it is not surprising that the principal features of this band system are not unlike those in that part of the photoelectron spectrum which concerns ionization of the $3t_2$ electron: a progression in $\nu_1(a_1)$ of 840 cm^{-1} with a ν(e) or $\nu(t_2)$ vibronic substructure of ~210 cm^{-1}. The $1t_1 \rightarrow 3s(R)$ transition corresponds to the structure on the low-energy side of band VI. It contains three peaks separated by ~950 cm^{-1}, a $\nu_1(a_1)$ frequency not detectably different from that of the ground state at 965 cm^{-1}. The $1e \rightarrow 3s(R)$ transition corresponds to the three well-resolved peaks on top of band VI and consists of a progression in $\nu_1(a_1)$ of ~870 cm^{-1}. Thus, in all transitions where vibrational structure is resolved, the band characteristics parallel those in the pes spectrum and we take this to indicate pseudo-ionic (*i.e.*, Rydberg) character.

The $3t_2 \rightarrow 3s$ and $1t_1 \rightarrow 3s$ Rydbergs are thought not to be resolved in RuO_4 and to lie within the compass of band VI. This is, perhaps, a convenient analysis but it is not inconsistent with the large half-width of this band or its large intensity.

Acknowledgment. The authors wish to express their gratitude to Hung-tai Wang and Petr Hochmann of these laboratories for considerable help with the Rydberg analysis. This work was supported by contract between the United States Atomic Energy Commission-Biology Branch and the Louisiana State University.

Electrogenerated Chemiluminescence. XIII. Electrochemical and Electrogenerated Chemiluminescence Studies of Ruthenium Chelates

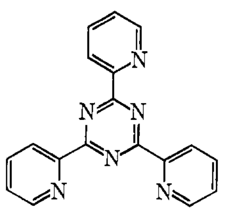
Nurhan E. Tokel-Takvoryan, Ronald E. Hemingway, and Allen J. Bard*

Contribution from the Department of Chemistry, University of Texas, Austin, Texas 78712. *Received January 18, 1973*

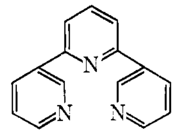
Abstract: The electrochemistry and electrogenerated chemiluminescence (ecl) of four ruthenium(II) chelates, RuL_x^{n+} ($x = 3$, $n = 2$, L = 2,2′-bipyridine (bipy); $x = 3$, $n = 2$, L = 1,10-phenanthroline (*o*-phen); $x = 2$, $n = 2$, L = 2,2′,2′′-terpyridine (terpy); $x = 2$, $n = 3$, L = 2,4,6-tripyridyl-*s*-triazine (TPTZ)), in acetonitrile solutions were investigated. All compounds showed evidence of several one-electron reduction and oxidation steps to form products stable during cyclic voltammetric scans. Coulometric and rotating ring-disk electrode (RRDE) studies of the bipy chelate were also carried out. The bipy, *o*-phen, and terpy chelates produce ecl *via* redox reactions of oxidized and reduced forms to form an emitting species, which has been identified as the triplet state by comparison to its luminescence spectrum; the ecl of the bipy chelate is the most intense. A study of ecl of the bipy chelate at the RRDE yielded an ecl efficiency of 5–6%.

The luminescence properties of a number of d^6 metal ions complexed to π-conjugated ligands have been reported. The second and third row transition d^6 metal complexes of Rh(III), Ir(III), Os(III), and Ru(II) display phosphorescence which is assigned to transitions which are "metal localized," (*i.e.*, $Rh(bipy)_2Cl_2^+$),[1,2] "ligand localized" ($Rh(o\text{-phen})_3^{3+}$),[3] and "charge transfer" in origin ($Ru(bipy)_3^{2+}$)[4,5] and ($Ir(bipy)_3^{3+}$).[6]

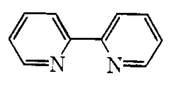
Previous reports of electrogenerated chemiluminescence (ecl) have demonstrated the generation of excited states by electrogenerated radical ion annihilation reactions of organic aromatic hydrocarbons and heterocyclic and macrocyclic[7] compounds in aprotic media. In a recent communication[8] we reported ecl obtained from the $Ru(bipy)_3Cl_2$ system in acetonitrile. We now wish to present the results of more detailed studies of the $Ru(bipy)_3^{2+}$ system and other $Ru(L)_x^{n+}$ systems in acetonitrile ($x = 3$, $n = 2$, L = 1,10-phenanthroline (*o*-phen); $x = 2$, $n = 2$, L = 2,2′,2′′-terpyridine, (terpy); $x = 2$, $n = 3$, L = 2,4,6-tripyridyl-*s*-triazine, TPTZ).



