Appendix
Novel photochemical reaction of itaconatopentamminecobalt(III) ion to produce a room temperature luminescent compound

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Abstract

Irradiation of itaconatopentamminecobalt(III) perchlorate complex in the ligand to metal charge transfer absorption band in aqueous solution using 254 nm radiation produced an oxidized ligand free radical, which further reacts with itaconatopentamminecobalt(III) ion and also by radical dimerisation reaction to form a compound which shows broad absorption at ~265 nm and emission at ~425 nm. The compound is identified to be a derivative of itaconic acid. The photoproduct shows two lifetimes of 1.5 ± 0.1 ns and 5.5 ± 0.5 ns indicating that the photoproduct decomposes at room temperature to give a second compound which is also luminescent. © 2001 Elsevier Science B.V. All rights reserved

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Cobalt(III) amine complexes coordinated to carboxylic acids are classic examples showing photoredox reactions originating from the ligand to metal-charge-transfer (LMCT) excited states [1,2].

\[ [[\text{NH}_4]_2 \text{Co(OCOR)}_2]^2- \rightarrow \text{Co(II)}^2+ + R + 5\text{NH}_3 + \text{CO}_2 \]

We have attempted to use this photochemical reaction for exploring the nature of the products formed using cobalt(III) complexes of amino acids [3,4] and unsaturated carboxylic acids. In this communication we report an interesting transformation of a photoproduced free radical from the itaconatopentamminecobalt(III) ion giving rise to a luminescent compound.

Iaconatopentamminecobalt(III) perchlorate. I (see [12]) was prepared by refluxing aquapentamminecobalt(III) perchlorate with an excess of the sodium salt of itaconic acid for two hours at 70 °C in aqueous solution [5,6]. The perchlorate salt of the complex precipitated on adding perchloric acid and was characterised satisfactorily by elemental analysis, IR and NMR spectral data. (Caution: all perchlorate salts are potentially explosive.

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protons at δ-5.92 (d, 4H, J = 3 Hz) and an acid proton which exchanged with D2O. The proton NMR spectrum of the compound at room temperature showed additional peaks showing that the compound had undergone decomposition. The 13C NMR spectrum obtained at 5 °C showed peaks at δ-178 for acidic carbons, olefinic carbons at δ-133.48, 129.08 and aliphatic carbons at δ-39.4. The GC-Mass spectrum of the compound shows two major compounds as shown in Fig 1(b). From the above observations it is inferred that the luminescent photoprodut is a conjugated molecule with olefinic groups. The presence of the carbonyl absorption in the 13C NMR spectrum and a band at 1700 cm⁻¹ in IR spectrum confirms the presence of a carbonyl group.

The photoprodut is suggested to form as a result of reactions of the primary photochemically produced free radical as shown in Scheme 1. Photochemical reactions of cobalt(III) ammine complexes with carboxylate ligands show decarboxylation of the coordinated ligand from the CTTM excited state and the resulting free radicals produce interesting photoproduts [7,8].

Itaconic acid is a nonfluorescent compound of importance in polymer industry as a monomer. Itaconic acid is a secondary metabolite in biological reactions [9,10]. At present no synthetic derivative of itaconic acid is known as a fluorescent molecule. However it has been reported more recently [11] that a long chain fluorescent derivative of itaconic acid has been isolated as a fungal metabolic product. The fluorescence spectrum reported for this metabolite is very similar to that observed for the photoprodut in the present investigation.

The proton NMR spectrum of the photoprodut obtained in a 400 MHz Bruker instrument using D2O as solvent and DSS as standard at 5 °C showed peaks at δ-2.22 (s, 4H) for -CH2- protons, a doublet for olefinic
In order to check the other characteristics of the photochemical product, we have estimated the lifetime of the emissive excited state of the compound by single photon counting technique by exciting at 375 nm and monitoring the emission at 430 nm. The emission decay profile does not fit to a single exponential and the bi-exponential fit with a chi square of 1.09-1.23 corresponds to lifetimes of 1.5 ± 0.1 ns and 5.5 ± 0.5 ns. This observation again confirms the presence of two products which have similar characteristics which manifest in the excited state emission behavior. The quantum yield for cobalt(II) formation in the photochemical process is determined to be 0.49 ± 0.02 using ferrosofate actinometry.

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References

[12] Supplementaries data for the complex investigated: HR NMR and elemental analyses data of N,N'-diaminopenic阳amidecobalt(III) complex the infrared spectrum showed strong C-H stretching absorption in the area of 2940-3010 cm⁻¹ N-H stretching at 3250-3400 cm⁻¹ the CH=CH absorption at 3000-3150 cm⁻¹ carboxylate anion asymmetric stretching at 1500-1620 cm⁻¹ and the coordinated perchlorate absorption at 1080-1200 cm⁻¹ H NMR data (D2O/DMSO, 400 MHz) the methylene protons appeared at δ 4.34 (s, 2H) the olefinic protons appeared at δ 6.04 (s, 1H) and δ 6.42 (s, 1H) Elemental analysis calculated for C,H,N,Co,Ni= C 11.68 H 4.43 N 14.79 Found C 11.69 H 4.03 N 14.57
[13] Hilasonic shows the following NMR spectral features: 1H NMR data a singlet at δ 3.14 for methylene protons the two singlets appeared at δ 5.89 and δ 6.6-6.7 for olefinic protons The two protons are exchanged with D2O 1H NMR data the two and carbonos appeared at δ 174.99 and δ 172.606 the two olefinic carbons appeared at δ 136.10 and δ 125.99 the aliphatic carbon at δ 39.97