



## Study of Luminescence Quenching of Tri's(4, 4'-di-phenyl-2, 2'-bi-pyridine Ruthenium (II) Chloride & Tris(4, 7-Diphenyl-1, 10-Phe.nanthroline)

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**Abstract:** Luminescence quenching of  $[Ru(\text{diphenyl-bpy})_3]Cl_2$  and of  $[Ru(\text{diphenyl-phen})_3]Cl_2$  by 19 transition metal complexes is reported. These complexes have properties which permit them to supplement the widely used  $[Ru9bpy)_3]^{2+}$  and  $[Ru(\text{phen})_3]^{2+}$  sensitizers. The excited state of these complexes can also be tuned significantly by solvent variation. Quenching is predominantly by diffusion. Decay times, excited state energies, Stern-Volmer constant, by molecular quenching constants and association constants are Quenching appears to by energy and electron transfer constants are reported.

### I. Introduction

Luminescence Ru(II), Os(II) and Ir(III) complexes have proved to be nearly ideal photo-sensitizers [1-20]. They emit with long life times in fluid solutions. They can transfer energy and undergo excited state electron transfer process to a variety of organic and inorganic systems. They promise to be useful in solar energy conversion [9], chemical actinometrical of high power lasers, [11] and teaching experiments [12]. To date most work has been done with the original sensitizer,  $[Ru(\text{bpy})_3]^{2+}$  (bpy=2, 2'-bi-pyridine) and with  $[Ru(\text{phen})_3]^{2+}$  (phen=1, 10-phenanthroline), [1-7, 9-12] but work On analogous Os(II) and Ir(III) complexes is advancing rapidly [8, 9a, 13, 14]. The latter complexes greatly intend the available excited state energies [8].  $[Ru(\text{diphenyl-bipy})_3]Cl_3$  and  $[Ru(\text{diphneyl-phen})_3]Cl_2$  have been used in energy transfer studies to  $O^{13}$  and to some Cr(III) complexes [17]. We present here a survey of quenching of these complexes by a number of inorganic complexes which establishes their values in supplementing and extending the work with  $[Ru(\text{bpy})_3]^{2+}$  and  $[Ru(\text{phen})_3]^{2+}$ . Quenching appears to by energy and electron transfer. The room temperature absorption and Cl emission spectra of  $[Ru(\text{diphenyl-bpy})_3]Cl_2$  and  $[Ru(\text{diphenyl-phen})_3]Cl_2$  are given in Figure-I. For the solvent series water, alcohols, DMF the absorptions and emission spectra in alcoholic and aqueous glasses are given in Figure-2; the pronounced red shift of the alcoholic vs, the aqueous glass is especially dramatic here because of the sharpness of the spectra, Usually the emission is orange in the aqueous glass a distinct red in the alcoholic and deep, dull red in the DMF one. In terms of using  $[Ru(\text{diphenyl-bpy})_3]Cl_2$  and  $[Ru(\text{diphenyl-phen})_3]Cl_2$  as luminescent photosensltizers. Figure-I and Table-I and II reveal Interesting features,. Unlike the previously very successful and widely used  $[Ru(\text{bpy})_3]^{2+}$  and the related  $[Ru(\text{phen})_3]^{2+}$  both complexes exhibit strongly solvate chromic shifts on their absorption spectra and the energy of their sensitizing emitting state. A significant and useful 1-1.3- $\mu\text{m}^{-1}$  (3 - 4) variation of the excited state energy arises on going from water to DMF; continuous tenability by used of mixed solvents should be possible. Thus, for detailed probing of acceptor excited state properties a single donor could be used ever a substantial and essentially continuous energy range merely by varying the solvent.

