Protonation Behaviour in the Ground and Excited States of some Os(II) Polypyridyl Complexes

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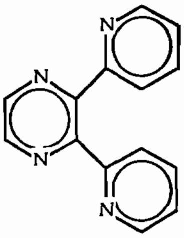
Abstract

Absorption spectral changes and emission intensity variations during the protonation in the ground and excited charge transfer states of $Os(dpp)_3^{2+}$ and $Os(44'\text{-}dcbpy)_3^{4-}$ {dpp = 2,3-bis(2-pyridyl)pyrazine and 44'-dcbpy = 4,4'-dicarboxy-2,2'-bipyridine} have been investigated in aqueous solution.

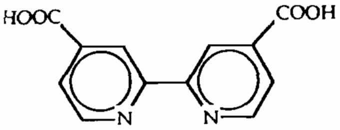
Introduction

Photophysics and photoredox chemistry of transition metal polypyridyl complexes have been extensively studied in the last two decades and a very detailed picture of the excited state features and dynamics is emerging [1, 2]. A distinguishing feature of these complexes is the presence of lowest excited state of metal-to-ligand charge transfer (MLCT) in nature. Acid–base properties of the coordinated ligands provide a direct measure of the interplay between the σ-donor strength and π-bonding properties in influencing the dπ–π* (MLCT) interactions. Studies on complexes with ligands that carry extra protonation sites are thus of much interest. There have been a few studies of Ru complexes from this viewpoint [3].

As part of our ongoing studies on the photophysics and photoredox chemistry of transition metal polypyridyl complexes, we recently examined the influence of such protonation equilibria on the ground and excited states of Ru complexes containing 2,3-bis(2-pyridyl)pyrazine (dpp) and 4,4'-dicarboxy-2,2'-bipyridine (44'-dcbpy) as protonatable ligands [4]. There has hardly been any related study on analogous Os complexes. In this report, we describe our observations on the acid–base behaviour of two tris-chelated Os(II) complexes $Os(dpp)_3^{2+}$ and $Os(44'\text{-}dcbpy)_3^{4-}$.



2,3-bis(2-pyridyl)pyrazine(dpp)



4,4'-dicarboxy-2,2'-bipyridine (44'-dcbpy)

Experimental

Materials

Ligands 2,3-bis(2-pyridyl)pyrazine (dpp) and 4,4'-dicarboxy-2,2'-bipyridine ($44'\text{-}dcbpyH_2$) were commercial sources (Strem) and were used as supplied. Os(II) complexes $Os(LL)_3^{n+}$, LL = dpp, 44-dcbpy were prepared according to the procedures described earlier [5]. Water used in absorption, emission studies were deionized and then distilled twice on quartz still before use. All other chemicals were of analytical grade from Fluka.

Methods

Absorption spectra were recorded on a Cary 214 spectrophotometer using 1 cm matched quartz cells. Emission spectra were recorded on a Spex Fluorolog spectrofluorimeter equipped with a Hamamatsu R948 photomultiplier tube. Emission spectral maxima quoted are corrected values. The pK_a, $pK_a^{*\prime}$ values for the deprotonation were calculated using the equation:

$$\begin{aligned} pH &= pK_a - \{\log[\text{acid}]\,[\text{base}]\} \\ &= pK_a - \{\log[I - I_0]/[I_f - I]\} \qquad (1) \end{aligned}$$

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where I_0 and I_f are the initial and final absorbances (or emission intensities) respectively. In cases of two closely spaced protonation equilibria, a graphical method of curve-fitting was employed. Monitoring of the ground state protonation in dpp complexes necessitated usage of aqueous H_2SO_4 solutions of varying concentrations. H_0 values for such mixtures were taken from the tabulations of Rochester [6].

Results and Discussion

Acid–base Properties of $Os(dpp)_3{}^{2+}$

The absorption spectrum of $Os(dpp)_3{}^{2+}$ in aqueous solution consist of several bands: MLCT ($d\pi$–π^*) at 480, 436 nm, ligand localized (π–π^*) transition at 304 nm and LMCT transition to the triplet state appearing as weak absorption in the red (574, 670 sh nm). The complex luminesces weakly in the red in aqueous solution at room temperature with a maximum at 767 nm (corrected.) The complex has two non-chelated pyrazyl and pyridyl N-centers on each dpp that can undergo protonation equilibria.

