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**TRANSFER OF TRISPOLYPYRIDINERUTHENIUM(II) CHELATES  
IN THEIR GROUND AND EXCITED STATES ACROSS  
THE WATER/1,2-DICHLOROETHANE INTERFACE**Josef HANZLÍK<sup>a</sup> and AnnaMaria CAMUS<sup>b</sup><sup>a</sup> *The J. Heyrovský Institute of Physical Chemistry and Electrochemistry,  
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*Dedicated to the memory of Prof. J. Heyrovský on the occasion of his centenary.*

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Transfer of trispolypyridineruthenium(II) chelates of the type  $[\text{Ru}(\text{chel})_3]^{2+}$ , where chel is 2,2'-bipyridine, 2,2'-bipyrimidine or 2,2'-bipyrazine, in their ground states across the water/1,2-dichloroethane interface was classified as the reversible transfer of a divalent cation. Thermodynamic and transport parameters characterizing this transfer were obtained from voltammetric measurements. Photoexcitation of these chelates gives rise to the photoinduced charge transfer across the water/1,2-dichloroethane interface.

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For a long time, trisbipyridine complex of ruthenium and its analogs have attracted a great deal of interest thanks to their properties, which can be utilized in photochemical and photophysical experimental studies. Extensive work focused on excited states of these complexes with the aim to achieve chemical conversion of the solar energy in liquid medium. For this purpose, micellar and polymer systems, as well as electrodes with modified surfaces of metals and semiconductors, have been also examined<sup>1</sup>.

Not left aside, electrochemical instrumentation has been developed for the study of the charge transfer across the interface of two immiscible electrolyte solutions, the water/organic solvent interface being the most frequent case<sup>2</sup>. Some time ago, the transfer of both alkylviologens as prospective mediators of electron transfer<sup>3</sup>, and trisbipyridine complexes of transition metals inclusive ruthenium<sup>4</sup> have been studied. Much attention has been paid to electron transfer across the interface between two immiscible electrolyte solutions, because this system is considered as the simplest model of biological charge transfer processes<sup>5</sup>. However, progress in this field has been slow, and only few systems of this type have been known and studied<sup>6-8</sup>.

The idea that the interface between two immiscible liquids can ensure the charge separation in the photochemical excitation, has been first implemented by Calvin<sup>9</sup>. Recently, several communications have appeared reporting the photoinduced charge transfer across the interface of two immiscible liquids, where the photoactive particle is represented by tetraphenylborate anion<sup>10</sup> or tris(bipyridine)Ru(II) complex<sup>11-12</sup>.

As shown earlier by Crutchley and Lever<sup>13</sup>, tris(bipyrazine)Ru(II) complex in its <sup>3</sup>MLCT state is a stronger oxidation agent than the corresponding bipyridine complex, the oxidation potential of which is close to 1.3 V. Effort to make use of systematic changes in properties, inclusive of changes in the redox potential, in a series of structurally similar compounds, has led us to the synthesis of symmetric trispolypyridine chelates of ruthenium with 2,2'-bipyridine (bpy), 2,2'-bipyrimidine (bpm) and 2,2'-bipyrazine (bpz), cf. Fig. 1.

The aim of this work has been firstly to deal with the transfer of trischelateruthenium(II) mentioned above across the water/1,2-dichloroethane interface. In the second part, the attention has been paid to the charge transfer in these systems under the conditions of photoexcitation.

## EXPERIMENTAL

### Chemicals

The ligands bpy and bpz were purchased from Fluka A.G. and Aldrich, bpm was prepared according to the procedure<sup>14</sup>. Chlorides of trispolypyridineruthenium(II) chelates, [Ru(chel)<sub>3</sub>]Cl<sub>2</sub> · x H<sub>2</sub>O, were prepared as described in literature for chel = bpy (ref.<sup>15</sup>), bpm (ref.<sup>16</sup>) or bpz (ref.<sup>17</sup>).