### II. Experimental Section

$[R.u(\text{diphenyl-bipy})_3]Cl_3$  and  $[Ru(\text{diphenyl-phen})_3]Cl_2$  were prepared by procedures described elsewhere [21]. All other reagents were the same as those described earlier [15]. The luminescence intensity quenching measurement were carried out using the procedures and equipment described earlier [15], data were corrected for the trivial absorption of exciting and emitted light by the quenchers [22]. Excitation and emission wave lengths were selected to minimize corrections 408-, 436-, 460-, and 480-nm ox-citation and 600- or 650- am emission), correction factors rarely amounted to more than a few percent change in  $K_{sv}\phi$ . For the decay time,  $\tau$ , measurements with  $[Ru(\text{diphenyl-phen})_3]Cl_2$  the xenon flash apparatus described elsewhere was used [12c]. The strobe was, however, run at  $\sim 10$  m $\theta$  which gave an - 0.7- $\mu\text{s}$  duration, the phototube was an RCA 7164 R, and photographic recording of the oscilloscope traces was used. For the decay time measurements with  $[Ru(\text{diphenyl-bpy})_3]Cl_2$ , a laser system described elsewhere [24], was used except that the oscilloscope used a sampling plug in setup as a screening boxer integrator; results were displayed directly or an x-y recorder. Low temperature emission were measured in either ethanol-methanol (4/1 v/v), or di-methanol-water (4/1, v/v), or di-methylformamide (DMF) -  $CH_2Cl_2$ (9/1, v/v) glasses at 77°K. Emission data were not corrected for the spectral sensitivity of the system. Our phototube has a flat response in this region, however and comparison of

low temperature uncorrected spectra with corrected ones falling in the same region suggests that the spectral response is relatively flat only falling off rapidly beyond 850 nm. Distortions should be minimal, and errors in measurement on the sharp spectral features at 77°K should be insignificant.

### III. Results

The room temperature absorption and Cl emission spectra of [Ru(diphenyl-bpy)<sub>3</sub>]Cl<sub>2</sub> and [Ru(diphenyl-phen)<sub>3</sub>]Cl<sub>2</sub> are given in Figure-1. For the solvent series water, alcohols, DMF the absorptions and emission spectra in alcoholic and aqueous glasses are given in Figure-2; the pronounced red shift of the alcoholic vs, the aqueous glass is especially dramatic here because of the sharpness of the spectra, Usually the emission is orange in the aqueous glass a distinct red in the alcoholic and deep, dull red in the DMF one. At low temperatures the energy of the highest energy, emission maximum is E<sub>max</sub>. The energy at which the emission intensity on the short wave length side of E<sub>max</sub> falls to 5% of the intensity at E<sub>max</sub> is E<sub>5%</sub>, E<sub>5%</sub> and E<sub>max</sub> are tabulated in Table-I for both sensitizers in the glasses at 77 K. Decay times, τ<sub>0S</sub> of the complex in deoxygenated water, methanol and DMF at - 21°C are given also in Table-1. The intensity stern-Volmer plots were linear except for Ni<sup>2+</sup>, CO<sup>2+</sup>, and Cu<sup>2+</sup> which exhibited the upward curvature characteristic of a system showing both static and dynamic quenching [10, 24]. Figure-3 shows typical (φ<sub>0</sub>/φ) - 1 and (τ<sub>0</sub>/τ) - lvs [Q] plots for [Ru(diphenyl-phen)<sub>3</sub>]Cl<sub>2</sub> with Ni<sup>2+</sup>, φ's and τ's are emission intensities and decay times, respectively. The subscript zero denotes values in the absence of quencher. Table-II summarizes our quenching results. All data were further aqueous solution except for the acetylacetonato complex quenchers which used a methanol solvent. Intensity stern-Volmer quenching constants, K<sub>sv</sub> φ (=((φ<sub>0</sub>/φ)/[Q])) and for select systems the decay time Stern-volmer quenching constants, K<sub>sv</sub> τ (=((τ<sub>0</sub>/τ)-1)/[Q]), are presented. Except in the cases of Ni<sup>2+</sup>, CO<sup>2+</sup> and Cu<sup>2+</sup>, K<sub>sv</sub> φ and K<sub>sv</sub> τ were equal within experimental error. By molecular quenching constants, K<sub>2</sub>'s were computed from K<sub>2</sub>=K<sub>sv</sub> φ/τ<sub>0</sub> except for Ni<sup>2+</sup>, CO<sup>2+</sup> and Cu<sup>2+</sup> quencher were the correct form K<sub>2</sub>=K<sub>sv</sub> τ/φ<sub>0</sub> was used. Systems exhibiting photosensitivity by changes of emission intensity with 1-2 rain of irradiation are indicated in Table-II. Other systems may be sensitive, but not detected by this procedure. Also indicated in Table-II are the observed Stern-Volmer quenching constants and then K<sub>2</sub>'s for deactivation at zero ionic strength for [Ru(diphenyl-phen)<sub>3</sub>]Cl<sub>2</sub> or [Ru(diphenyl-bpy)<sub>3</sub>]Cl<sub>2</sub> Date are reported for the sensitizers with the largest K<sub>sv</sub>'s. with [Ni(CN)<sub>4</sub>]<sup>2-</sup>, [Ru(diphenyl-bpy)<sub>3</sub>]Cl<sub>2</sub> precipitated. With [Cr(NH<sub>3</sub>)<sub>2</sub>(NCS)<sub>4</sub>] both [Ru(diphenyl-bpy)<sub>3</sub>]Cl<sub>2</sub> and [Ru(diphenyl-phen)<sub>3</sub>]Cl<sub>2</sub> precipitated and no data are available.

