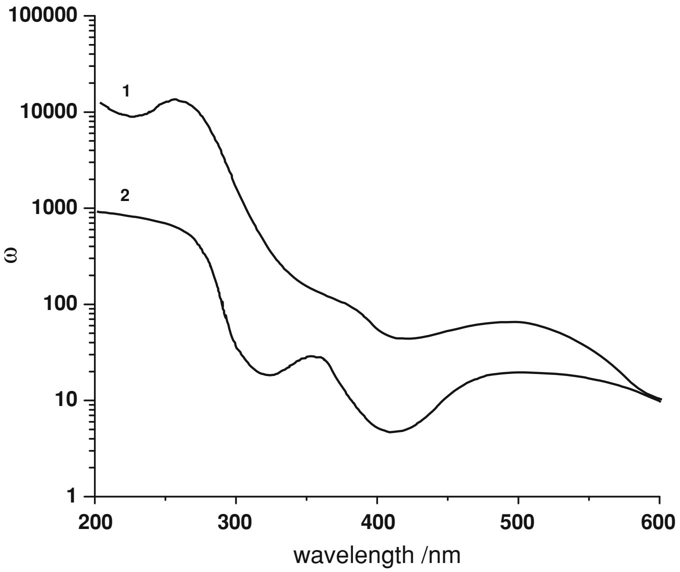


Fig. 1 Electronic spectra of complexes **1** $[Co(NH_3)_5It](ClO_4)_2$ and **2** $[Co(NH_3)_5SR](ClO_4)_2$

Synthesis of carboxylatopentaamminecobalt(III) complexes **1** and **2**

The complexes employed in this investigation were prepared by following the general procedure reported in the literature [9–11, 15–17], and, in some cases, a modified procedure was adopted. The general procedure for the synthesis of carboxylatopentaamminecobalt(III) complexes involves the treatment of 20 mol of the carboxylic acids (itaconic acid and sorbic acid) with 1.75 N sodium hydroxide (10 ml), heating at 80 °C for 10 min, and then filtering. The pH of the filtrate was adjusted to <6.5 and the filtrate was added to a solution of aquapentaamminecobalt(III) perchlorate (1.0 g) in hot water (2 ml). The mixture was kept at 75–80 °C for ~4 h, then was cooled, and then added to a large separating funnel containing a mixture of water (5 ml), 70 % $HClO_4$(25 ml), and ether (150 ml). The unreacted parent carboxylic acid becomes dissolved in the ether layer on shaking. On standing for 30 min, the layers separated and the aqueous layer was extracted again with 200 ml of ether. The solution was cooled and then added to precooled 70 % perchloric acid (15 ml), and the mixture was allowed to stand overnight at −10 °C. The precipitated complex was filtered off, washed with ice cold water, dissolved in a minimum quantity of hot water (90 °C), and the solution was cooled to 0 °C. The recrystallized complex was then filtered off and dried in vacuum at 35 °C for 10 h.

The parent carboxylic acid compound is present as an impurity which had to be removed, after several recrystallizations. The purity of the sorbatopentaamminecobalt(III) complex was acceptable when $\in_{502}$ had a value in the 65–70 M^{-1} cm^{-1}

range. The above procedure with slight modification is used for the itaconatopentaamminecobalt(III) complex. In the case of itaconic acid, since two carboxylic acid groups are present, in order to avoid the formation of bidentate coordination, an excess amount of itaconic acid was used and the pH of the medium was maintained at 6.5. The complex was recrystallized from distilled water at 60 °C. Recrystallization was repeated until the measured molar absorptivity remains unchanged ($\lambda_{\max}$ 500 nm; $\in_{500} = 63\ M^{-1}\ cm^{-1}$). The yields tend to be small, often <20 %. The presence of vinyl group in the unsaturated carboxylic acids leads to the formation of polymers at higher temperatures. In order to avoid the polymerization of free acid, the synthesis of these complexes was carried out under dark conditions and at a moderate temperature of 70–80 °C. (*Caution:* perchlorate is a potentially highly dangerous oxidant in the presence of organic material; hence, care should be taken in the handling of these complexes).

Continuous photolysis

Continuous photolysis experiments for complexes **1** and **2** were performed at the intense ligand to metal charge transfer bands using a 254-nm low-pressure mercury pen-ray lamp (Ultraviolet Products Inc) in acidic aqueous medium (pH = 1) at 5 °C. The apparatus used for photolysis is shown as supplementary material S1. Light intensities were measured using ferrioxalate actinometry [18–20].

