Non-luminescent mixed complexes of [Ru(bpy)_3]^2+ and anionic metal complexes

R Ramaraj*
School of Chemistry, Madurai Kamaraj University,
Madurai 625 021

and

A Kira & M Kaneko*
The Institute of Physical and Chemical Research (RIKEN),
Wako, Saitama, 351-01, Japan

Received 22 April 1991; revised and accepted 12 August 1991

Mixed complexes of [Ru(bpy)_3]^2+ and anionic metal complexes ([ML]_n^m-) such as [PtCl_6]^{2-}, [Fe(CN)_6]^{4-} and [Fe(CN)_6]^{3-} were isolated. The emission from the excited [Ru(bpy)_3]^2+ was completely quenched in the solid state of the mixed complexes in contrast to the very long emission lifetime of the mixed complex of [Ru(bpy)_3]^2+ [Hg_2Cl_6]^{2-} reported before.

Recently we have isolated a new complex, [Ru(bpy)_2Cl_2]^2+[Hg_2Cl_6]^{2-} (denoted as Ru-Hg) formed from [Ru(bpy)_3]^2+ and HgCl_2. The main characteristics of [Ru(bpy)_3]^2+ are maintained in Ru-Hg, but the solubility and emission behaviour are very different. Crystalline Ru-Hg shows a single exponential emission decay with an unusual long lifetime of 1740ns at room temperature, while [Ru(bpy)_3]^2+ shows a double exponential decay with lifetimes of 975ns (73.7%) and 475ns (26.3%) .

The luminescence quenching of the excited state [Ru(bpy)_3]^2+ by [PtCl_6]^{2-}, [Fe(CN)_6]^{4-} and [Fe(CN)_6]^{3-} in solution has already been reported. With most of the anionic metal complexes, there is evidence of extensive ion pairing with [Ru(bpy)_3]^2+ in solution resulting in some static quenching of the excited states. With static quenching the emission yields decrease without appreciable changes in lifetime. The energy of the shorter wavelength emission maximum for [Ru(bpy)_3]^2+ is about 18 kK. Since the low-lying excited state energy levels of the quencher molecules ([PtCl_6]^{2-},

Experimental

Ru(bpy)_3Cl_2.H_2O was prepared by the reported procedure and commercially available purest chemicals were used for the preparation of the ion pair complexes. An aqueous solution of 50 mM [Ru(bpy)_3]^2+ (10 ml) and an aqueous solution of 100-200 mM K_2PtCl_6, K_4Fe(CN)_6 or K_3Fe(CN)_6 (10 ml) were mixed with stirring, when a precipitate was obtained immediately. The stirring was continued for another 15 min and the precipitate was filtered, washed with a small amount of cold water and dried in vacuo at 25°C.

Absorption and emission spectra were recorded on a Hitachi 320 spectrophotometer and Hitachi F-2000 fluorescence spectrophotometer respectively and IR spectra on a Shimadzu spectrophotometer (IR-27G). For emission decay measurements, a computer-controlled single-photon counting system equipped with a 1ns pulsed hydrogen lamp (10 atm hydrogen) (Hitachi-Horiba, Model NAES-1100) was used.

Results and discussion

The ion pair complex isolated from [Ru(bpy)_3]^2+ and [PtCl_6]^{2-} is yellow-orange in colour, insoluble in water and ethanol but soluble in DMF and acetonitrile. It analysed for [Ru(bpy)_3]^2+.[PtCl_6]^{2-} (denoted as Ru-Pt) (Found: C, 36.60%; H, 2.48%; N, 8.51%; Reqd: C, 36.85%; H, 2.46%; N, 8.60%). The ion pair complex isolated from [Ru(bpy)_3]^2+ and [Fe(CN)_6]^{4-} is brown in colour, fairly soluble in water, but insoluble in DMF and acetonitrile. It analysed for 2[Ru(bpy)_3]^2+.[Fe(CN)_6]^{4-}.8H_2O (denoted as Ru-Fe(II)) (Found: C, 52.97%; H, 4.28%; N, 16.85%; Reqd: C, 52.46%; H, 4.05%; N, 16.56%). The ion pair complex isolated from [Ru(bpy)_3]^2+ and [Fe(CN)_6]^{3-} is bright orange in colour, and fairly soluble in water, DMF and acetonitrile, and analysed for 3[Ru(bpy)_3]^2+.[Fe(CN)_6]^{3-}.13H_2O (denoted as Ru-Fe(III)) (Found: C, 51.76%; H, 3.95%; N, 16.58%; Reqd: C, 51.36%; H, 4.19%; N, 17.62%).