### IV. Discussion

In systems exhibiting both static and dynamic quenching the following equations are obeyed [10, 12c, 24].

$$K_{sv} \tau = ((\tau_0/\tau) - 1)/[Q] \quad (1)$$

$$K_{sv} \phi = ((\phi_0/\phi) - 1)/[Q] \\ = (K_{sv} \tau + \beta K_{eq}) + K_{sv} \tau (\beta K_{eq})[Q] \quad (2)$$

Where [Q] is the quencher concentration and K<sub>eq</sub> is the first association constant between donor and quencher, β varies from 1.000 to ε<sub>DQ</sub>/ε<sub>D</sub> for optically dilute to dense solutions where ε<sub>D</sub> and ε<sub>DQ</sub> are the molar extinction coefficients of donor ant] donor-quencher association pair, respectively, at the excitation wave length. These expressions assume that the formal quencher concentration is always much greater than the donor concentration and that the association pair is not luminescent and can not dissociate on excitation to give free excited donor. K<sub>sv</sub>τ equals K<sub>2</sub>τ<sub>0</sub>, the normal Stern, Volmer quenching constant, under these conditions.

With Co<sup>2+</sup>, Ni<sub>2+</sub> and Cu<sub>2+</sub> where both dynamic and static quenching were present, (K<sub>sv</sub> + β K<sub>eq</sub>) was obtained from the intercepts of the K<sub>sv</sub>φ vs [Q] plots which were linear within experimental error. Using K<sub>sv</sub>τ evaluated from τ measurements (eq-1), β K<sub>eq</sub> was then calculated. K<sub>sv</sub>τ(β K<sub>eq</sub>) obtained from the slope of the K<sub>sv</sub> φ vs [Q] plot agreed within experimental error with the product evaluated from the separately obtained terms. Since our experiments were always run under optically dilute conditions (< 0.1), β=1. The calculated K<sub>eq</sub>'s are summarized in Table-III.