During photolysis, the electronic absorption spectral changes were recorded in the UV–visible region for definite intervals of time. The formation of cobalt(II) was confirmed by analyzing the reduced metal ions spectrophotometrically on complexation with thiocyanate ions (molar absorptivity at 625 nm for $[Co(NCS)_4]^{2-} \approx 1{,}868\ M^{-1}\ cm^{-1}$).

Photolysis of complexes **1** and **2** in acidic medium liberates ammonia, which is dissolved in the photolysis solution. The pH of the photolysed solution increased after photolysis due to the presence of ammonia in the solution. To confirm the presence of ammonia, the solution was photolysed for about 75 % decomposition of the complex and, through this solution, dry nitrogen was passed and the resulting gas was passed through Nessler's reagent. During this process, a few pellets of sodium hydroxide were added to the photolysed solution. Ammonia was liberated and a red–brown color developed in the Nessler's reagent. This test confirmed the liberation of ammonia during photolysis.

After the completion of photolysis, following separation of the oxidized photoproduct from cobalt(II) ions, the photolysed solution was passed through a column loaded with a cation exchange resin (Dowex 50W-X4, 200–400 mesh). The column temperature was maintained at 5 °C by circulating cold water and the organic photoproducts in the column were eluted with cold water at 5 °C in the dark. Then, the solution was concentrated and evaporated to dryness by means of a freeze-drying.

Results and discussion

Of the carboxylatopentaamminecobalt(III) complexes used in the present investigation, complex **1** shows two low-intensity absorption bands in the visible region (500 nm, $\varepsilon = 62.89\ \mathrm{M^{-1}\ cm^{-1}}$, d–d transition) and one in the near-ultraviolet region (350 nm, $\varepsilon = 61.88\ \mathrm{M^{-1}\ cm^{-1}}$, CT transition), which are illustrated in Fig. 1. These two low-intensity bands are assigned as the spin-allowed ligand field transitions, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$, and the intense charge transfer band in the ultraviolet region as the charge transfer transition. In the case of complex **2** [501 nm, $\varepsilon = 61.94\ \mathrm{M^{-1}\ cm^{-1}}$, d–d transition, and 350 (sh). 275 (sh)nm, CT transition], the charge transfer absorption is shifted to the longer wavelength region due to the presence of conjugation in the carboxylic acid.

IR (KBr, $\mathrm{cm^{-1}}$): 1,700 (–C=O stretching of free –COOH group), 1,600 (–C=O stretching of coordinated $–\mathrm{COO^-}$ group). For complex **1**: 1,580 (–C=O stretching of

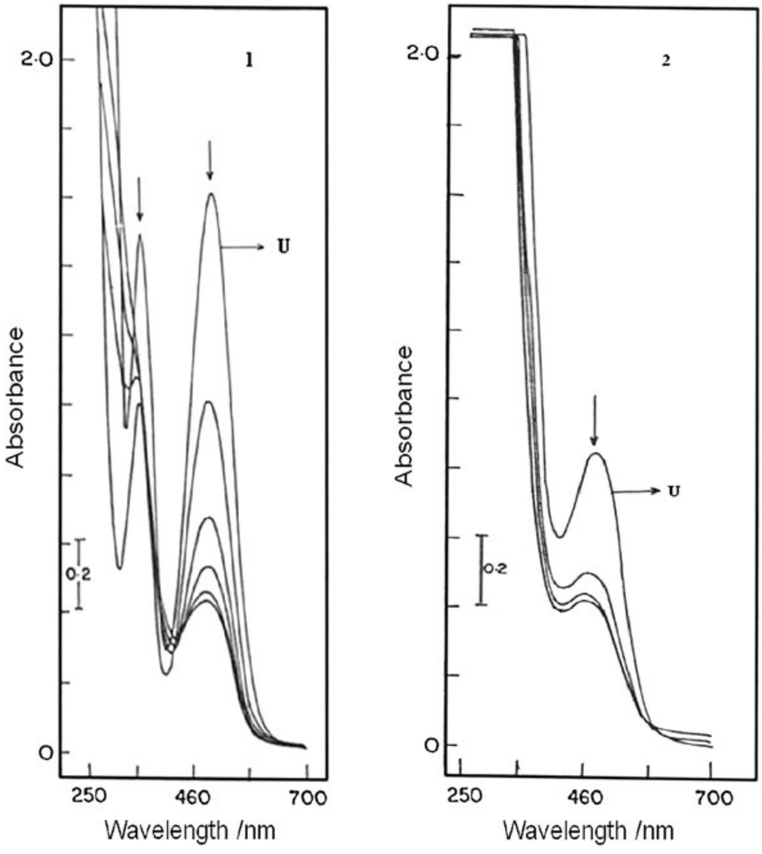


Fig. 2 Electronic spectral changes accompanying 254-nm photolysis of complexes **1** $[\mathrm{Co(NH_3)_5It](ClO_4)_2}$ and **2** $[\mathrm{Co(NH_3)_5SR](ClO_4)_2}$ in acidic aqueous solution at 5 °C. *U* unphotolysed solution

