Inorganica Chimica Acta, 33 (1979) L139–L140
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Preparation, Reactions and Photoreactions of Bis(bipyridyl)poly-4-vinylpyridine Ruthenium(II) Complexes

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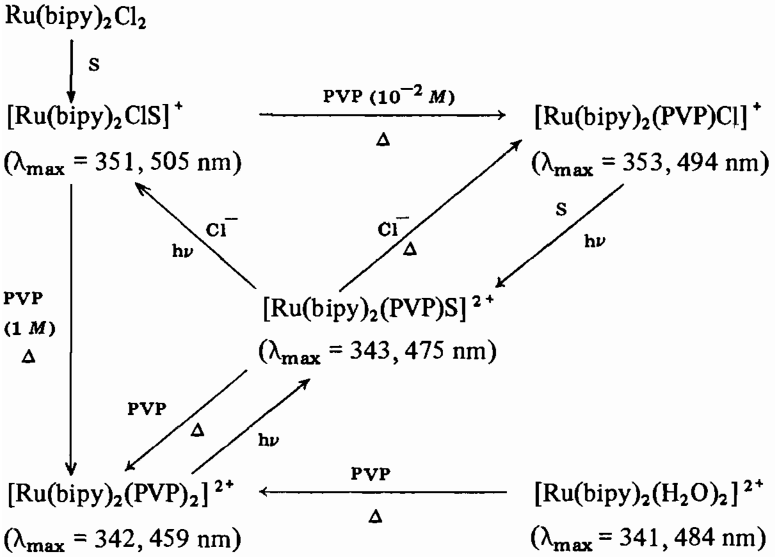
Received December 4, 1978

Transition metal complexes are of interest as potential 'catalysts' for the photodissociation of water by visible light [1–3]. It is generally recognised that for such catalysts to be effective it will be desirable to immobilise the complexes in order to inhibit non-productive back reactions and to promote efficient energy capture by the reactive complex. Already bipyridyl complexes of ruthenium have been incorporated into monolayer assemblies [2] and into micelles [4] where they exhibit modified photophysical properties while retaining much of the chemical behaviour of the parent compounds. We believe that polymer-bound complexes will also be of interest in this connection. Although it has been demonstrated that such compounds, either in soluble or in insoluble forms, are effective catalysts for a wide variety of reactions [5], there has been little reported work on their photochemical and photophysical properties. We have, therefore, embarked on a programme to study the photochemistry of transition metal complexes attached to synthetic macromolecules, and to assess their potential as photocatalysts. In this communication we present the results for bis(bipyridyl)ruthenium complexes of poly(4-vinylpyridine).

In a series of experiments, in which the PVP:Ru stoichiometry[†] was varied from 80:1 to 2:1, methanolic solutions of atactic poly(4-vinylpyridine)[≠] (10^{-2} *M*) and Ru(bipy)$_2$Cl$_2$ were allowed to reflux for periods of up to 100 hours, the uv/visible spectra of aliquots being recorded periodically. In each case the final product was a soluble complex, the uv/visible spectrum of which indicates that the ruthenium is present as [Ru(bipy)$_2$(PVP)Cl]$^+$. The solid complex was isolated as its chloride by solvent evaporation and as its perchlorate by precipitation from aqueous methanol by sodium perchlorate. Although the nature of the complex appears to be independent of the PVP:Ru ratio, complete conversion to the polymer-bound compound is achieved more rapidly with mixtures having higher PVP:Ru ratios. We have therefore examined the chemistry and photochemistry of 20:1 complexes in greatest detail. At higher concentrations of poly(vinyl)pyridine (*e.g.* 1.0 *M*) reaction mixtures of



Scheme 1. Reactions of bis(bipyridyl)[poly(4-vinylpyridine)] ruthenium(II) complexes in methanol solution (S = Solvent).

