Luminescence of Cesium(I) Tetraphenylporphyrin

SEKHAR BASU, JYOTSNA BASU & K K ROHATGI-MUKHERJEE*
Physical Chemistry Section, School of Energy Studies, Jadavpur University, Calcutta 700 032
and
I LOPEZ ARBELOA
Departmento de Quimica-Fisica, Facultad de Ciencias, Universidad del Pais Vasco, Apartado 644, Bilbao, Spain
Received 10 April 1986; revised and accepted 28 July 1986

Cesium(I) tetraphenylporphyrin of 2 : 1 (metal : TPP) composition has been synthesised in pure crystalline form, and its spectral characteristics have been studied. The absorption spectrum of Cs2TPP exhibits two extra bands of low intensity besides the Soret and Q bands. It emits weak fluorescence ($\phi_F = 0.07$) but no low temperature phosphorescence is observed. From the excitation polarisation spectrum a $S_{2h}$ symmetry is assigned to this compound.

Porphyrrins and metalloporphyrins, in view of their crucial role in photosynthesis, are now being developed as biomimetic systems for solar energy conversion and storage. This has created added impetus for the study of photophysics of the complexes. However, todate there are only a few publications on Group IA alkali metal porphyrins and data obtained so far are not sufficient to predict the structure of these compounds. Rothemund reported the spectra of a green solution containing a mixture of methanolic cesium hydroxide and porphyrin in pyridine but the isolation and analysis of the complex was not attempted.

The present paper reports on the synthesis, absorption, fluorescence and polarisation spectra of cesium tetraphenylporphyrin (Cs2TPP) and in particular presents the estimates of natural radiative lifetime, quantum yield, radiative and non-radiative pathways as well as a tentative geometry of this metalloporphyrin.

Materials and Methods
Preparation of the metal complex
Tetraphenylporphyrin (H2TPP) was prepared from freshly distilled pyrrole (Fluka) and benzaldehyde (LR, Glaxo, India) by the method of Adler et al. Cesium-TPP was prepared by refluxing H2TPP and CsCl in dimethyl sulphoxide under nitrogen atmosphere for 72 hr. The precipitate obtained was dissolved in chloroform and purified by chromatography over alumina (Gr V) column to get cesium-TPP in pure crystalline form. The analysis by atomic absorption spectroscopy (AAS) suggests the composition of the complex to be 1.2 (TPP:Cs) (Found: C, 60.12; N, 6.5; H, 3.2. Calc.: C, 60.12; N, 6.37; H, 3.4%). Two large sized monovalent cesium ions replace the two pyrrolic hydrogens of the porphyrin ring.

The complex Cs-TPP was synthesised a number of times and each time AAS gave reproducible results confirming Cs2TPP configuration.

Solutions of Cs-TPP were prepared by stirring a known amount of the compound in a N2-purged methycyclohexane solvent for 24 hr in the dark. The solutions were not very stable in the presence of light or air. The absorption and emission properties change on storage.

Methods
Absorption spectra were recorded on a Perkin-Elmer spectrophotometer (Hitachi model 200) and the fluorescence spectra on a Perkin-Elmer MPF 44B spectrophotofluorimeter. The fluorescence quantum yields were measured relative to tetraphenylporphyrin in methycyclohexane ($\phi_F = 0.13$), using the optically dilute solution. A solute concentration of about $10^{-5}$ $M$ in methycyclohexane was used to record the emission spectra at 77K. The polarization measurements were carried out using polaroid polarizer and analyzer supplied with the instrument. The degree of polarization ($p$) was calculated using expression (1) proposed by Azumi and McGlynn.

$$p = \frac{I_{EE} - I_{EB}(I_{BE}/I_{BB})}{I_{EE} + I_{EB}(I_{BE}/I_{BB})}$$

where the subscripts E and B represent the polarisation directions perpendicular and parallel to the plane formed by the excitation beam and observed beam respectively.

Results and Discussion
Absorption spectra
The absorption spectrum of Cs2TPP in methycyclohexane (Fig. 1) at room temperature exhibits peaks
fluorescence emission spectra of Cs₂ TIP in methylcyclohexane at 300 K (---) and at 77 K (-----).