Table 1 Quantum yield of cobalt(II) ion formation for carboxylatopentaamminecobalt(III) complexes

Complex	ϕ_{Co}^{2+}	
	Graphical	Experimental
$[Co(NH_3)_5It]\ (ClO_4)_2$	0.49 ± 0.02	0.50 ± 0.02
$[Co(NH_3)_5SR]\ (ClO_4)_2$	0.19 ± 0.02	0.19 ± 0.02

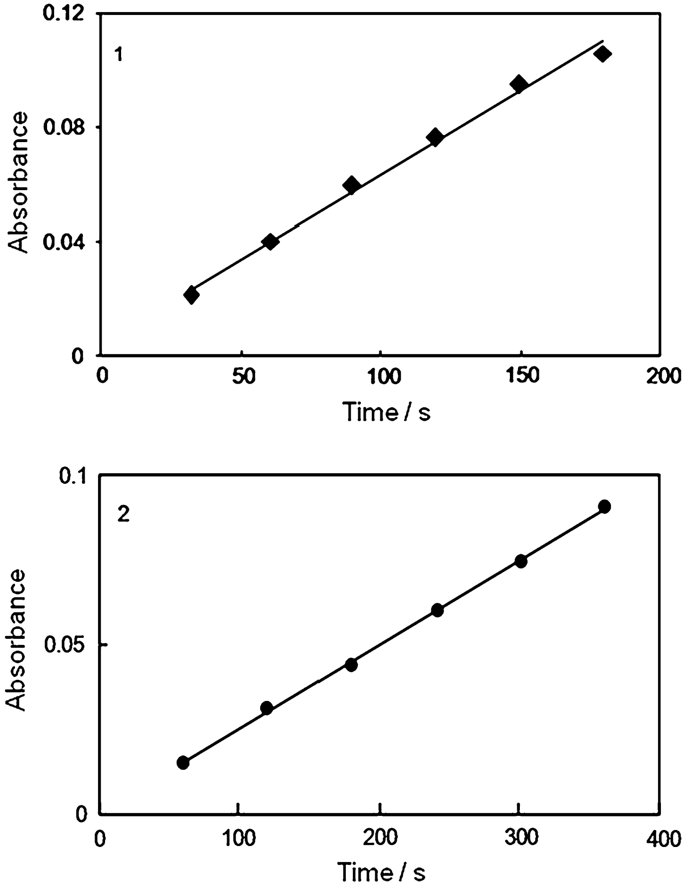


Fig. 3 Formation of cobaltous ions on the photolysis of carboxylatopentaamminecobalt(III) complexes (change of absorbance at 625 nm vs. time of photolysis): **1** $[Co(NH_3)_5It]^{2+}$ ions and **2** $[Co(NH_3)_5SR]^{2+}$ ions

coordinated –COO$^-$ group), 1,700 (uncoordinated carboxylic acid). For complex **2**: 1,618 (–C=O asymmetric stretching of coordinated –COO$^-$ group), 1,396 (–C=O symmetric stretching of coordinated –COO$^-$ group), 1,100 (stretching mode of ClO4–).

