J. inorg. nucl. Chem. Vol. 43, No. 10, pp. 2355–2358, 1981
Printed in Great Britain.

0022-1902/81/102355–04$02.00/0
Pergamon Press Ltd

TRIS(2,2′-BIPYRIDINE) RUTHENIUM(II) ELECTRON-TRANSFER IN A LAYERED ZIRCONIUM PHOSPHATE LATTICE

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(*Received* 29 *December* 1980; *received for publication* 23 *January* 1981)

Abstract—The preparation of a crystalline zirconium phosphate containing apparent monolayers of tris(2,2′-bipyridine) ruthenium (II) is described. ESR and photoacoustic spectral data indicate the ruthenium complex retains its octahedral symmetry in this new host environment. Electron spin resonance data also indicate that under visible illumination triethylamine transfers an electron to the ruthenium complex to form a free radical amine cation.

INTRODUCTION

Use of sunlight and inorganic complexes such as tris-bipyridyl ruthenium ions to photocatalyze water "splitting" has been an elusive goal[1]. Many such studies have treated homogeneous solutions[2], but it has gradually become evident that heterogeneous systems involving micellar[3], membranous[4], or colloidal[5] surfaces facilitate the photochemical process by one or more of the following effects: retarding or suppressing back reactions that destroy the photoexcited state, separating oxidized and reduced species, and catalyzing reaction steps. Rather than a single cyclic photoredox process most of the recent heterogeneous systems[6] involve several coupled cycles usually including the Ru(II)–Ru(III) couple and the methylviologen couple Mv^{2+}/Mv^{+} where the latter is a radical cation.

An obvious extrapolation of this interest in surfaces would be the inclusion of the photoexcitable metal ion in a layered crystalline environment. Tris(2,2′-bipyridyl) ruthenium(II) has been characterized[7] on the clay mineral hectorite. Although exchange of this complex ion into the clay is stoichiometric at low loadings and the complex retains its solution spectral characteristics on the clay, the resulting material does not dissociate water into its elements under visible illumination. The present paper describes the sometimes contrasting properties of tris(2,2′-bipyridyl) ruthenium(II) incorporated into a layered zirconium phosphate (ZrP) lattice. The impetus for this work was the hope that a layered synthetic system would have electron transport properties analogous to the ordered chlorophyll molecules in a plant leaf. It was also hoped that such an opaque solid would demonstrate the usefulness of visible photoacoustic spectroscopy (PAS)[8, 9].

EXPERIMENTAL

The $Ru(bipy)_3Cl_2$ used was prepared by refluxing $RuCl_3 \cdot 1\text{-}3\ H_2O$ obtained from Alfa Products, in an excess of 2,2′-bipyridine, obtained from Pfaltz & Bauer, for 1–2 hr at 230°C. The product was rinsed repeatedly with benzene to remove excess 2,2′-bipyridine, dissolved in water, filtered and the water was then evaporated.

Attempts to exchange the large $Ru(bipy)_3^{2+}$ ion into commercially available zirconium phosphate (ICN) from a ~ 3×10^{-3} M solution of the ion in both H_2O and methanol at ambient temperature proved fruitless. It was therefore determined to incorporate the $Ru(bipy)_3^{2+}$ ion into the ZrP lattice during crystallization of the latter. Zirconyl sulfate was prepared by refluxing 0.6 g ZrO_2 in 3 ml conc. H_2SO_4 and 4.6 g $(NH_4)_2SO_4$ at 320°C until the ZrO_2 dissolved. The solution was diluted with water to 20 ml and cooled to room temperature. Three grams of $Ru(bipy)_3Cl_2$ were added to the 20 ml of zirconyl sulfate solution. Subsequently 3.3 ml of conc. HCl and 6.6 ml of 85% H_3PO_4 were added and a gel formed. This was refluxed at ~75°C for three days and the resulting red crystals were filtered and rinsed with H_2O. X-ray powder patterns were obtained on a Phillips XRG-3000 powder pattern diffractometer using Ni-filtered Cu radiation.

Electron paramagnetic resonance (EPR) measurements were obtained on a Varian E-3 EPR spectrometer: Modulation amplitude 10 G, modulation frequency 100 kHz, time constant 1 sec, scan time 4 min, microwave power 20 mW, and at ambient temp.