Evidence for upward curvature. Additionally with [Ru(diphenyl-phen)<sub>3</sub>]Cl<sub>2</sub> and dam show that no labile chloro, amine, acetylacetonato, cyano, oxalato and thiocyanato complexes all quench predominantly (> 90%) by dynamic process over the concentration ranges examined. The species studied included the open square-planar [Ni(CN)<sub>4</sub>]<sup>2-</sup> and Cu(4Acac)<sub>2</sub> which conceivably could bond through their free trans sites. Thus, we inter that static quenching is at most a sin or quenching component for all no labile quenchers with both complexes,

For evaluating the detailed quenching mechanism, knowledge of the energies of the donor sensitizing levels is needed. The room temperature data do not give good information on this quantity. The emissions of the donors are board and structure less, and their emitting states are too weak to resolve in absorption. We have therefore, used low temperature emission spectra coupled with the Fleischer sirloin for estimating zero point excited state energies E<sub>0</sub>'s [28]. Fleischer *et. al.* set. E<sub>0</sub> equal to E 5%. Thus, E<sub>0</sub>'s for sensitizers in water, methanol and DMF can be estimated from the E 5% values of Table-I. These E<sub>0</sub>'s compare with the solvent independent E<sub>0</sub>'s of

1.80 and 1.84  $\mu\text{M}_1$ ; for  $[\text{Ru}(\text{diphenyl-bpy})_3]\text{Cl}_2$  and  $[\text{Ru}(\text{diphenyl-phen})_3]\text{Cl}_2$ , respectively [15]. A word of caution is necessary. Measurements of  $E_0$ 's based on low temperature emission spectra rest on the assumption that the metal complex and solvent reorganization energies following excitation are small. If this is not true, then at room temperature, were the solvent and donor can relax fully, the available excitation energy will be substantially less than that indicated from the low temperature emission data. At 77°K the solvent and complex are clamped into a rigid environment that can not relax during the life time of the excited state. We believe this to be a minor problem since the emission and absorption change on going from room temperature to 77°K are very similar for both the complex.

In terms of the detailed diffusional quenching mechanisms, the result with  $[\text{Ru}(\text{diphenyl-phen})_3]\text{Cl}_2$  and  $[\text{Ru}(\text{diphenyl-bpy})_3]\text{Cl}_2$  are similar to and expand  $[\text{Ru}(\text{bpy})_3]^{2+}$  and  $[\text{Ru}(\text{phen})_3]^{2+}$ . The essentially non-quenching nature of I-demonstrates again that heavy atom quenching is unimportant in these heavy atom containing Ru(II) sensitizers. Further, the failure to find any consistent co-relation between the degree of quencher paramagnetism and quenching ability seems to rule out the existence of paramagnetic quenching of the Ru(II) sensitizers. For example, the paramagnetic  $\text{Ni}(\text{acac})_2$ ,  $\text{Co}(\text{acac})_2$ ,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  are substantially weaker quenchers than the diamagnetic  $\text{Co}(\text{acac})_3$  and  $[\text{Ni}(\text{CN})_4]^{2-}$ .

Excluding heavy atom or paramagnetic quenching, there remain three basic diffusional quenching mechanisms possible for our systems energy transfer ( $^*D + Q \rightarrow D + ^*Q$ ), oxidative electron transfer quenching ( $^*D + Q \rightarrow D^+ + Q^-$ ), reductive electron transfer quenching ( $^*D + Q \rightarrow D^- + Q^+$ ). All have been observed unambiguously with  $[\text{Ru}(\text{bpy})_3]^{2+}$  [3, 4, 10] and are possible with  $[\text{Ru}(\text{diphenyl-bpy})_3]\text{Cl}_2$  and  $[\text{Ru}(\text{diphenyl-phen})_3]\text{Cl}_2$ . Ex-diplex formation should not be possible on steric grounds, except possibility for the square-planar complex quenchers. We discount this possibility, however because all those quenchers have low-lying energy levels which should promptly deactivate the donor before an ex-diplex could form. The only quenching mechanism possible for  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}(\text{acac})_2$ ,  $[\text{PtCl}_4]^{2-}$  and the Cr(III) complexes is energy transfer. Reduction or oxidation should be too difficult. We attribute all quenching in these cases to energy into ligand field excited state.