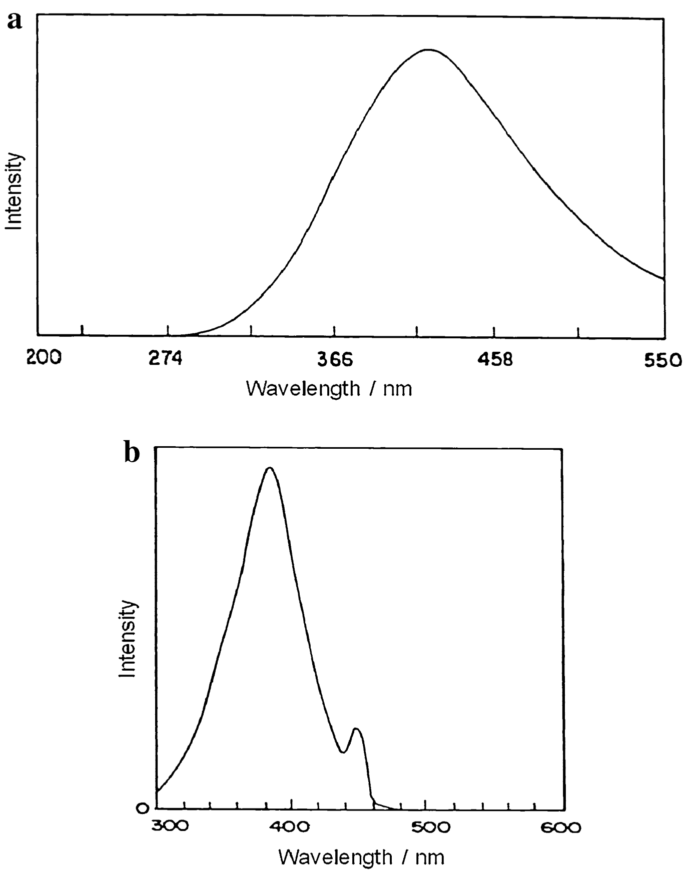


Fig. 4 The emission spectrum (**a**) and the excitation spectrum (**b**) of organic photoproduct obtained from $[Co(NH_3)_5It]^{2+}$ ions excited at 290 nm in water

^{1}H-NMR (300 MHz, D_2O, δ/ppm) for complex **1**: 3.9 (2H, s, $–CH_2$), 6.04, 6.42 (1H, s, two olefinic protons) and also one of the acid protons is exchanged with solvent D_2O. ^{1}H-NMR (300 MHz, acetone d_6, δ/ppm) for complex **2**: 1.9 (3H, s, CH_3), 7.12, 6.67 (1H, m, two olefinic protons).

Elemental analysis for complex **1**: anal. calcd. for $C_5H_{20}N_5O_4$: C, 12.68; H, 4.23; N, 14.79; found: C, 12.48; H, 4.13; N, 14.47. Elemental analysis for complex **2**: anal. calcd. for $C_6H_{22}N_5O_2$: C, 15.82; H, 4.83; N, 15.38; found: C, 15.42; H, 4.78; N, 15.32.

Continuous photolysis of cobalt ammine complexes

Most of the ultraviolet photochemistry of cobalt(III) complexes arising from the irradiation of ligand-to-metal charge transfer bands at 254 nm results predominantly in leading to photoreduction, with the formation of cobalt(II) ions and the oxidized free radical of the ligand [21–23]. Carboxylatopentaamminecobalt(III) ions, on

Table 2 The relative mass peak intensity of the photoproducts from carboxylatopentaamminecobalt(III) complexes

Photoproduct from **1** $[Co(NH_3)_5It](ClO_4)_2$		Photoproduct from **2** $[Co(NH_3)_5SR](ClO_4)_2$	
Mass peak	% intensity	Mass peak	% intensity
152	3.22	324	10.50
138	4.83	309	4.20
124	6.45	295	2.52
115	3.27	285	2.31
111	14.51	283	9.24
97	20.96	282	19.33
83	25.80	281	71.00
69	33.87	268	3.15
55	83.87	267	6.09
41	100.00	265	15.55
		251	5.04
		249	9.87
		222	1.68
		221	7.77
		207	13.86
		177	6.09
		147	34.87
		133	5.88
		74	9.45
		73	100.00

excitation of the carboxylato-to-cobalt(III) charge transfer bands, lead to carboxylate radical (RCOO$^{\bullet}$) and cobalt(II) complex [24–26] in acidic aqueous solution.

A homolytic bond fission mechanism for the charge transfer to the metal-excited state is generally proposed for the photochemical reactions of all the carboxylatopentaamminecobalt(III) complexes. This involves a one-electron transfer from the carboxylate ligand to the central cobalt(III) metal ion, leading to a reduced species producing cobalt(II) ions and oxidized ligand radicals. The typical absorption spectral changes are shown in Fig. 2. The photoproducts were analyzed by various spectral techniques.

Quantum yield of cobalt(II) ion formation

The photolysis of cobalt(III) complexes in acidic aqueous solution in the LMCT band leads to the formation of cobalt(II) ions, and the amount of cobalt(II) ions formed on photolysis was determined by Kitson's method by complexing it with ammonium thiocyanate. The quantum yield values of cobalt(II) ion formation on 254-nm irradiation of carboxylatopentaamminecobalt(III) complexes **1** and **2** are given in Table 1, and the plots of absorbance versus time are shown in Fig. 3. The