The absorption spectrum of the complex is pH independent in aqueous solution over the pH range 0–10. Os complexes like their Ru analogs are weak bases undergoing protonation in the ground state only in acidic solutions. The process is accompanied by distinct spectral changes: a red shift of the M-PL band from 480 to 528 nm. Quantitative analysis of the absorption growth at 528 nm indicate a single titration with an inflection point (pK_a) at -4.60

$$[Os(dpp)_2(dppH)]^{3+} \rightleftharpoons [Os(dpp)_3]^{2+} + H^+ \qquad (2)$$
$$pK_a = -4.60$$

Of the two possible protonation sites, the low pK_a value suggest possible protonation at the pyrazyl N-centers. (It is also likely that pyridyl N-centers protonate first but due to the remote nature of this protonation site, the process is not accompanied by any distinct spectral changes). The free ligand dpp has two pK_a values [4]: 2.90 and 0.80. The shift in the ground state pK_a upon chelation of dpp in the Os complex ΔpK_a is very significant, over 7 pK_a units.

$$\Delta pK_a = pK_a(Os) - pK_a(PL) \qquad (3)$$

Above pH 7.0, the emission of the $Os(dpp)_3{}^{2+}$ complex is pH independent. Unlike the absorption, the emission intensity of the complex varies significantly in dilute acidic solutions. Figure 1 (bottom) presents typical pH dependence of emission. The emission intensity decreases rapidly in mildly acidic solutions and no detectable emission is observed in acidic (pH 0) solutions.

Figure 1 (top) presents emission intensity versus pH titration curve. The curve passing through the experimental points is the calculated intensity curve for the deprotonation process occurring according to eqn. (2)

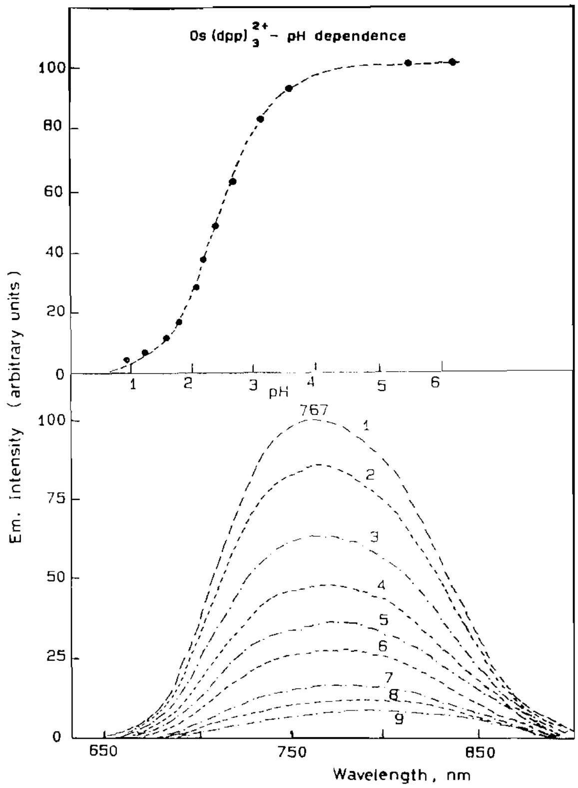

Fig. 1. Emission spectra of $Os(dpp)_3{}^{2+}$ in aqueous solution at various pH values: 5.50 (1), 3.17 (2), 2.68 (3), 2.41 (4), 2.20 (5), 2.08 (6), 1.78 (7), 1.58 (8), 1.23 (9) (bottom). Variation of emission intensity (at 767 nm) with pH for $Os(dpp)_3{}^{2+}$ in aqueous solutions (top).

$$[Os(dpp)_2(dppH)^+]^* \rightleftharpoons [Os(dpp)_3]^* + H^+ \qquad (4)$$
$$pK_a{}^{*\prime} = 2.45$$

The calculation is based under the following assumptions: (i) single titration point (pK_a) exists in the pH range 0–7; (ii) the emission intensity of the basic form ($pH \geqslant 7$) is normalized at 100% and emission from the protonated form is negligible at the wavelength of monitoring analysis. In the pH range examined 0–10, it can be noted that the variation in the emission intensity can be quantitatively accounted by a single inflection point ($pK_a{}^{*\prime}$).

In principle, the inflection point, denoted as $pK_a{}^{*\prime}$, derived from emission titration curves, needs to be corrected for the differences in the excited state lifetime of the unprotonated (τ') and protonated forms (τ) according to eqn. (5)

$$pK_a{}^{*\prime} = pK_a{}^* - \log(\tau/\tau') \qquad (5)$$

Absence of any detectable emission in acidic solutions corresponding to the monoprotonated form of the complexes does not permit evaluation of