Absorbance measurements to determine $Ru(bipy)_3Cl_2$ concentrations in solutions were made on a Beckman DB spectrophotometer ($\epsilon = 14355\ M^{-1}\ cm^{-1}$ at $\lambda = 453$ nm[10]). Visible spectra of dry, opaque, crystalline $Ru(bipy)_3\ Zr(PO_4)_2$ were obtained by dispersive photoacoustic spectroscopy. PAS measurements were made with a 500 W xenon arc lamp, intensity modulated at 138 Hz. The light was wavelength selected by a Bausch and Lomb monochromator (33-86-40) and focused, through a glass window in a sealed cell, onto the sample. The signal from a sensitive Brüel and Kjaer 4165 microphone, also contained in the cell, was processed by a PARC 124A lock-in amplifier to yield a dispersive PA spectrum. The PA spectra were source normalized by point by point rationing with the PA spectra (over the same range of wavelengths) of Norite A decolorizing carbon.

RESULTS AND DISCUSSION

The synthesis of crystalline zirconium phosphate, its structure, and ion-exchange properties have been extensively studied[11]. Precipitation of crystalline ZrP from the ZrP gel in the presence of sulfate ion at *ca.* 75°C appears to be a suitable method of synthesis[12]. The crystals thus formed are layered two-dimensional crystals with an interlayer distance of 7.56 Å[12]. Single crystals large enough for X-ray studies have not been produced.

Direct exchange of NH_4^+, K^+, Hg^{2+}, Ce^{3+}, and other cations into crystalline ZrP has been reported[12–15 respectively]. The interlayer distances are dependent on cation size, e.g. the NH_4^+ exchanged form has an interlayer distance of 9.48 Å[12]. The cation must therefore, push the layers of the crystal apart in order to exchange with the H^+ ion present in ZrP.

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The exchange of large complex ions, such as the Ru(bipy)$_3^{2+}$ complex into an intact ZrP lattice is energetically unfavorable. This difficulty was overcome by incorporating the complex into the crystal during formation as described above in Experimental. Spectrophotometric analyses at $\lambda = 453$ nm of the filtrate showed ~50% incorporation of the complex. With the availability of H$^+$ ions many times greater than that of the Ru(bipy)$_3^{2+}$ ion, this high degree of ruthenium complex incorporation indicates a high thermodynamic favorability towards the formation of Ru(bipy)$_3$ Zr(PO$_4$)$_2$. Other syntheses[11] of zirconium phosphates of the form Zr(R – PO$_3$)$_2$ and Zr(R – OPO$_3$) have been carried out using R – PO(OH)$_2$ or R – OPO(OH)$_2$ (where *R* is a hydrocarbon) in place of H$_3$PO$_4$ in the synthesis. The synthetic method reported in the present paper produced X-ray powder diffraction peak placements and intensities consistent with those of Alberti *et al.*[11].

The sharp, well defined peaks in the X-ray powder diffraction pattern (Fig. 1) are indicative of a well defined crystalline structure. The first peak in the pattern has been interpreted[11, 16] as the *d*-spacing between the layers of the crystal. The interlayer *d*-spacing value obtained for the Ru(bipy)$_3$ Zr(PO$_4$)$_2$ is 15.9 Å as expected for a complex of this size. In order to exchange Ru(bipy)$_3^{2+}$ into the hydrogen form of ZrP the layers would have to be separated by 15.9–7.6 = 8.3 Å, thus the complex cannot directly be exchanged as was at first hoped.

A comparison of diffraction patterns for the H$^+$ form and the Ru(bipy)$_3$ Zr(PO$_4$)$_2$ showed many similarities. Distortions were caused by the presence of the bulky Ru(bipy)$_3^{2+}$ ion located in sites previously occupied by the small H$^+$ ion. Additional X-ray peaks also arise because of the uniform orientation of the Ru(bipy)$_3^{2+}$ ion in this crystal lattice. The interplanar spacings indicate that the complex is bonded to phosphate ions on two facing planes. Bonding to adjacent phosphate ions (of the same plane) would probably create a larger interlayer distance than that observed.