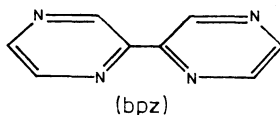
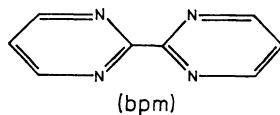
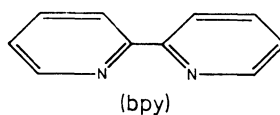


FIG. 1

Chemical formulas of ligands: bpy is an abbreviation for 2,2'-bipyridine; bpm for 2,2'-bipyrimidine; bpz for 2,2'-bipyrazine

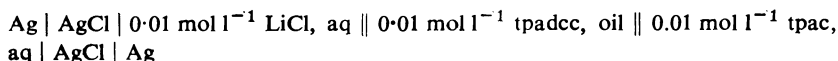
For the sake of photoactivity or better solubility, it was necessary to replace chloride as the counter ion by tetraphenylborate or by 7,8,9,10,11,12-hexabromo-1-carba-*closo*-dodecaborate(1-) (abbreviated hereafter as ccd). A small excess of the aqueous solution of sodium tetraphenyl borate or caesium ccd was added to the aqueous solution of the chloride salt of the corresponding complex. The resulting precipitate was sucked off, washed with water and dried in vacuum over phosphorus pentoxide.

Lithium chloride was used as the base electrolyte in the aqueous phase, and tetrabutylammonium chloride (abbreviated here after as tbac) or tetraphenylarsonium chloride (tpac) were used for the preparation of the reference electrode. All these compounds were purchased from Fluka A.G. as puriss. p.a. grade chemicals. Three compounds were used as the base electrolyte in the organic phase. Tetrabutylammonium tetraphenylborate (tbatpb) was prepared as described in literature<sup>18</sup>. Tetraphenylarsonium dicarbollycobaltate (tbadcc)<sup>19</sup> and caesium ccd<sup>20</sup> were prepared in the Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Řež near Prague. Tetrabutylammonium salt of ccd was precipitated from the solution of Cs ccd in a water-ethanol mixture by the 10% aqueous solution of tetrabutylammonium hydroxide. The isolation of this quaternary salt proceeded as in case of quaternary tetraphenylborate.

1,2-Dichloroethane (puriss. p.a., Fluka A.G.) was used without further purification. Acetonitrile (for UV spectroscopy, Fluka A.G.), which served as the solvent in some voltammetric measurements, was desiccated by fractional distillation from its mixture with phosphorus pentoxide. Water was doubly distilled from a quartz glass apparatus. All other components were purchased as reagent grade chemicals from Lachema, Brno, Czechoslovakia.

#### Apparatus

Methods and the four-electrode assembly for voltammetric measurements at the interface between two immiscible electrolyte solutions were described previously<sup>2,4</sup>. The water-organic solvent interface had an area of 10.21 mm<sup>2</sup>. In case of the transfer of complexes in their ground states, the potential difference  $E$  of the galvanic cell



was controlled, which is the Galvani potential difference between the aqueous (w) and the non-aqueous (o) phase defined as  $\Delta_o^w \varphi = \varphi(w) - \varphi(o)$ , related to the formal potential difference for tetraphenylarsonium cation,

$$E = \Delta_o^w \varphi - \Delta_o^w \varphi_{\text{tpa}^+}^{\theta} .$$

The value  $\Delta_o^w \varphi_{\text{tpa}^+}^{\theta} = 0.364 \text{ V}$  was obtained from extraction data<sup>21</sup>.

In case of the transfer of complex ions under the conditions of photoexcitation, tpadcc in the galvanic cell above was replaced by tbatpb or tbaccd, and the corresponding quaternary chlorides were used for the preparation of the reference electrode.

The stationary disc platinum electrode, which was made of the platinum wire having a diameter of  $7 \cdot 10^{-9} \text{ m}$  sealed into glass, was used as the working electrode in the classical three-electrode voltammetric measurements<sup>22</sup>. UV-VIS spectra were measured by means of the spectrophotometer SPECORD M40 (Zeiss, Jena). The Schlenk flask technique<sup>23</sup> was applied whenever the presence of inert atmosphere was required.