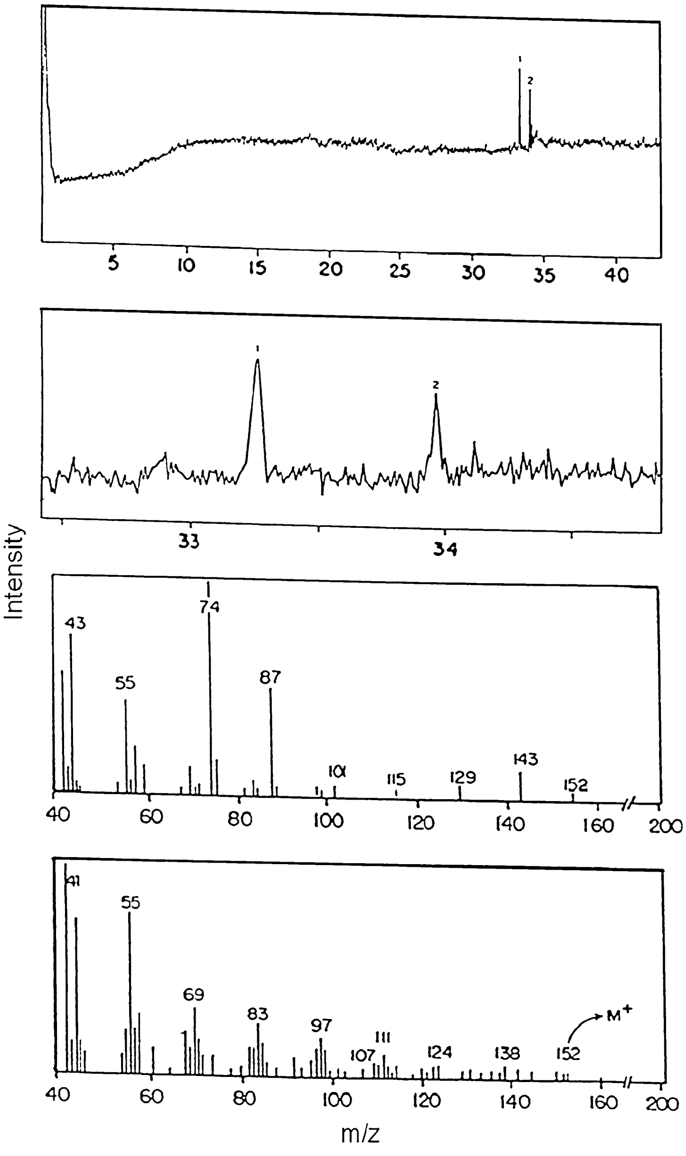


Fig. 5 The gas chromatography/mass spectrometry (GC-Mass) spectrum of organic product from $[Co(NH_3)_5It]^{2+}$ ions in methanol

linear plot observed shows that no significant secondary photolysis occurs under these conditions.

Analysis of photoproduct from complex **1**

The absorption maximum for the photoproduct is observed at 270 nm. The emission maximum observed at 420 nm is shown in Fig. 4.

