

## Bis(bipyridine)ruthenium(II) Cyanobridged Polymeric Cations

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*Polymeric cations made up of Ru(bpy)<sub>2</sub> units linked by cyanide bridges can be prepared by reacting Ru(bpy)<sub>2</sub>(CN)<sub>2</sub> with Ru(bpy)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. The reaction yields a mixture of polymeric cations of various chain lengths. Polymeric cations of this type have emitting excited states in solution, with lifetimes in the 50–100 ns range.*

### Introduction

Dicyanobis(2,2'-bipyridine)ruthenium(II), Ru(bpy)<sub>2</sub>(CN)<sub>2</sub>, has received a considerable deal of attention in recent years. Particularly, Demas and co-workers have studied the spectroscopic properties, the excited-state protolytic equilibria, and the behaviour in excited-state bimolecular processes of this molecule [1–3]. More recently, there has been a renewed interest on this complex due to the possibility of binding additional metal centers to the complex *via* cyanide bridges, while retaining the useful excited-state properties of the main chromophore [4–6].

In the usual procedure for the synthesis of Ru(bpy)<sub>2</sub>(CN)<sub>2</sub>, which involves reaction of cyanide ions with oxalatebis(2,2'-bipyridine)ruthenium(II), Ru(bpy)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> [7], substantial amounts of a brown, unidentified by-product are invariably formed. Based on our experience with bi- and tri-nuclear bimetallic complexes formed by Ru(bpy)<sub>2</sub>(CN)<sub>2</sub>, we suspected this by-product to be some polymeric or oligomeric species made up of Ru(bpy)<sub>2</sub> units connected *via* cyanide bridges. We report here on our attempts to arrive at such polymers by a direct route, and on the properties of the products obtained.

### Experimental

#### Materials

Ammonium hexachlororuthenate(IV) (Fluka), sodium cyanide and 2,2'-bipyridine (Baker), potassium oxalate (Carlo Erba), were commercial products

of reagent grade. Ru(bpy)<sub>2</sub>(CN)<sub>2</sub> [7] and Ru(bpy)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> [8], were prepared according to literature procedures.

#### Chromatography

Thin-layer chromatography was performed by using aluminium oxide IB-F 0.25 mm thick. All R<sub>f</sub> values were estimated to the center of the spot. The spots were visible by their own colors under visible light. Chromatographic columns were prepared with aluminium oxide 90 active neutral (70–230 mesh ASTM) (Merck).

#### Apparatus and Procedures

UV-VIS spectra were recorded with a Varian Cary 219 spectrophotometer. The emission spectra were measured with a Perkin Elmer MPF3 spectrofluorimeter equipped with a R928 Hamamatsu tube. The emission lifetimes were measured with a J.K. system 2000 ruby laser (frequency doubled; pulse half-width, 25 ns) in a single shot mode with oscillographic recording. Infrared spectra were recorded with a Perkin Elmer mod. 283 spectrophotometer in nujol mull. Potential sweep voltammetric curves were recorded by means of an Amel 448 three electrode oscillographic polarograph. A saturated calomel electrode (SCE) was used as reference electrode and the potentials are referred to it. The auxiliary electrode was a piece of platinum wire, and the indicator electrode was a platinum electrode with periodical renewal of the diffusion layer. Before each experiment, the platinum electrode was conditioned according to previously described procedures [9]. 0.1 M tetraethylammonium perchlorate was used as supporting electrolyte, and DMF solutions of the complexes were examined. Halfwave potentials for the reversible couples were taken as the mean of the anodic and cathodic peaks.

### Results and Discussion

The synthetic route chosen was to react Ru(bpy)<sub>2</sub>(CN)<sub>2</sub> with Ru(bpy)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, since Ru(bpy)<sub>2</sub>(CN)<sub>2</sub> is known to bind *via* cyanide bridges to 'naked' transi-

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tion metal ions [3, 4] and to react with transition metal complexes by displacing labile ligands [5, 6]. The oxalate ligand in  $\text{Ru}(\text{bpy})_2\text{C}_2\text{O}_4$  is relatively easily displaced by other ligands, such as free cyanide. This feature is used in the standard method for the preparation of  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  [7].