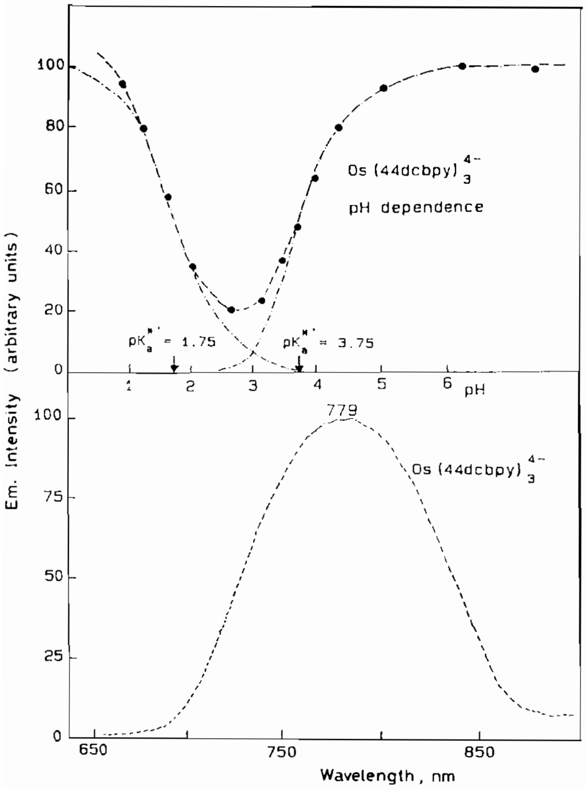

Fig. 2. Emission spectra of $Os(44'\text{-}dcbpy)_3^{4-}$ in aqueous solution at pH 7.60 (bottom). Variation of emission intensity at 780 nm of $Os(44'\text{-}dcbpy)_3^{4-}$ with pH in aqeuous solutions (top).

absolute pK_a^* values. In the excited state, the dpp complex is considerably more basic ($\Delta pK_a > 5$ pK_a units). Such pronounced shifts are in agreement with the localized electron description of MLCT excited state.

Acid–Base Properties of [Os(44'-dcbpy)$_3$]$^{4-}$

In aqueous solution at pH $\geqslant 7.0$, the carboxyl groups are fully deprotonated and the complex carries a nett 4– charge. The absorption spectrum is characterized by several bands: MLCT transitions at 498, 444 nm and ligand-localized π–π^* transitions at 304 nm. The complex exhibits a weak emission in the red as shown in Fig. 2. Over the pH range of 0–10 examined, the absorption spectral changes are too small to allow meaningful measurements of protonation equilibria. Hence we resorted to monitoring of the protonation changes by conventional pH titration on an automated pH-titroprocessor. By this technique, over the pH range 0–10, we could detect only one ground state deprotonation at pH *c.* 1.70 (eqn. (6))

$$[Os(44'\text{-}dcbpy)_2(44'\text{-}dcbpyH_2)]^{2-} \rightleftharpoons [Os(44'\text{-}dcbpy)_3]^{4-} + 2H^+ \qquad (6)$$
$$pK_a = 1.70$$

Over the same pH range of 0–10.00, the emission from $[Os(44'\text{-}dcbpy)_3]^{4-}$ shows more pronounced variation in intensity and emission maxima. Starting at pH 7.0, lowering of pH leads to a decreased emission intensity and small red shifts upto pH of about 2.90. Further lowering of pH leads to enhanced emission intensity and small blue shifts. The emission maximum at pH 0 is very similar to that observed at pH $\geqslant 7$ with regaining of > 95% intensity. Figure 2 also presents the emission intensity variation monitored at $\lambda = 780$ nm as a function of pH. A two pK_a^* analysis similar to that carried out on the tris(dpp) complex (fit shown in the upper part of Fig. 2), leads to identification of two excited state pK_a^* values of 3.75 and 1.75 corresponding to eqns. (7) and (8):

$$[Os(44'\text{-}dcbpy)_2(44'\text{-}dcbpyH_2)]^{2-*} \rightleftharpoons [Os(44'\text{-}dcbpy)_3]^{4-*} + 2H^+ \qquad (7)$$
$$pK_a^* = 3.75$$

$$[Os(44'\text{-}dcbpy)(44'\text{-}dcbpyH_2)_2]^{0*} \rightleftharpoons [Os(44'\text{-}dcbpy)_2(44'\text{-}dcbpyH_2)]^{2-*} + 2H^+ \qquad (8)$$
$$pK_a^* = 1.75$$

It is intersting to compare the ground state and excited state pK_a values of the tris-chelated Os(II) complexes with those of analogous Ru(II) tris chelates. For the dpp, 44'-dcbpy complexes of Os, the pK_a^* values shift to lower pH values by *c.* 1 pH unit, in accordance with the expected s-donor and π-backbonding effects of Os. In each of the tris-chelates, there are six protonation sites. Over the limited pH range examined, we could determine utmost two pK_a and pK_a^* values. According to the localized electron model for the MLCT excited state of these complexes, only one of the three ligands receives the promoted electron (eqn. (9))

$$[Os^{II}(PL)_3]^{2+} \longrightarrow [Os^{II}(PL)_2(PL\text{-}\cdot)]^{2+*} \qquad (9)$$

Hence this ligand alone is expected to experience significant variations in the local electron density (basicity) upon formation of the excited state.

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