$\text{Cu}(\text{acac})_2$  and  $\text{Cu}^{2+}$  in addition to having low-lying d-d levels to act as energy transfer quenchers can be readily reduced [29, 30] to Cu(I) species by the powerful reducing excited donors with  $\text{Cu}^{2+}$ . and  $^*[\text{Ru}(\text{bpy})_3]^{2+}$  flash photolysis shows a large component of oxidative quenching [31], we infer that  $\text{Cu}^{2+}$  also quenches  $[\text{Ru}(\text{diphenyl-bpy})_3]\text{Cl}_2$  and  $[\text{Ru}(\text{diphenyl-phen})_3]\text{Cl}_2$  at least in part by oxidative quenching to yield  $\text{Cu}^+$ .  $\text{Cu}(\text{acac})_2$  is also very readily reduced although the polarographic wave is irreversible, [30]. We assume quenching in these cases is at least in part by electron transfer. For  $\text{Cu}^{2+}$  in after, the substantially higher  $K_2$ 's compared to hexaquo  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  which can only quench by energy transfer to d-d states also supports the presence of a large component of electron transfer quenching with  $\text{Cu}^{2+}$ . Similarly for  $\text{Cu}(\text{acac})_2$ .  $K_2$  is much larger than for  $\text{Ni}(\text{acac})_2$  and  $\text{Co}(\text{acac})_2$  which can only quench by energy transfer this supports oxidative quenching by  $\text{Cu}(\text{acac})_2$ .  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{CoCl}(\text{NH}_3)_5]^{2+}$  and  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  are all photosensitive and quench with much higher  $K_2$ 's than most of the complexes which can quench by only energy transfer. We attribute a measure quenching component in these system to oxidative quenching to yield  $\text{Co}^{2+}$ . as has been established with quenching of  $[\text{Ru}(\text{bpy})_3]^{2+}$  by  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Co}(\text{Br}(\text{NH}_3)_6)]^{2+}$ . and  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  [3, 23]. Since energy transfer quenching is possible in all those cases, however some quenching by this path way can not be ruled out.

Thermodynamically  $[\text{Fe}(\text{CN})_6]^{3-}$  can quench  $[\text{Ru}(\text{bpy})_3]^{2+}$  and  $[\text{Ru}(\text{phen})_3]^{2+}$  by both energy and oxidative electron transfer [15], this should also be true for the  $[\text{Ru}(\text{diphenyl-bpy})_3]\text{Cl}_2$  and  $[\text{Ru}(\text{diphenyl-phen})_3]\text{Cl}_2$ . The essentially diffusion limited rate constant for quenching of these two complexes, however, is so much greater than most observed energy transfer quenching process that we believe electron transfer must be the dominant-quenching path way. For  $[\text{Fe}(\text{CN})_6]^{4-}$  with  $[\text{Ru}(\text{bpy})_3]^{2+}$  reductive quenching is possible [4c, d] and has been assigned as the major quenching path way, but flash photolysis evidence for reductive quenching is negative [31]. Alternatively, we have suggested based on the absence of any low temperature emission from  $[\text{Fe}(\text{CN})_6]^{4-}$ , that a low-lying d-d state is responsible for deactivation. Although reductive quenching of  $[\text{Fe}(\text{CN})_6]^{4-}$  is possible for  $[\text{Ru}(\text{diphenyl-bpy})_3]\text{Cl}_2$  and  $[\text{Ru}(\text{diphenyl-phen})_3]\text{Cl}_2$  [17].