This parallel ordering and close spacing of the Ru(bipy)$_3^{2+}$ complex in the ZrP lattice makes it especially suitable for redox reactions requiring more than one electron transfer[17]. It has previously been found that certain ruthenium complexes in the excited state, Ru(bipy)$_3^{2+}\xrightarrow{h\nu}$*Ru(L)$_3^{2+}$, can either accept[18], *Ru(L)$_3^{2+}$ + D → Ru(L)$_3^{+}$ + D$^+$, or donate[19], *Ru(L)$_3^{2+}$ + A → Ru(L)$_3^{3+}$ + A$^-$, an electron. Which of these two possible reactions of the photoexcited species occurs depends on the ligand, the quencher, and the solvent. Many of these processes give rise to no net reaction because of rapid back transfer of the electron. There are, however, reactions both oxidative and reductive for which a product of electron transfer has been isolated[18].

The reaction examined here is the transfer of an electron from liquid triethylamine to the excited state of solid Ru(bipy)$_3$ Zr(PO$_4$)$_2$:

$$\mathrm{Ru(bipy)_3\,Zr(PO_4)_2 + et_3N{:}} \xrightarrow{h\nu} \mathrm{Ru(bipy)_3\,Zr(PO_4)_2\,Et_3N\cdot}$$

where everything shown on the right hand side is in the solid lattice and the actual products are Ru(bipy)$_3^{+}$ and the Et$_3$N$^{\cdot+}$ free radical.

The Ru(bipy)$_3^{2+}$ complex has the electron configuration t_{2g}^6 and is therefore diamagnetic. EPR spectra of the Ru(bipy)$_3$ Zr(PO$_4$)$_2$(s) exhibited no prominent signal so it was concluded that the octahedral symmetry of the Ru(bipy)$_3^{2+}$ complex is unaffected by its location in the ZrP lattice. Et$_3$N run neat at ambient temperature also produced no EPR signal. However, when Et$_3$N(*l*) is added to the Ru(bipy)$_3$ Zr(PO$_4$)$_2$(s) in the EPR sample tube and the sample is irradiated with a 75 W G.E. visible spotlight an informative spectrum results (see Fig. 2). The very strong, sharp signal with a *g*-value equal to 2.002 corresponds to the free radical Et$_3$N$^{\cdot+}$ since a sharp signal with a *g*-value of 2.0025 is characteristic of an organic free radical[20]. A Ru(I) ion in a strong octahedral field has one more electron than the t_{2g} state can accommodate. This electron must enter the e_g state giving the complex a net spin of 1/2. For this state the *g*-values are close to the free spin value, i.e. 2.002. A slight shift can be caused by the spin-orbit coupling to the $t_{2g}^5\,e^2$ state[21].

In Fig. 3 the visible absorption spectrum (Cary 14) of an aqueous ~10^{-5} M Ru(bipy)$_3$ Cl$_2$ solution and a literature chloroform solution are compared with photoacoustic spectra of the Ru(bipy)$_3^{2+}$ loaded crystalline zirconium phosphate and the solid Ru(bipy)$_3$ Cl$_2$. These spectra are similar to visible spectra of aqueous

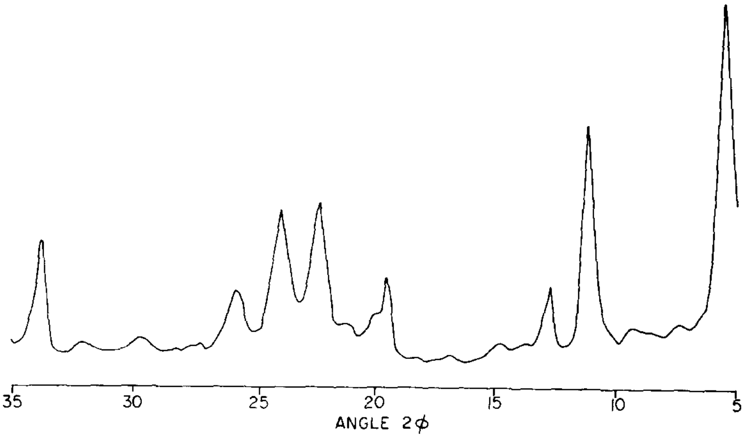

Fig. 1. X-Ray powder diffraction pattern of Ru(bipy)$_3$ Zr (PO$_4$)$_2$. The peak at $2\phi \cong 6°$ is shifted from ~11° reported in the hydrogen form of the zirconium phosphate, and from the Bragg relationship indicates an interplanar spacing of 15.9 Å.