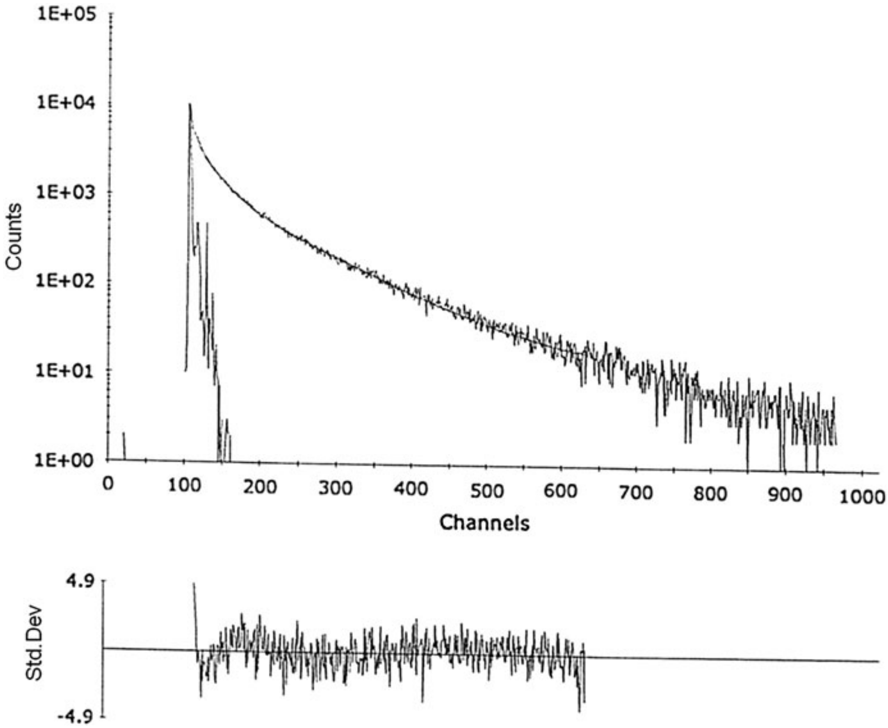


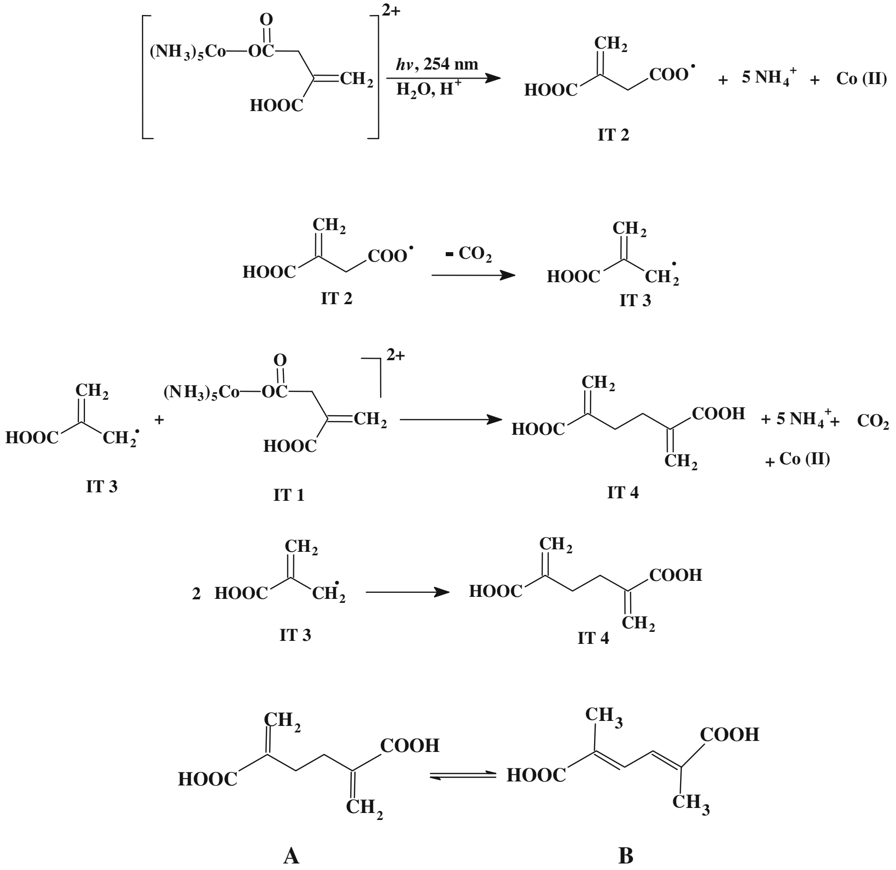
Fig. 6 The fluorescence emission decay profile of organic photoproduct excited at 375 nm

IR (KBr, cm^{-1}): 1,700 (–C=O stretching). ^{1}H NMR (300 MHz, D_2O, δ/ppm): 2.32 (–CH_2–), 5.92 (d, 44, $j = 3$ Hz) olefinic protons and acid protons are exchanged with D_2O. ^{13}C-NMR (300 MHz, D_2O, δ/ppm at 5 °C): 178 (acidic carbons), 133.48, 129.08 (olefinic carbons), and 39.4 (aliphatic carbons).

The GC-Mass spectrum of the photoproduct was recorded using methanol as the solvent, and the relative mass intensity is shown in Table 2. The GC trace of the compound shows two major compounds at retention periods (rt) of 33.28 and 33.92, as shown in Fig. 5. This indicates the presence of two major compounds in the organic photoproduct. From the GC-Mass spectra, it is confirmed that the photoproduct is a mixture of isomers. The mass spectra of the compound showed a molecular ion peak at *m*/*z* 152.

The lifetime of the emissive excited state of the compound was measured by exciting at 295 nm and monitoring the emission at 420 nm. The emission decay profile does not fit a single exponential and fits to the biexponential with lifetimes of 1.5 ± 0.1 and 5.5 ± 0.5 ns, respectively. This observation, again, supports the presence of two products that have similar character in the excited state emission. The fluorescence emission decay profile of organic photoproduct of complex **1** excited at 375 nm is shown in Fig. 6.

From the above spectral studies, a mechanism is proposed for the formation of photoproduct (IT 4), as shown in Scheme 2. The primary photoproduct A



Scheme 2 Formation of photoproduct from complex **1**

isomerizes to structure B to give a signal at *m*/*z* 138, due to the loss of $H^\bullet$ and $CH_3^\bullet$ from $M^{+\bullet}$.

