Inorganica Chimica Acta, 31 (1978) L423–L424
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Bis(8-quinolinolato)platinum(II): a Novel Complex Exhibiting Efficient, Long-Lived Luminescence in Fluid Solution

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Received September 13, 1978

The bimolecular electron-transfer processes of electronically excited coordination compounds are currently under active investigation [1–6], mainly due to the interest of these systems as photocatalysts for solar energy conversion [7–9]. So far, these studies have been essentially limited to a number of polypyridine complexes of Cr(III), Ru(II), Os(II), and Ir(III) [6]. Actually, these are among the few complexes known that have relatively long-lived excited states and which allow an easy monitoring of excited-state processes by their emission in fluid solution. As a part of a systematic investigation aimed at finding new types of complexes suitable for excited-state bimolecular reaction studies, we report here on the properties of a Pt(II) complex exhibiting efficient, long-lived luminescent emission in fluid solution.

When 8-quinolinol (QQH) dissolved in a small volume of ethanol is added to an aqueous alkaline (pH 10) solution of K_2PtCl_4 in a mol ratio of 2:1, and the resulting solution is heated on a steam bath for a few minutes, a brownish-orange precipitate is formed. The precipitate is moderately soluble in a variety of organic solvents and highly soluble in DMF, from which it can be recrystallized to give a red crystalline compound. Elemental analysis confirms the formulation of this compound as bis(8-quinolinolato)platinum(II) ($Pt(QO)_2$).

The absorption spectrum of $Pt(QO)_2$ in DMF (Fig. 1) shows two prominent features, namely, a structured absorption with maximum at 346 nm (ϵ_{max}, 7510) and a structureless band at 480 nm (ϵ_{max}, 6540). The spectrum is quite different from that of free QO^-, QOH, $QHOH^+$ [10], as well as from the spectra of $M(QO)_2$ complexes where M is a closed shell metal [11].

DMF solutions of $Pt(QO)_2$ exhibit a luminescent emission which is strongly enhanced by deaeration. The bright red luminescence of deaerated solutions can be easily detected visually. The emission spectrum (Fig. 1) consists of a broad band with a maximum at 650 nm which shifts to 620 nm and becomes structured (vibrational spacings of about 900 cm^{-1}) upon cooling to 77 °K (Fig. 1). The lifetime of the emission in DMF at 20 °C is 3.5 μsec [12]. In these experimental conditions, the emission quantum yield can be estimated as ~0.01 [13]. The excitation spectrum matches well the absorption spectrum of the complex. The emission is totally different from that of free ligand, as well as from the fluorescence of

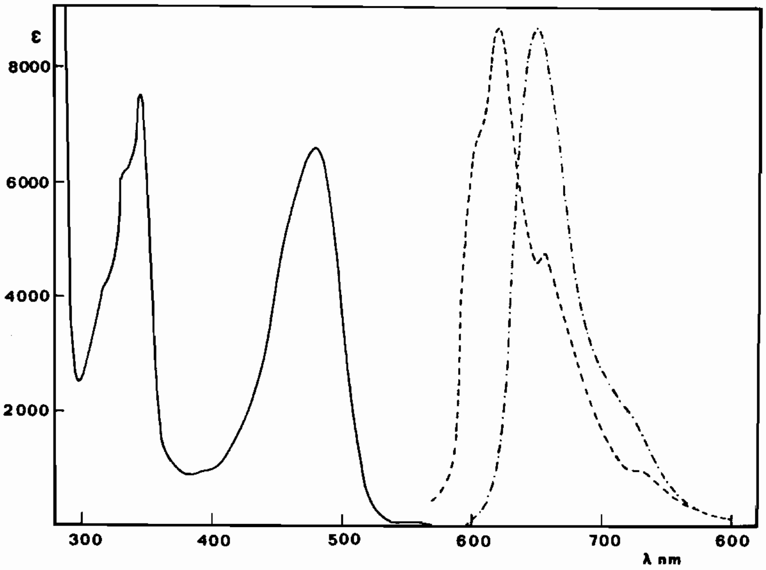

Figure 1. Absorption spectrum (——) and room temperature (·—·—·) and 77 °K (– – –) emission spectra (arbitrary units) of $Pt(QO)_2$ in DMF solution.

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several $M(QO)_2$ complexes where M is a closed-shell metal (λ_{max}, 530–570 nm; τ, 3–28 nsec) [11]. The long lifetime of the emission strongly suggests its attribution to a formally spin-forbidden transition (phosphorescence) of the $Pt(QO)_2$ chromophore.

Further work is in progress towards the characterization of this and similar systems, which, in view of their strong visible absorption and long excited-state lifetime, appear to be promising candidates for use in bimolecular excited-state reaction studies and in energy conversion problems.

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10 The spectra of the free ligand have the following maxima: QO^-, 349 and 403 nm; QOH, 315 nm; $QHOH^+$, 310, 321, and 362 nm. QO^-, QOH, and $QHOH^+$ are assumed to be the dominant species in the following media, respectively: DMF saturated with KOH, neat DMF, and DMF containing 3% concentrated $HClO_4$.

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13 The rough estimate of the emission quantum yield has been performed by comparison of the $Pt(QO)_2$ emission with the known [14] luminescence of tris(2,2'-bipyridine)ruthenium(II).

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