The two Q-bands at 514 and 547 nm are the first excited state transitions with \( \varepsilon_{514} = 3.6 \times 10^3 \) and \( \varepsilon_{547} = 2.8 \times 10^3 \) dm\(^3\) mol\(^{-1}\) cm\(^{-1}\) respectively. The lower energy band at 547 nm is the electronic origin of this (\(\pi\pi^*\)) transition termed Q(0,0) and confirmed by polarization spectra. The two weak extra bands at 480 and 590 nm are rather uncommon and not observed for other Group I metalloporphyrins. Such anomalous absorption spectra and extra 'allo' type bands have been reported for transition metal porphyrins such as Mn(II), Fe(II), Mo(IV), W(V) Re(V), Cr(III) which have odd number of electrons. The anomalous absorption is attributed to the coupling of the unpaired metal electron with the \(S = 1\) spin of the excited porphyrin triplet. The extra bands at 480 and 590 nm indicate a fairly strong interaction between the Cs(I) ion and the porphyrin system. When the energy \(E_B\) of the Soret band, is plotted as a function of energy \(E_Q\) of Q band, for various reported Group I metal tetraphenylporphyrins, the points fit reasonably well on a linear plot with unit slope for Li, Na and K but for Cs the point is shifted above the line. This further confirms the perturbation of its energy levels. The observed difference \(E_B - E_Q = 5756\) cm\(^{-1}\) is smaller than that reported for K, Na or Li complex of TPP.

**Fluorescence spectra**

Figure 2 presents the fluorescence emission spectra of Cs₂ TIP in methylcyclohexane at 300 and 77 K. At 300K the fluorescence spectrum is structured and consists of two bands located at 652 and 716 nm. No mirror symmetry relationship between absorption and emission spectra is apparent and the calculated Stoke's shift is approximately 1612 cm\(^{-1}\). The fluorescence characteristics of Cs₂ TIP are similar to those of other typical metalloporphyrins emitting \(\pi\pi^*\) fluorescence. The observed fluorescence quantum yield, \(\phi\), in degassed methylcyclohexane solution is 0.07. At 77K nature of fluorescence is the same but the shorter wavelength band at 652 nm is shifted by about 215 cm\(^{-1}\) towards higher energy. Furthermore, no good correlation exists between low temperature excitation spectrum and the room temperature absorption spectrum throughout the visible region. No phosphorescence is observed at 77K in deoxygenated solution, even when heavy atom perturbation technique is applied.

The emission is more intense and blue-shifted at 77K than at 300K. To explain the discrepancy between room temperature and low temperature emission it may be suggested that at low temperature the emission from Cs₂ TIP occurs from the vibrational levels of \(S_I\) which are not in thermal equilibrium with the zero level of \(S_I\). Quimby et al. have reported emission of this type from Zn-tetraarylporphyrins where the emission at 77K is suggested to originate from the group of vibronic levels of \(S_I\) associated with Q(1-0) absorption band. In recent years anomalous fluorescence emission has been observed in some metalloporphyrins which has been explained as \(S_I \rightarrow S_0\) fluorescence from the Soret band. But this explanation is not valid in our case.
The mean radiative lifetime ($\tau^0$) and the rate constant ($k_f$) for fluorescence emission of Cs$_2$TPP have been calculated from the absorption and emission spectra by the Strickler-Berg equation\textsuperscript{14}. In a real system, other competitive processes reduce the observed mean radiative lifetime, which is given by Eqs (2) and (3)

$$\tau = \frac{1}{k_i + \Sigma k_i} = \frac{\tau^0 k_f}{k_i + \Sigma k_i} \quad \ldots (2)$$

$$\tau = \tau^0 \phi_f \quad \ldots (3)$$

where $\Sigma k_i$ is the summation of rate constants for all modes of deactivation of the excited state by non-radiative pathways and $\phi_f$ is the quantum yield of fluorescence. The values for Cs$_2$TPP are listed in Table 1 and compared with the published data for TPP.