From the Scheme 2, it is inferred that the luminescent photoproduct is a conjugated molecule with olefinic groups. The presence of the carbonyl absorption in the ^{13}C NMR spectrum and a band at 1,700 cm^{-1} in the IR spectrum confirms the presence of a carbonyl group. The formed photoproduct is stable at low temperature and the proton NMR spectrum of the compound at room temperature showed additional peaks, which confirm that the photoproduct had undergone decomposition.

Analysis of photoproduct from complex **2**

After continuous photolysis of complex **2**, the separated photoproduct was analyzed by the spectral methods. The organic photoproduct dissolved in methanol was analyzed by the GC-Mass spectral method. In GC, the major peak was obtained with

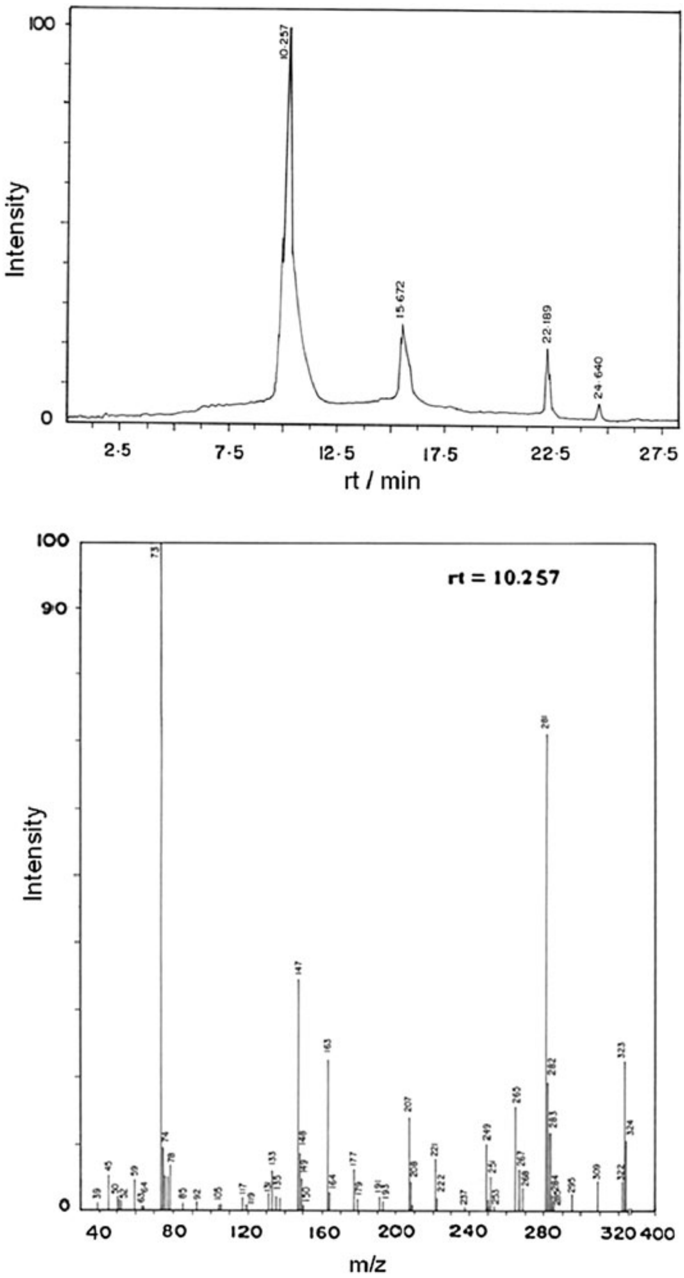
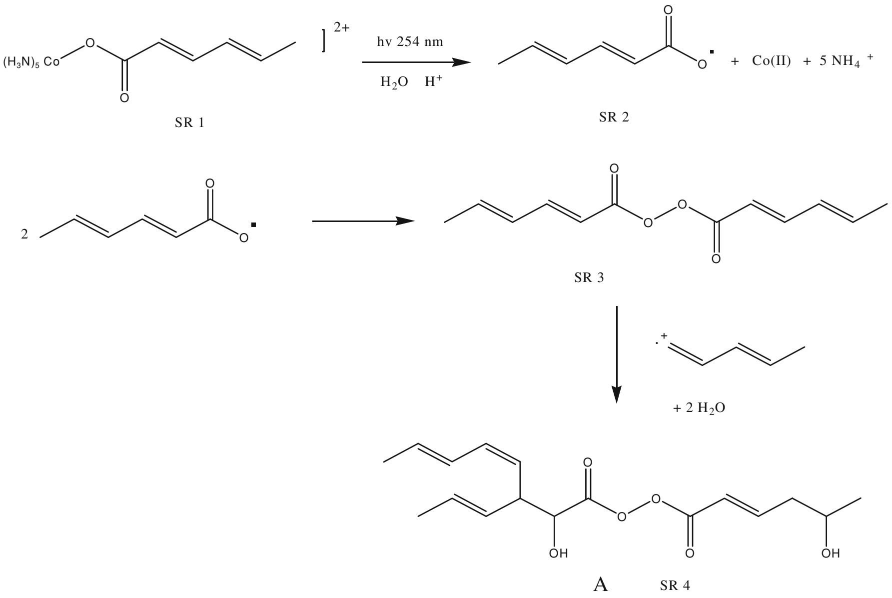