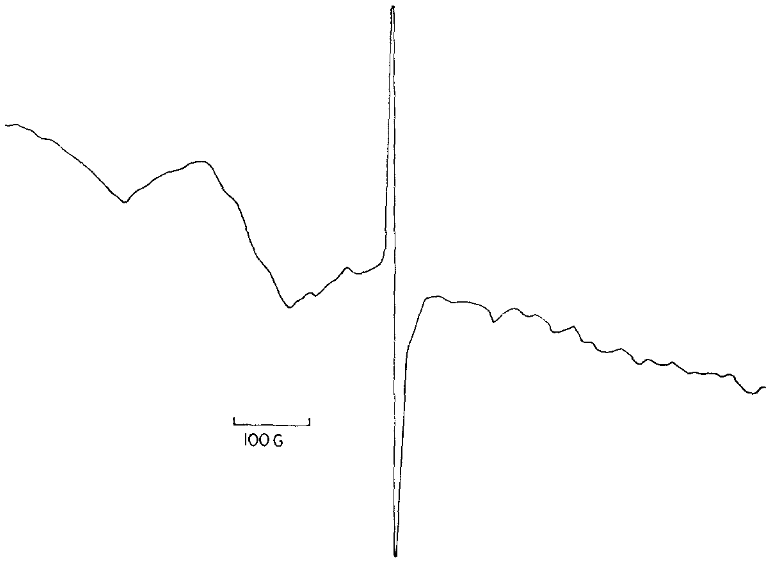

Fig. 2. EPR spectrum of solid Ru(bipy)$_3$ Zr (PO$_4$)$_2$ in the presence of liquid triethlamine that has been irradiated with visible light. The sharp peak at $g = 2.002$ indicates the presence of the Et$_3$N$\cdot^+$ free radical.

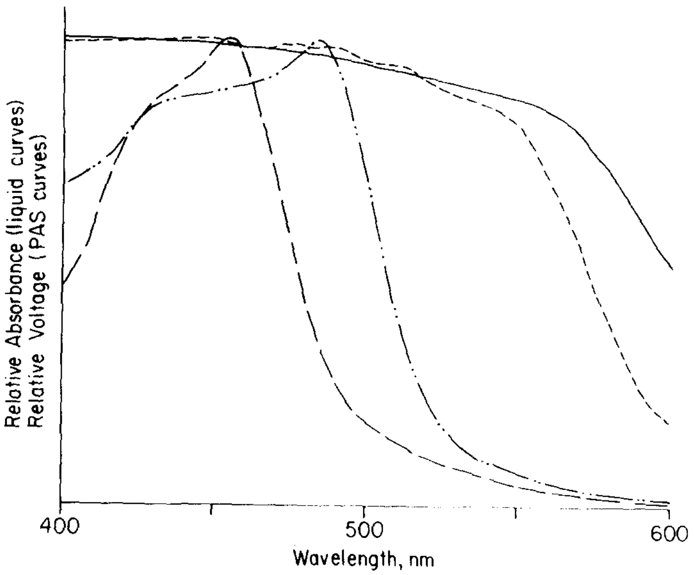

Fig. 3. Superposition of: absorption spectrum of aqueous Ru(bipy)$_3^{2+}$– – –; absorption spectrum of Ru(bipy)$_3^{2+}$ in chloroform – · · – · · –; dispersive photoacoustic spectrum of solid Ru(bipy)$_3$ Cl$_2$ – – – –; and dispersive photoacoustic spectrum of solid Ru(bipy)$_3$ Zr (PO$_4$)$_2$ —. The similarity of the spectra indicates the presence of an octahedral complex in the Ru(bipy)$_3$ Zr (PO$_4$)$_2$ as is more conclusively demonstrated by an EPR spectrum of the material (not shown).

Ru(bipy)$_3^{2+}$ previously reported[22] as well as to recently reported reflectance spectra of this same species incorporated into zeolite Y[9]. Thus one may assume that the octahedral environment of the ruthenium cation has not been altered by the incorporation of the Ru(bipy)$_3^{2+}$ ion into the zirconium phosphate lattice as is also indicated by the EPR spectral measurements described above.

The irradiation of the crystal in water with visible light results in the evolution of gas for a period of ~1 hr. Studies are presently underway to identify the photochemical products and to determine the mechanism of this reaction.

Acknowledgments—Financial support from the Department of Energy (Office of Basic Energy Sciences) and the Research Committee, University of Utah is gratefully acknowledged. We are also grateful for the use of K. L. DeVries' EPR spectrometer.

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