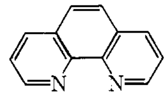
2,4,6-tripyridyl-*s*-triazine (TPTZ)



2,2′,2′′-terpyridine (terpy)



2,2′-bipyridine (bipy)



1,10-phenanthroline (*o*-phen)

Experimental Section

$Ru(bipy)_3Cl_2 \cdot 6H_2O$ and $Ru(o\text{-phen})_3Cl_2$ were purchased from G. F. Smith Chemical Co., and each was purified by triple recrys-

---

[1] G. A. Crosby and D. H. W. Carstens, "Molecular Luminescence," F. C. Lim, Ed., W. A. Benjamin, New York, N. Y., 1969, p 309.

[2] D. H. W. Carstens and G. A. Crosby, *J. Mol. Spectrosc.*, **34**, 113 (1970).

[3] M. K. DeArmond and J. E. Hillis, *J. Chem. Phys.*, **49**, 466 (1970).

[4] F. E. Lytle and D. M. Hercules, *J. Amer. Chem. Soc.*, **91**, 253 (1969).

[5] J. N. Demas and G. A. Crosby, *J. Mol. Spectrosc.*, **26**, 72 (1968).

[6] K. R. Wunschel, Jr., and W. E. Ohnesorge, *J. Amer. Chem. Soc.*, **89**, 2777 (1967).

[7] N. E. Tokel, C. P. Keszthelyi, and A. J. Bard, *J. Amer. Chem. Soc.*, **94**, 4872 (1972).

[8] N. E. Tokel and A. J. Bard, *J. Amer. Chem. Soc.*, **94**, 2862 (1972).

tallization from distilled water before use. $Ru(bipy)_3(CiO_4)_2$ and $Ru(o\text{-}phen)_3(ClO_4)_2$ were prepared by metathesis with excess $NaClO_4$ in a H_2O–EtOH mixture. They were recrystallized from the same solvent mixture four times before use. 1,10-Phenanthroline and 2,2′-bipyridine were purchased from J. T. Baker Chemical Co., and 2,2′,2′′-terpyridine and TPTZ were supplied by G. F. Smith Chemical Co. and were used as received. $RuCl_3$ (lot 31), 40.80%, was purchased from Engelhard Corp. and metallic Ru (60 mesh) from Alfa Inorganics Ventron. $Ru(terpy)_2(ClO_4)_2$ and $Ru(TPTZ)_2(ClO_4)_3$ were synthesized according to published procedures.[9,10] The former was recrystallized from H_2O three times, while $Ru(TPTZ)_2(ClO_4)_3$ was purified with hot dioxane extraction nine times. 10-Methylphenothiazine (10-MP) (Eastman Organic Chemicals) was recrystallized three times from benzene. Spectroquality grade acetonitrile (Matheson Coleman and Bell) was purified by the method of Osa and Kuwana.[11] The amount necessary for each experiment was vapor transferred directly into the appropriate electrochemical or ecl cell on the vacuum line. The solvent, *N*,*N*-dimethylformamide (DMF), from Matheson Coleman and Bell, was purified by the same procedure as that reported previously.[12] Tetra-*n*-butylammonium fluoborate ($TBABF_4$), polarographic grade, used as the supporting electrolyte, was supplied by Southwestern Analytical Chemicals, Austin, Texas. The $TBABF_4$ was employed without further purification but was dried in a vacuum oven for 36 hr at a temperature of 120° and then stored in a desiccator over magnesium perchlorate.

Preliminary ecl studies were carried out in a three-electrode cell with Pt wires serving as the working and auxiliary electrodes and a Ag wire as the reference electrode using previously reported experimental procedures.[12] The electrochemistry was performed in a cell[13] with a three-electrode configuration consisting of a Pt disk microelectrode surrounded by a helical Ag wire quasi-reference and a concentrically arranged Pt loop as a counter electrode. A Princeton Applied Research Corp. Model 170 electrochemistry system (PAR) was used for cyclic voltammetry experiments. For the coulometric experiments a three-compartment cell was used. A side arm was used for freeze–pump–thaw degassing of the solutions. The reference electrode was a sce connected by a KNO_3 salt bridge in a medium fritted compartment and the auxilliary compartment was separated by two 10-mm medium porosity sintered glass frits. Determination of overall ecl efficiency, ϕ_{ecl}, has been conducted by employing the rotating ring–disk electrode (RRDE) technique. The ecl cell described earlier[14] was placed in a light-tight box with all the controls located outside the box. The RRDE was driven with a Motomatic Model E 150 tachometer–generator motor (Electro-craft Corp., Hopkins, Minn.) using feedback control. A Tacussel Electronique Bipotentiostat, Model Bipad 2, was employed to control the potentials of the disk and ring electrodes simultaneously. The emitted light was measured with a UDT-500 (United Detector Technology, Inc.), a combination of a PIN silicon Schottky photodiode (1-cm² area) and an operational amplifier with variable gain. The output of this device was read directly from a Fairchild Model 7050 high impedance digital voltmeter. Bias for the UDT-500 was provided by a Harrison 6205B dual power supply (±15 V) (Hewlett-Packard).