Photoelectrochemical experiments were carried out in the four-electrode cell shown in Fig. 2. The cell has been designed so as to allow electrochemical measurements of the charge transfer

across the interface between two immiscible electrolyte solutions under the simultaneous introduction of the light beam into a defined part of the system. This was accomplished by means of the optical guide, which was a rod of 5 mm in diameter and 12 cm in length made of the optically pure quartz. In order to minimize the optical losses, the rod was silver-plated<sup>24</sup> and then coated with a layer of the silicon rubber. The optical guide was fixed to advantage with the help of the screw GL connections, which are vacuum-tight and enable a gradual change in the position of the optical guide relative to the interface. This construction ensures that the illumination of the reference electrodes is avoided, and hence their special shading is unnecessary. A water-cooled mercury pressure lamp HBO 1500 (Narva, Berlin), equipped with a screen adapted to the optical guide, was used as the source of the light.

## RESULTS AND DISCUSSION

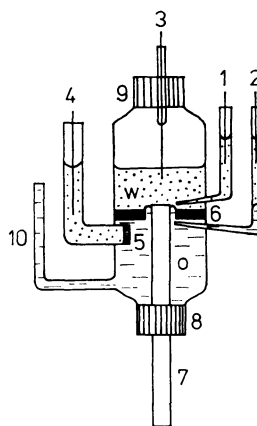
### *Transfer of Trispolypyridine Complexes of Ruthenium across the Water/1,2-Dichloroethane Interface*

Transfer of  $[\text{Ru}(\text{chel})_3]^{2+}$  cation, where chel is bpy, bpm or bpz, from the aqueous phase to 1,2-dichloroethane was studied by cyclic voltammetry. All quantitative data were obtained from single-scan measurements. Figure 3 displays the cyclic voltammogram of a solution containing the 1 : 1 mixture of complexes with chel bpy and bpm. The potential range (window) is controlled by processes referred to as C and D. In these processes the base electrolyte ions are transferred, those formed from tpadcc most probably prevail.

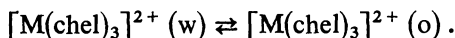
The processes A and B are due to the transfer of chelates themselves. The transfer of tris-(bipyridine)Ru(II) cation and of analogous chelates of other transition metals was investigated previously with an aim to trace the effect of nature of the central metal atom on the transfer process<sup>4</sup>. From the mechanistic point of view, trisbipyridine complexes were shown to fall into two groups. For Co(II), Cu(II) and Zn(II),

FIG. 2

Cell for photoelectrochemical experiments at the interface between two immiscible electrolyte solutions: 1, 2 reference argenchloride electrodes; 3, 4 counter platinum electrodes; 5 sintered glass (G5) separating the counter electrode from the non-aqueous phase; 6 the glass barrier with the round hole ensuring the geometry of the phase boundary formed between water and the organic solvent; 7 quartz optical guide; 8, 9 GL connections; 10 the adjustment of the interface; w the aqueous phase; o the non-aqueous phase



the transfer of the complex ion is complicated by its chemical equilibria with the ligand. In case of Ru(II), as well as Os(II), Fe(II) and Ni(II), the transfer of the complex  $[M(\text{chel})_3]^{2+}$  from water to dichloroethane exhibits the behaviour, which is characteristic for a simple, diffusion-controlled process without any chemical complication



The processes A or B in Fig. 3 correspond to the transfer of tris-(bipyridine)Ru(II) or tris(bipyrimidine)Ru(II) ion, respectively. Diagnostic voltammetric criteria for a reversible electron transfer reaction at an electrode<sup>25</sup> apply also to the simple ion transfer across the interface of two immiscible liquids<sup>26</sup>. On their basis, the transfer reactions of trischelateruthenium(II) with chel bpm and bpz proceed according to the same mechanism as with chel bpy. The only remarkable difference between the cases for bpy and bpm, which is apparent from Fig. 3, is the considerable difference in formal potentials of the ion transfer, cf. the processes A and B. On the other hand, the difference in diffusion coefficients is rather small.