### Synthesis

When methanolic solutions containing  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  and  $\text{Ru}(\text{bpy})_2\text{C}_2\text{O}_4$  in a 2:1 molar ratio were refluxed at 70 °C, no appreciable spectral change was observed, even after long periods of time. Thin layer chromatography on alumina plates with methanol, showed two well-separated components: a yellow-orange one with a  $R_f$  value corresponding to that of  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  ( $R_f = 0.73$ ) [7], and  $\text{Ru}(\text{bpy})_2\text{C}_2\text{O}_4$  which appeared as a dark purple crescent.

If 1 M  $\text{H}^+$  ( $\text{HClO}_4$  or  $\text{H}_2\text{SO}_4$ ) was added to this solution, an instantaneous change in the absorption spectrum occurred. This instantaneous change is exactly the sum of the changes exhibited by the separate components upon acidification and can be explained in terms of protonation of the cyanide [1, 2] and protonation or partial dechelation of the oxalate groups. On refluxing the solution at 70 °C, slower spectral changes were observed, which were related to a reaction occurring between  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  and  $\text{Ru}(\text{bpy})_2\text{C}_2\text{O}_4$ .

Three fractions were resolvable on alumina plates with methanol. Two were identified as the unreacted  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  and the  $\text{Ru}(\text{bpy})_2\text{C}_2\text{O}_4$ , which still appeared as a dark purple crescent. The third fraction appeared between the two reactants as a broad-tailed brown spot. After four hours no appreciable variations of the absorption spectra of the reaction mixture were observed. The reaction mixture was neutralized with KOH. The final volume of the solution was brought to approximately 10 ml (by evaporating the solvent at room temperature); the precipitate which formed (potassium oxalate and potassium sulphate) was filtered off and the solution was passed through a  $2 \times 100$  cm neutral aluminium oxide chromatographic column and eluted with methanol.

The reaction products could be efficiently separated from the unreacted starting materials,  $\text{Ru}(\text{bpy})_2\text{C}_2\text{O}_4$  and  $\text{Ru}(\text{bpy})_2(\text{CN})_2$ , since the first one remained absorbed in the column while the second was the first eluted species. The reaction products appeared on the column as a very broad band containing several components. Since the components were not resolvable in these conditions, the whole broad band was collected as a single fraction. This fraction was dried at room temperature. The solid products were soluble in water and very soluble in most polar organic solvents. Attempts to separate the product fraction into single components by using weakly acidic cationic exchange resins with various types of eluents failed to give better results.

Strongly acidic cationic exchange resins gave irreversible retention of the components, suggesting that these components were highly charged products.

In all the experiments no appreciable difference could be observed if head or tail portions of the product fraction were used instead of the whole fraction. In view of the unsatisfactory separation of the fraction all experiments reported here refer to the material recovered from the whole fraction. In this sense, the results reported below are to be taken as average properties of a mixture of distinct but remarkably similar products.

### Characterization of the Products

The visible spectra are not very useful for elucidation of the structures of these products. In fact they are dominated by the typical  $d-\pi^*$  transitions of the  $\text{Ru}(\text{bpy})_2\text{X}_2$  chromophore. Also the solvent effect (Fig. 1) is as expected for all the chromophores of this type [6, 7, 10, 11].

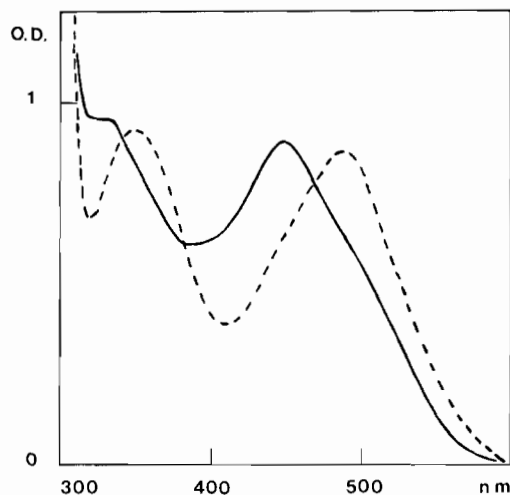
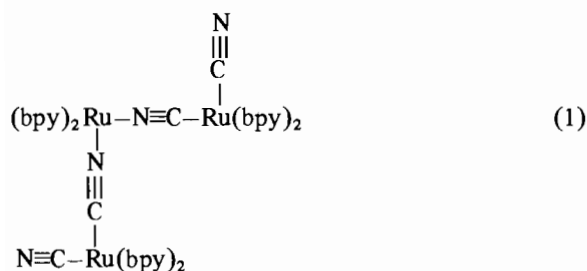


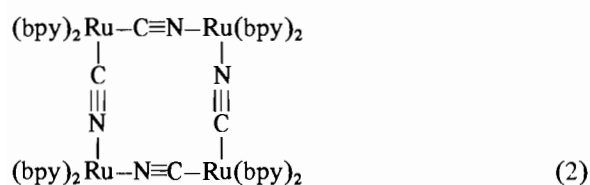
Fig. 1. Product absorption spectra in DMF (---) and water (—) solutions.