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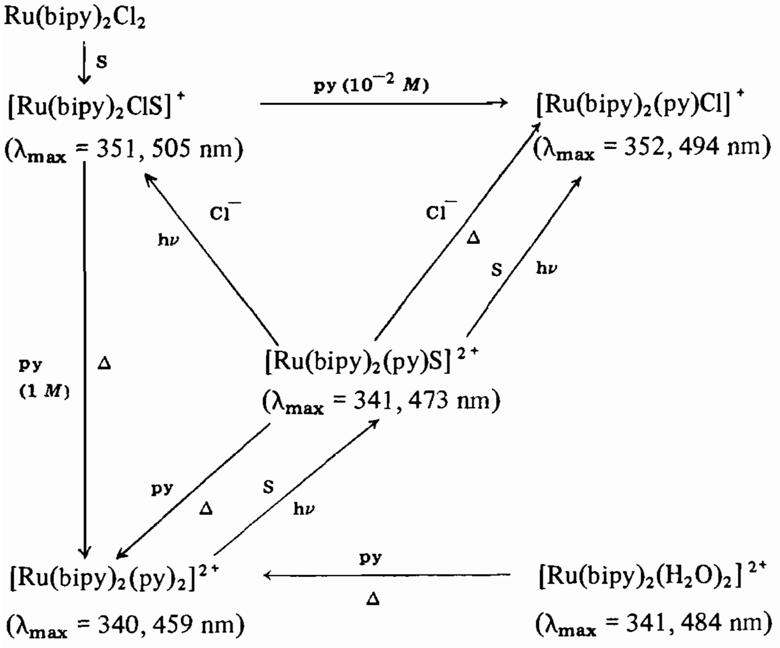
[†] PVP is used here to indicate the unit –CH$_2$CH(C$_5$H$_4$N)–. Concentration of polyvinylpyridine is here its 'base molarity', *i.e.* it refers to the concentration of this unit in solution.

[≠] Prepared by AIBN-initiated radical polymerisation of 4-vinylpyridine: molecular weight, from viscosity measurements, 9000. Experiments with polyvinylpyridine having molecular weight of 50,000 gave essentially similar results.



Scheme 2. Reactions of bis(bipyridyl)pyridine)ruthenium(II) complexes in methanol solution (S = Solvent).

20:1 stoichiometry yield a product which we have identified by uv/visible spectroscopy as the complex containing two polymeric ligands *viz.* $[Ru(bipy)_2(PVP)_2]^{2+}$. The same compound is formed when $[Ru(bipy)_2(H_2O)_2](ClO_4)_2$ is allowed to react with polyvinylpyridine (10^{-2} or 1 *M*). These PVP complexes cleanly undergo substitution upon irradiation, and these reactions and other chemical and photochemical transformations are summarised in Scheme 1.

In order to compare the reactions of these PVP-complexes with those of their non-polymeric analogues we have prepared and isolated a series of pyridine (py) complexes, $\{[Ru(bipy)_2(py)_2](ClO_4)_2$, $[Ru(bipy)_2(py)Cl](ClO_4)$, $[Ru(bipy)_2(py)(H_2O)](ClO_4)_2\}$ using literature methods where available [6, 7]. These complexes also undergo thermal- and photo-substitution in methanol solutions. These reactions, which are summarised in Scheme 2, appear to be very similar to those of their polymer-bound analogues, the systems only differing in their rates of reaction.

In conclusion, the results of this preliminary study show that polymer-bound complexes of ruthenium bipyridyl can be prepared in which the chemical and photochemical properties closely resemble those of analogous non-polymeric complexes. These systems are thus most suitable for a detailed study of the effect of polymer complexation on the photochemical and photophysical properties of transition metal compounds. Therefore, we are now engaged in the determination of quantum efficiencies for the reactions in Schemes 1 and 2, in order to assess how such properties depend on factors such as the molecular weight and the tacticity of the polymer and the 'concentration' of $Ru(bipy)_2$ units attached to the polymer chain. We are also carrying out experiments to determine the stereochemistry of the ruthenium complexes reported here.

It is, of course, clear that the photosubstitution reactions of these polyvinylpyridine complexes make them unsuitable as solar energy converters. We are therefore at present synthesising polymers containing bipyridyl groups, the bis(bipyridyl)ruthenium complexes of which should be essentially inert to photosubstitution.

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