Theory of the cyclic voltammetry<sup>25</sup> allows to evaluate the formal potential of the ion transfer  $E^\theta$  for the system studied.  $E^\theta$  is closely related to the formal Galvani potential difference  $\Delta_o^w \varphi_{\text{compl}}^\theta$ ,

$$E^\theta = \Delta_o^w \varphi_{\text{compl}}^\theta - \Delta_o^w \varphi_{\text{ref}}^\theta$$

which can be obtained from  $E^\theta$ , provided that the formal potential difference of the reference  $\text{tpa}^+$  ion is known.

Table I summarizes reversible half-wave potentials  $E_{1/2}^{\text{rev}}$ , formal Galvani potential differences  $\Delta_o^w \varphi_{\text{compl}}^\theta$ , diffusion coefficients in water  $D_w$  and the standard Gibbs energies of the  $[\text{Ru}(\text{chel})_3]^{2+}$  ion transfer from water to 1,2-dichloroethane, which were calculated according to the relationship

$$\Delta G_{\text{tr, compl}}^{\theta, \text{w} \rightarrow \text{o}} = 2F \Delta_o^w \varphi_{\text{compl}}^\theta .$$

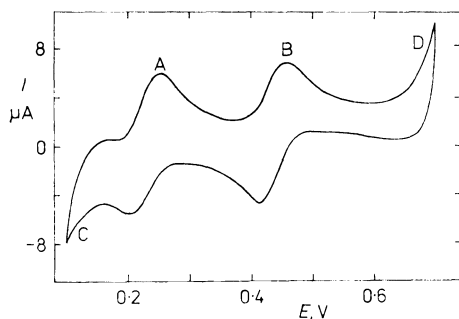


FIG. 3  
Cyclic voltammogram of the mixture of two complexes  $[\text{Ru}(\text{chel})_3]\text{Cl}_2$ , where chel is bpy and bpm. Composition of the aqueous phase:  $0.01 \text{ mol l}^{-1}$  lithium chloride,  $2 \cdot 10^{-4} \text{ mol} \cdot \text{l}^{-1}$  complex in the mixture at a concentration ratio of 1 : 1. Composition of the organic phase:  $0.01 \text{ mol l}^{-1}$  tpadcc in 1,2-dichloroethane. Polarization rate:  $0.05 \text{ V s}^{-1}$ , multi-sweep mode

Values of the transfer Gibbs energy in Table I imply that the complex with bpy has a rather hydrophobic character, in contrast to complexes of bpm and bpz, which are strongly hydrophilic. Assuming the same and unchangeable structure of complexes in an analogous series, such a behaviour can be ascribed to a change in the ligand structure. Note that nitrogen atom substitutes for C—H group in *meta* or *para* positions relative to the coordinating atom in case of bpm or bpz, respectively. The change in structure leads first of all to a change in bonding, inducing a change in energy of the redox orbitals, which can be evidenced by the electrochemical reduction of these complexes<sup>27</sup>. While the solvation of the complex with bpy occurs without pronounced electrostatic interactions, a strong bonding interaction between the lone  $sp^2$  electron pair localized on nitrogen and the solution species can be expected for complexes with bpm and bpz. It is known that through this electron pair, the chelate can coordinate another central atom, thus forming polynuclear complexes<sup>28</sup>.

There is a competition for this acceptor site between molecules of water and penta-aqualithium(I) ion, which is present in the aqueous solution of lithium chloride used here as the base electrolyte<sup>29</sup>. Somewhat lower values of diffusion coefficients of complexes with heteroligands bpm or bpz indicate that the size of these particles increased. Another argument favouring the interaction with the more voluminous solvated lithium ion is that on comparing the heteroligands bpm and bpz, the complex with the latter ligand is more hydrophilic. Such a behaviour stems obviously from the existence of steric barriers, which are higher for solvation of the complex with bpm, where the coordination centres are adjacent to each other, than in case of the complex with bpz, where these centres are more distant. Such a location mechanism of changes in solvation properties along the series of analogous complexes appears to be quite probable<sup>30,31</sup>.