The IR spectra were very similar to that of the starting  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  reactant, except for the presence of additional characteristic sulphate anion bands, and for small but definite shifts of the cyanide stretching bands towards high energy ( $\nu_{\text{CN}} = 2060, 2095 \text{ cm}^{-1}$  to be compared with 2050, 2070  $\text{cm}^{-1}$  for  $\text{Ru}(\text{bpy})_2(\text{CN})_2$ ). These shifts are typical of cyanide bridge formation [4–6, 12, 13]. The oxalate bands (in the 1600–1700  $\text{cm}^{-1}$  region), which are present in the starting  $\text{Ru}(\text{bpy})_2\text{C}_2\text{O}_4$  reactant, were completely absent in the spectra of the products. These IR results seem to indicate that all the reaction products contain polynuclear species in which the oxalate ligand of  $\text{Ru}(\text{bpy})_2\text{C}_2\text{O}_4$  has been completely replaced by cyanide bridges from  $\text{Ru}(\text{bpy})_2(\text{CN})_2$ .

Two possible general structures for these poly-nuclear species can be envisioned: (i) open-chain polymers of formula  $[\text{Ru}_n(\text{bpy})_{2n}(\text{CN})_{n+1}](\text{SO}_4)_{(n-1)/2}$ , with  $n \geq 3$ , odd; e.g. for  $n = 3$ ,



(ii) cyclic polymers of formula  $[\text{Ru}_n(\text{bpy})_{2n}(\text{CN})_n](\text{SO}_4)_{n/2}$  with  $n \geq 4$ , even; e.g. for  $n = 4$ ,



The elemental analyses of the product mixture are reported in Table I. For comparison, the theoretical analyses of  $\text{Ru}(\text{bpy})_2(\text{CN})_2$ , the cyclic polymer (any  $n$  value), and open chain polymers of various chain length ( $n = 3, 5, 7, \infty$ ) are also reported in Table I. It is to be noted that the theoretical analyses of the various type of polymers are not very different. Within this difference, the elemental analyses of the product mixture seems to fit best (see especially the O and S analyses) those of either a cyclic polymer (any value of  $n$ ) or an open-chain polymer of high length ( $n \rightarrow \infty$ ).

In conclusion, the available evidence indicates that the reaction between  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  and  $\text{Ru}(\text{bpy})_2\text{-C}_2\text{O}_4$  yields a complex mixture of polymers of the type shown in eqns. (1) and (2), of various chain length. It can be noted that molecular weight or electronic charge [14] are of very limited value for determining the chain length in systems of this kind, because of their poly-electrolyte nature.

Of some interest from a photochemical standpoint is the fact that the polymeric species obtained in this work are luminescent in solution at room temperature. The emission spectra of the products in aqueous and DMF solution are shown in Fig. 2. The shape and the solvent shifts are rather typical of a  $d-\pi^*$  emission of  $\text{Ru}(\text{bpy})_2\text{X}_2$  chromophores [6, 7]. Interestingly, the emission is red-shifted with respect to that of  $\text{Ru}(\text{bpy})_2(\text{CN})_2$ . Since it has been shown that binding metals to  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  via cyanide bridges invariably causes blue-shifts in the emission of this chromophore [2, 4, 6], this result seems to indicate that the emitting chromophores in the polymeric compounds are the  $\text{Ru}(\text{bpy})_2$  units containing N-bonded cyanides. If N-bonded cyanide can be considered as a pseudo-amine ligand, this chromophore is expected to have lower lying excited states than the C-bonded one [15].

Emission lifetimes of the products are shorter than those of  $\text{Ru}(\text{bpy})_2(\text{CN})_2$ , being typically in the 50–100 ns range. These relatively short lifetimes may be related either to some interaction between the individual chromophores in the polymer, or to the relatively low position expected for the ligand field levels in the N-bonded  $\text{Ru}(\text{bpy})_2$  chromophore.