For TPP, the quantum yield for fluorescence ($\phi_f$) is high although that for triplet formation ($\phi_T$) is also considerable\textsuperscript{7}. In the case of Cs$_2$TPP, the incorporation of heavy atom reduces $\phi_f$ and increases the rate constants for fluorescence emission ($k_f$) as well as that for non-radiative ($\Sigma k_i$) pathways.

**Polarization spectrum**

For examination of the symmetry of Cs$_2$TPP molecule and assignment of its absorption transition dipoles, fluorescence limit polarization method was used. The excitation polarization spectrum of Cs$_2$TPP in methylecyclohexane at $77K$ is shown in Fig. 3. The emission monochromator was set on $652$ nm band for fluorescence. The absolute values of degree of polarization at the different absorption bands are $-0.01$, $+0.16$, $-0.12$, $-0.17$ and $-0.21$ respectively for $590$, $547$, $514$, $480$ and $416$ nm bands.

The larger $p$-value (+0.16) is observed around $547$ nm absorption band which is the lowest singlet ($S_1$) state in absorption. The emission is also expected to involve the same electronic transitions, which have nearly collinear moments. The lower $p$-values are obtained upon excitation into higher electronic states, which are generally not the state responsible for fluorescence emission. The peak at $416$ nm in absorption spectrum showing the minimum value of $p(-0.21)$ is the $S_2$ Soret band. Also the band around $590$ nm is not the Q(0,0) band as indicated by its negative polarization value compared to $547$ nm band.

The $D_{2h}$ symmetry of the free base tetraphenylporphyrin may be transformed into $D_{2h}$ by introduction of a metal atom. The limit polarization of the fluorescence of low symmetry molecules (not higher than two) has to agree approximately with the theoretical value $1/2$, with reference to the sum of randomly located linear oscillators. When the symmetry is higher than two, limit polarisation may not be higher than $1/7\textsuperscript{15}$. The lower limit is $-1/3$ for both the symmetries. In the work of Gouterman and Stryer\textsuperscript{16}, the symmetry of $D_{2h}$ and lower were observed in porphyrin derivatives examined. In the paper by Gurinovich et al\textsuperscript{17}, photoselection of porphyrin under variety of condition was examined and a rather distinct division was achieved into those possessing $D_{4h}$ symmetry and those possessing $D_{2h}$ or lower.

In the case of Cs$_2$TPP the upper limit of polarisation is 0.16 which is greater than $1/7$ and lower limit is $-0.21$, indicating its deviation from four-fold ($D_{4h}$) symmetry. For this reason, a $S_{2h}$ symmetry is suggested for this complex instead of $D_{4h}$.

**Structure**

Porphyrins have a central hole of essentially fixed size. In certain cases the metal is unable to fit into this hole and as has been shown by Hoard\textsuperscript{18}, lies out of the porphyrin plane. In haemoglobin\textsuperscript{19}, for example, the iron atom in the oxygenated form lies roughly in plane, while the metal lies out-of-plane in the deoxy form. It has been suggested that anomalous absorption spectra of lead and mercury porphyrins\textsuperscript{20} can be related to non-planar arrangement of the central metal with respect to the porphyrin skeleton. It is therefore expected that the two bulky cesium atoms are unable to fit into the porphyrin central hole and sit above and below the porphyrin ring generating a species of symmetry $S_{2h}$.
The overlap between π-orbitals of the porphyrin ring and metal orbitals of proper symmetry produces a moderately high ligand field strength which can explain complex formation of Cs with tetraphenylporphyrin molecules. The stability of Cs₂TPP can be nicely explained from Pearson's theory of 'hard and soft acids and bases' (HSAB). According to this theory hard acids prefer to bind with hard bases, while soft acids prefer soft bases. The unsaturated porphyrin ring permits sufficient polarizability to the four pyrrole nitrogen atoms due to extensive electron delocalization and thus each nitrogen acts as a soft base. The Cs⁺ is a soft acid as compared to Li⁺, Na⁺ and K⁺ due to its high ionic radii and lower electron density. The Y-values of softness follow the order: Cs⁺ (2.73) > Na⁺ (0.93) > K⁺ (0.92) > Li⁺ (0.36). Therefore a soft acid soft base complex of Cs⁺ and TPP can be sufficiently stable to exist.

References