The IR spectra of all the three complexes are characteristic of the mixed complexes. The absorption and emission spectra and the lifetime of complexes recorded in DMF solution are almost the same as those of [Ru(bpy)_3]^2+. However, all three complexes Ru-Pt, Ru-Fe(II) and Ru-Fe(III), in the solid state do not show emission at all.

The luminescence quenching of the excited state [Ru(bpy)_3]^2+ by [PtCl_6]^{2-}, [Fe(CN)_6]^{4-} and [Fe(CN)_6]^{3-} in solution has already been reported. With most of the anionic metal complexes, there is evidence of extensive ion pairing with [Ru(bpy)_3]^2+ in solution resulting in some static quenching of the excited states. With static quenching the emission yields decrease without appreciable changes in lifetime. The energy of the shorter wavelength emission maximum for [Ru(bpy)_3]^2+ is about 18 kK. Since the low-lying excited state energy levels of the quencher molecules ([PtCl_6]^{2-},

References

[Fe(CN)₆]⁴⁻ and [Fe(CN)₆]³⁻ are around or below 18 kK⁹, the luminescence quenching process is very efficient in solution.

For the mixed complex Ru-Hg, even though the absorption and emission characteristics are not changed in solution, the emission lifetime of Ru-Hg is much longer than that of [Ru(bpy)₃]²⁺ in the solid state as described before¹-². The different photochemical properties of Ru-Hg may be due to the structural reformation¹-¹⁴ of HgCl₂ to a di-µ-chloro-dinuclear [Hg₂Cl₆]²⁻; whereas such change is not observed in the case of Ru-Pt, Ru-Fe(II) and Ru-Fe(III). It is proposed that the complete absence of luminescence from the ion pair complexes Ru:Pt (1:1), Ru:Fé(II) (2:1), Ru:Fe(III) (3:2) is due to the formation of ion-pair complex between Ru(bpy)₃²⁺ and ML₆²⁻; the processes responsible for the complete quenching are the intramolecular non-radiative decay in nature and the present results, thus, support the conclusions arrived at in references 7-13. However, in solution, the ion pair complexes exist in equilibrium (Eq.1) and the emission would occur from free *[Ru(bpy)₃]²⁺ .

\[ p[Ru(bpy)_3]^{2+} + q[ML_6]^{2-} \rightleftharpoons p[Ru(bpy)_3]^{2+} \cdot q[ML_6]^{2-} \]

... (1)

For [PtCl₆]²⁻ and [Fe(CN)₆]⁴⁻, the low-lying excited state energy (E₀) has been suggested as ~ 18 and below 18 kK respectively⁹; however, the efficient quenching of the *[Ru(bpy)₃]²⁺ by [PtCl₆]²⁻ and [Fe(CN)₆]⁴⁻ like the other complex [Fe(CN)₆]³⁻ suggests that the low-lying excited state energy for [PtCl₆]²⁻ and [Fe(CN)₆]⁴⁻ also will be well below 18 kK.

Acknowledgement

RR acknowledges the Institute of Physical and Chemical Research for providing financial support for a three-month stay and the CSIR, New Delhi for partial financial support.

References

14 Kaneko M (submitted to Inorg Chem).