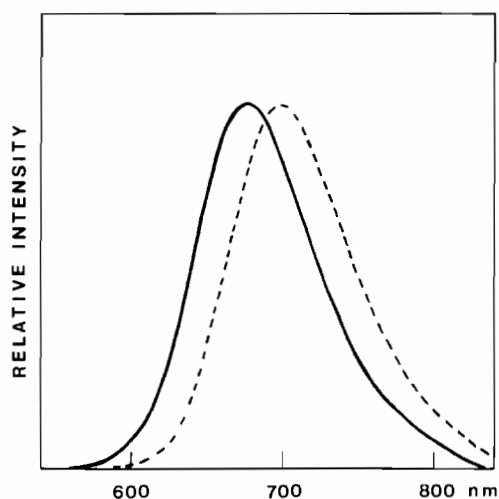


Fig. 2. Product emission spectra in DMF (---) and water (—) solutions.

TABLE I. Elemental Analyses for Bis(bipyridine)ruthenium(II) Complexes.

Compound	C	H	N	Ru	S	O
$\text{Ru}(\text{bpy})_2(\text{CN})_2^a$	56.72	3.44	18.05	21.70		
$[\text{Ru}_n(\text{bpy})_{2n}(\text{CN})_n]^{n+}(\text{SO}_4)_{n/2}$ , $n \geq 4$ , even <sup>a</sup>	51.69	3.28	14.36	20.73	3.28	6.56
$[\text{Ru}_3(\text{bpy})_6(\text{CN})_4](\text{SO}_4)^a$	53.32	3.33	15.55	21.05	2.22	4.44
$[\text{Ru}_5(\text{bpy})_{10}(\text{CN})_6](\text{SO}_4)_2^a$	52.66	3.31	15.07	20.92	2.65	5.30
$[\text{Ru}_7(\text{bpy})_{14}(\text{CN})_8](\text{SO}_4)_3^a$	52.38	3.30	14.87	20.87	2.83	5.66
$[\text{Ru}_n(\text{bpy})_{2n}(\text{CN})_{n+1}]^{(n-1)+}(\text{SO}_4)_{(n-1)/2}$ , $n \rightarrow \infty^a$	51.69	3.28	14.36	20.73	3.28	6.56
Reaction products <sup>b</sup>	51.67	3.55	13.52	21.16	3.45	6.89

<sup>a</sup>Theoretical values.

<sup>b</sup>Experimental values.

Cyclic voltammetry has not been able to differentiate between N-bonded and C-bonded Ru(bpy)<sub>2</sub> chromophores in the polymers. In fact, the products exhibit an apparently single oxidation wave at +0.83 V vs. SCE. At this stage it is not possible to decide whether this result comes from effective delocalization between adjacent Ru atoms or from experimental limitations. Preliminary experiments have shown that solutions of the products, on partial oxidation with PbO<sub>2</sub> or other oxidants, change from brown to blue-green, with the appearance of a broad, intense band in the red and near IR region ( $\lambda_{\text{max}} = 950 \text{ nm}$ , halfwidth 5000 cm<sup>-1</sup>) which seems to be typical of a Robin and Day Class II mixed valence species [16].

As pointed out before, in the preparation of the Ru(bpy)<sub>2</sub>(CN)<sub>2</sub> complex given by Demas and co-workers [7], a brown unidentified byproduct was obtained. This product is usually separated from Ru(bpy)<sub>2</sub>(CN)<sub>2</sub> by column chromatography on silica gel. We have obtained solutions of this by-product by extracting it from the solid substrate with boiling CH<sub>3</sub>CN or DMF. All the experiments performed on this 'compound' (absorption spectra, luminescence spectra, lifetimes, IR spectra) gave results identical to those described here, indicating that the 'by-product' of the synthesis of Ru(bpy)<sub>2</sub>(CN)<sub>2</sub> has the polymeric cyano-bridged structure described in this work.

## Conclusion

This work shows that polymeric cations made up of Ru(bpy)<sub>2</sub> units bonded *via* cyanide bridges can be very easily obtained. These polymeric cations still have long-lived excited states and redox properties similar to those of the monomeric unit. This makes such species quite interesting from the standpoint of photophysics and mixed-valence chemistry. It seems likely that careful control of the reaction conditions (pH, temperature) coupled with improvements in separation techniques, will allow the isolation and

characterization of single, discrete polymeric species. Also, more sophisticated synthetic routes involving the sequential addition of building units seem to be feasible in the future.

## Acknowledgments

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