TABLE I

Thermodynamic and transport constants for the transfer of  $[\text{Ru}(\text{chel})_3]^{2+}$  ion ( $1 \cdot 10^{-4} \text{ mol l}^{-1}$ ) from water to the non-aqueous phase. Base electrolytes:  $0.01 \text{ mol l}^{-1}$  lithium chloride in water and  $0.01 \text{ mol l}^{-1}$  tpadcc in 1,2-dichloroethane

chel	$E_{1/2}^{\text{rev}}$ V	$\Delta_{\text{O}}^{\text{w}} \varphi_{\text{compl}}^{\beta}$ V	$\Delta G_{\text{tr, compl}}^{\beta, \text{w} \rightarrow 0}$ kJ mol <sup>-1</sup>	$D_{\text{w}} \cdot 10^6$ cm <sup>2</sup> s <sup>-1</sup>
bpy	0.245	0.118	-22.70	2.50
bpm	0.430	0.067	12.90	2.35
bpz	0.450	0.087	16.80	2.35

*Photoinduced Transfer of Trispolypyridineruthenium(II) Chelates across the Water/1,2-Dichloroethane Interface*

Transfer of trispolypyridineruthenium(II) chelates across the water/1,2-dichloroethane interface assisted by white light (UV, VIS) illumination was studied under the potentiostatic conditions. Electrical current, which flows through the photoelectrochemical cell (Fig. 2), was measured at a constant potential difference between the aqueous and the organic solvent phase. By definition, the electrical current connected with the transfer of the positive charge from the aqueous to the non-aqueous phase is considered as positive. The cell design allows to bring the light beam close to the phase boundary from either phase side.

As the base electrolytes, lithium chloride and tbatpb (photoactive anion) or tbaccd (photoinactive anion) were present in water and the organic solvent, respectively. Upon the illumination of the non-aqueous phase containing tbatpb, the photocurrent was observed, which was ascribed to the transfer of the excited tetraphenylborate anion or products of its photodecomposition<sup>10</sup>. In the presence of the photoinactive ccd anion, no photocurrent was detected.

When the light beam was introduced into the aqueous phase close to the boundary of the immiscible base electrolyte solutions, no photocurrent was observed in the potential range available, cf. the curve 1 in Fig. 4. However, upon an addition of

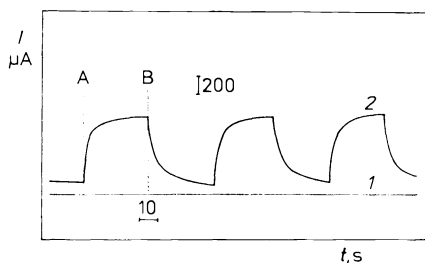


FIG. 4

Time dependence of the photocurrent at a constant potential of 0.25 V. Composition of the aqueous phase: curve 1  $0.01 \text{ mol l}^{-1}$  lithium chloride, curve 2  $0.01 \text{ mol l}^{-1}$  lithium chloride and  $1 \cdot 10^{-3} \text{ mol l}^{-1}$  tris(bipyrazine)Ru(II) chloride. Composition of the non-aqueous phase:  $0.01 \text{ mol l}^{-1}$  tbatpb in 1,2-dichloroethane. Illumination: A - switched on, B switched off