Fig. 7 The GC-Mass spectrum of organic product from $[Co(NH_3)_5SR]^{2+}$ ions in methanol

the retention period (rt) of 10.25, whereas the other peaks were of low intensity and the corresponding mass spectrum of the major peak is given in Fig. 7. In this case also, the major GC-Mass peaks are considered for detailed interpretation. The



Scheme 3 Formation of photoproduct from complex **2**

relative intensity of the mass peaks is given in Table 2 and the fragmentation schemes are given in supplementary material S2. The structure of the photoproduct was also confirmed by IR spectra and NMR spectra.

IR (KBr, cm^{-1}): 1724, 1,709 (–C=O stretching), and 1,637 (–C=C–H stretching), 1,430 (C–H bending vibration CH_3), 3,050–3,500 (C–H stretching vibrations CH_3 and O–H stretching vibrations, broad signal).

^{1}H NMR (300 MHz, D_2O, δ/ppm): 6.21–7.98 (m, olefinic protons), 1.23 and 1.87 (d, CH_3). The methylene protons and methyne protons appear as multiplets in the respective regions. ^{13}C-NMR, the compound "SR 4" shows peaks for two carbonyl carbons at δ 195.65 and 198.29. Eight olefinic carbons appear in the olefinic region separately. The methyl, methylene, and methyne carbons appear in the respective regions δ 17.57, 21.73, 23.25, 58.31, and 58.49. From the above spectral studies, the structure of the photoproduct is confirmed as SR 4. Based on the spectral analysis, Scheme 3 has been proposed for the structure of the major compound SR 4.

In Scheme 3, the two sorbato carboxyl radicals undergo dimerization reaction before the loss of carbon dioxide to form the compound SR 3. This compound abstracts $OH^\bullet$ radical from the solvent. This abstracted $OH^\bullet$ radical attacks the double bond conjugated to the carbonyl group at the α-position, thereby generating a radical in the β-carbon. The new radical abstracts CH_3–CH=CH–CH=$CH^\bullet$ radical formed from sorbatocarboxylic radical after the elimination of carbon dioxide molecules. The addition of water is subjected to the δ-carbon. The mass spectra illustrate that the addition of water takes place on the δ-carbon based on the mass unit *m*/*z* 309 signal. Hence, the proposed structure of the major compound (SR 4) "A" is named as 7,8-dioxahexadeca-4,12,14-trien-6,9-dione.

Conclusion

The photolysis of carboxylatopentaamminecobalt(III) complexes in their LMCT band results in the reduction of the cobalt(II) ions and the oxidation of ligand carboxyl radicals. This work gives evidence that the two possible mechanisms for the formation of photoproduct from carboxyl radicals depends on the nature of the coordinating ligand. In the case of complex **1**, the photoproduct is suggested to form as a result of photochemical reactions of cobalt(III) ammine complex with carboxylate ligand, showing decarboxylation of the coordinated ligand from the CTTM excited state and the resulting free radicals produce interesting photoproducts. But for complex **2**, the photoproduct was formed as the result of dimerization of carboxyl radicals. This is the first report where dimerization of the carboxyl radical has been observed.

The observation of the difference in the photoproducts formed from complexes **1** and **2** is attributed to the stabilization of the carboxyl radicals by the presence of the olefinic bonds in the neighboring carbons. Itaconic acid is a non-fluorescent compound of importance in the polymer industry as a monomer. At present, no synthetic derivative of itaconic acid is known as a fluorescent molecule. However, it has been reported more recently that a long-chain fluorescent derivative of itaconic acid has been isolated as a fungal metabolic product [27, 28]. The fluorescence spectrum of the photoproduct shows a similar spectrum of the existing metabolite.

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