For  $[\text{Ni}(\text{CN})_4]^{2-}$  with  $[\text{Ru}(\text{bpy})_3]^{2+}$  reductive quenching has also been postulated although potentiometric data do not support this claim [4c]. Energy transfer quenching is possible from both complexes to the  $-1.8 \mu\text{m}^{-1}$  lowest triplet of  $[\text{Ni}(\text{CN})_4]^{2-}$  [15]. The  $K_2$ 's for  $[\text{Ru}(\text{diphenyl-bpy})_3]\text{Cl}_2$  and  $[\text{Ru}(\text{diphenyl-phen})_3]\text{Cl}_2$  seem anomalously high for energy transfer to a ligand field excited state, approaching the diffusion limit. Also for  $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$   $K_2$  is quite large even though energy transfer is presumably involved. We hope by means of flash photolysis to determine the quenching mechanisms in these systems unambiguously.

## V. Conclusion

In terms of using  $[\text{Ru}(\text{diphenyl-bpy})_3]\text{Cl}_2$  and  $[\text{Ru}(\text{diphenyl-phen})_3]\text{Cl}_2$  as luminescent photosensitizers. Figure-I and Table-I and II reveal interesting features. Unlike the previously very successful and widely used  $[\text{Ru}(\text{bpy})_3]^{2+}$  and the related  $[\text{Ru}(\text{phen})_3]^{2+}$  both complexes exhibit strongly solvate chromic shifts on their absorption spectra and the energy of their sensitizing emitting state. A significant and useful 1-1.3  $\mu\text{m}^{-1}$  (3-4) variation of the excited state energy arises on going from water to DMF; continuous tenability by use of mixed

solvents should be possible. Thus, for detailed probing of acceptor excited state properties a single donor could be used over a substantial and essentially continuous energy range merely by varying the solvent. Both complexes also have very efficiencies of population of their sensitizing states [32]. Singlet oxygen production efficiencies in methanol set lower bounds of 0.68 and 0.80 for  $[\text{Ru}(\text{diphenyl-bpy})_3]\text{Cl}_2$  and  $[\text{Ru}(\text{diphenyl-phen})_3]\text{Cl}_2$  respectively [13]. Also in methanol at room temperature  $[\text{Ru}(\text{diphenyl-bpy})_3]\text{Cl}_2$  shows no variation in luminescence yield ongoing from the principal Ct band to below the zero point energy of the excited state [32].

**Table-1: Spectroscopic Properties of Sensitizers**

|   | $[\text{Ru}(\text{diphenyl-bpy})_3]\text{Cl}_2$ | $[\text{Ru}(\text{diphenyl-phen})_3]\text{Cl}_2$ |
|---|---|--|
| E5% (DMF) <sup>a</sup> , M <sup>-1</sup>                  | 1.698   | 1.700  |
| 0 (DMF) <sup>b</sup> , μS                                 | 0.19  | 1.62   |
| E 5% (CH <sub>3</sub> OH) <sup>a</sup> , μM <sup>-1</sup> | 1.815   | 1.810  |
| 0 (CH <sub>3</sub> OH) <sup>b</sup> , μS                  | 0.38  | 1.46   |
| E5% (H <sub>2</sub> O) <sup>a</sup> , μM <sup>-1</sup>    | 1.825   | 1.831  |
| 0 (H <sub>2</sub> O) <sup>b</sup> , μM <sup>-1</sup>      | 0.23  | 0.62   |

- a. E5% 'S are obtained from appropriate glass at 77  
 b. 0'S are in the deoxygenated pure solvent at ~ 21<sup>0</sup>C(19974)