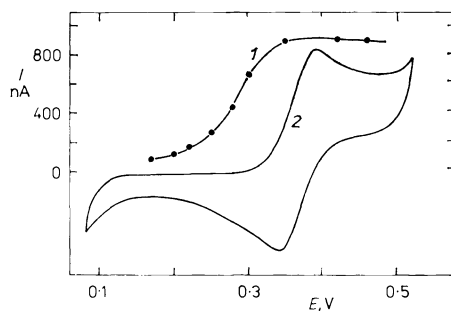


FIG. 5

Dependence of the limiting photocurrent on the applied potential (1), cyclic voltammogram of the transfer of tris(bipyrazine)Ru(II) in its ground state (2). Composition of the aqueous phase:  $0.01 \text{ mol l}^{-1}$  lithium chloride and  $1 \cdot 10^{-3} \text{ mol l}^{-1}$  tris(bipyrazine)Ru(II). Composition of the non-aqueous phase:  $0.01 \text{ mol l}^{-1}$  tbatpb in 1,2-dichloroethane

trispolypyridineruthenium(II) chelates in a concentration of  $1 \cdot 10^{-3} \text{ mol l}^{-1}$  to the aqueous phase, the positive photocurrent rises up as illustrated by the curve 2 in Fig. 4. Its dependence on time does not exhibit any lag period. The response of the system to illumination is immediate both when the light is switched on (the screen open), and when it is switched off (the screen closed). The limiting value is reached in twenty seconds from the beginning of illumination. The limiting photocurrent is proportional to the concentration of the ruthenium chelate in the concentration range from  $1 \cdot 10^{-4}$  to  $5 \cdot 10^{-3} \text{ mol l}^{-1}$ .

The effect of the applied voltage on the limiting photocurrent at a constant light intensity and a constant concentration of the chelate was studied to advantage with bpz and pbm, which complexes are transferred at more positive potentials than those with bpy. A maximum value of the limiting photocurrent – cf. the curve 1 in Fig. 5 – was observed close to the potential where the transfer from the aqueous to the non-aqueous phase of the ruthenium chelate in its ground state starts to occur. At more positive potentials, the photocurrent remains constant, but its rise-time increases and even doubles. Within about ten minutes of illumination of the solution, we observed only a small decrease of the peak current of the ground state chelate and the corresponding increase of the positive current at more negative potentials.

These experimental results show that photoactive particle is definitely the trispolypyridine chelate. For most of these substances, the particle with a relatively long life time is that in the lowest excited state  $^3\text{MLCT}$  (ref.<sup>32</sup>). The continuous production of this state in the close vicinity to the water/1,2-dichloroethane interface sets up conditions for its direct transfer across the interface and the inactivation in the organic solvent. In this mechanism, an essential role is played by resolution processes when the excited state arises in the aqueous solution and when it decays in the organic phase. The study of these processes is in progress. An important role in quenching the excited state  $^3\text{MLCT}$  is played by bimolecular chemical reactions. The solutions used were deaerated so that the quenching effect of oxygen was kept at minimum. On the other hand, a very strong effect of other quenchers in the solution on the magnitude of the photocurrent was demonstrated. The utilization of well-known reactions between the excited state  $^3\text{MLCT}$  of the trispolypyridine complexes and hexacyanochromium(III) cation<sup>33</sup> or 1,1'-dimethyl-4,4'-bipyridinium dication (methylviologen)<sup>34</sup> resulted in a decrease of the photocurrent measured at a constant potential with the increasing concentration of the quencher. The photocurrent was suppressed completely at the concentration ratio of the quencher to the complex equal to 166 or 2 for hexacyanochromium(III) or methylviologen cation, respectively.

Since the base electrolyte concentration exceeded the concentration of the photoactive particle by order of magnitude, we cannot neglect the possibility of photo-substitution reactions<sup>35</sup> inducing the facilitated transfer of the anion from the organic phase to water, which also gives rise to a positive electrical current. The interfacial region is probably a medium with the low dielectric constant, which would favour



such a process. The complete formation of ion pairs in this medium is also indicated by the difference in UV-VIS spectra of trispolypyridineruthenium(II) chelates in the aqueous and the non-aqueous solutions, as well as by the very low solubility of their tetraphenylborate salts in 1,2-dichloroethane. Quantitative photoexperiments would probably throw more light on the mechanism of the photoinduced charge transfer. They will be reported in a subsequent communication.

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