**Table-II: Luminescence Quenching Data at-21<sup>0</sup>C**

| Quencher  | $[\text{Ru}(\text{diphenyl-bpy})_3]\text{Cl}_2$ |   | $[\text{Ru}(\text{diphenyl-Phen})_3]\text{Cl}_2$ |   |
|---|---|---|--|---|
|   | $K_{sv} \phi (K_{svt}), \text{M}^{-1}$          | $\text{IO}^{-9}K_2\text{M}^{-1}\text{S}^{-1}$ | $K_{sv} \phi (K_{svt}), \text{M}^{-1}$           | $\text{IO}^{-9}K_2\text{M}^{-1}\text{S}^{-1}$ |
| $[\text{Co}(\text{NH}_3)_4] (\text{ClO}_4)_3$       | 368 ± 9   | 1.32  | 161550 ± (1500)                                  | 2.01  |
| $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$           | 875 ± 30  | 3.02  | 2750 ± 150 (2750)                                | 3.15  |
| Co Cl <sub>2</sub>                                  | 13.5 ± (1.65 ± 0.15)                            | 0.0052  | 25.9 ± (6.5 ± 1.7)                               | 0.008   |
| CuSO <sub>4</sub>                                   | 371 ± 20 (96 ± 10)                              | 0.31  | 760 ± 35 (320)                                   | 0.42  |
| NiSO <sub>4</sub>                                   | 138 ± 0.5 (2.2 ± 0.2)                           | 0.007   | 50 ± 7 (14.0 ± 1.0)                              | 0.170   |
| Ni(acac) <sub>3</sub>                               | 50 ± 3  | 0.11  | 92 ± 2   | 0.04  |
| Co(acac) <sub>3</sub>                               | 317 ± 10  | 0.75  | 1060 ± 8   | 0.61  |
| Co(acac) <sub>2</sub>                               | 15 ± 2  | 0.038   | 128 ± 3  | 0.075   |
| Cr(acac) <sub>3</sub>                               | 168 ± 2   | 0.40  | 1040 ± 25  | 0.61  |
| Cu(acac)  | 420 ± 30  | 0.95  | 2415 ± 30 (2580)                                 | 1.3   |
| NaI   | 0.38 ± 0.001                                    | 0.0012  | 0.23 ± 0.01                                      | 0.0002  |
| $\text{K}[\text{Cr}(\text{NH}_3)_2(\text{NCSO}_4)]$ | 520 ± 10  | 1.75  | 2300 ± 120 (2300)                                | 3.1   |
| $\text{K}_2[\text{PtCl}_4]$                         | 155 ± 6   | 0.523   | 680 ± 20   | 0.85  |
| $\text{K}_2[\text{Ni}(\text{CN})_4]$                | 1100 ± 8  | 4.12  | 3920 ± 128 (3900)                                | 5.15  |
| $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$     | 750 ± 35  | 2.15  | 2250 ± 200 (2100)                                | 2.95  |
| $\text{K}_3[\text{Co}(\text{CN})_6]$                | 0.65 ± 0.20                                     | 0.0012  | 1.8 ± 0.1  | 0.0022  |
| $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$     | 40 ± 4  | 0.12  | 180 ± 10   | 0.21  |
| $\text{K}_3[\text{Cr}(\text{CN})_6]$                | 75 ± 4  | 0.25  | 275 ± 10   | 0.35  |
| $\text{K}_3[\text{Fe}(\text{CN})_6]$                | 1840 ± 140                                      | 63.   | 4600 ± 10  | 6.15  |
| $\text{K}_4[\text{Fe}(\text{CN})_6]$                | 155 ± 5   | 0.55  | 320 ± 20 (320)                                   | 0.45  |

**Table-III: Association Constants for aqueous  $[\text{Ru}(\text{diphenyl-bpy})_3]\text{Cl}_2$  and  $[\text{Ru}(\text{diphenyl-phen})_3]\text{Cl}_2$**

| Metal Ion        | $K_{eq}, \text{M}^{-1}$                         |  |
|------------------|---|--|
|                  | $[\text{Ru}(\text{diphenyl-bpy})_3]\text{Cl}_2$ | $[\text{Ru}(\text{diphenyl-phen})_3]\text{Cl}_2$ |
| $\text{CO}^{2+}$ | 10  | 15   |
| $\text{Ni}^{2+}$ | 10  | 18   |
| $\text{Cu}^{2+}$ | 180   | 260a   |

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