Fluorescence and ecl spectra were taken using an Aminco-Bowman spectrophotofluorometer (SPF) in conjunction with a Hamamatsu TV Corp. R456 photomultiplier tube having uv-improved S-20 spectral response.

Results

Electrochemical. Peak potentials for all systems studied are given in Table I. Typical voltammograms of the ruthenium–bipyridyl, -terpyridyl, -TPTZ, and *o*-phenanthroline complex systems are given in Figures 1–4 and tabulations of cyclic voltammetric parameters, peak current ratios, $i_p/(V^{1/2}C)$, and ΔE_p are made in Tables II–IV; the *o*-phenanthroline complex shows complications in its behavior (Figure 4) which prevents meaningful tabulation of these parameters.

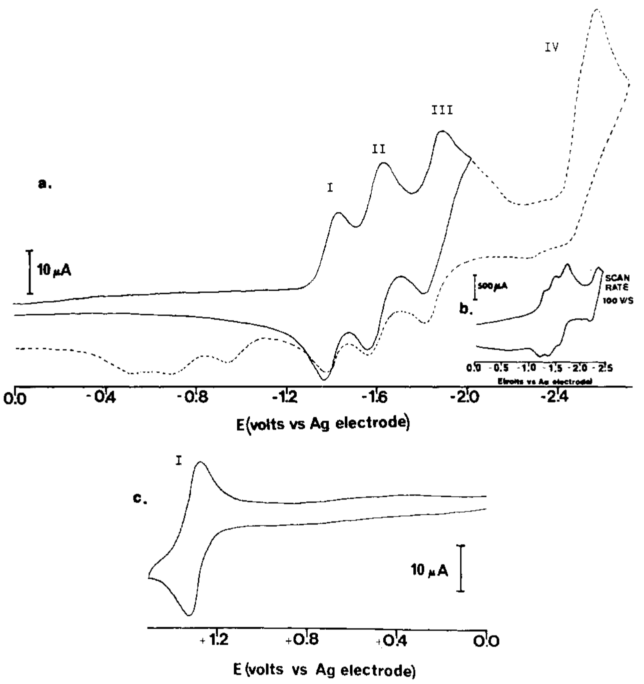


Figure 1. Cyclic voltammogram of 1 m*M* $Ru(bipy)_3(ClO_4)_2/CH_3CN/0.1\ M\ TBABF_4$ at a Pt disk microelectrode: (a) scan from 0.0 to −2.6 V, scan rate = 200 mV/sec; (b) scan as a, scan rate = 100 V/sec; (c) scan from 0.0 to +1.4 V, scan rate = 200 mV/sec.

Table I. Cyclic Voltammetric Peak Potentials (E_p) for Ruthenium Chelates and Ligands in 0.1 *M* $TBABF_4$–Acetonitrile Solutions at a Platinum Electrode

	E_p, V *vs.* sce				
	Oxidation	Reductions			
Species	I	I	II	III	IV
$Ru(bipy)_3{}^{2+}$	+1.354	−1.332	−1.517	−1.764	−2.4
$Ru(o\text{-}phen)_3{}^{2+}$	+1.40	−1.41	-1.54^a	-1.84^b	-2.24^c
$Ru(terpy)_2{}^{2+}$	+1.28	−1.43	−1.70		
$Ru(TPTZ)_2{}^{3+}$	+1.52	−0.84	−1.00	−1.66	−1.91
Bipyridine	None to +1.9	−2.13			
o-Phenanthroline	None to +2.1	-2.1^c			
Terpyridine	None to +2.1	-2.15^c			
TPTZ	None to +2.1	−1.56	-2.05^c		

[a] Desorption spike on reversal. [b] Broad peak of low current. [c] Irreversible.

Coulometric oxidation of the bipyridyl complex at 1.40 V gave an n_{app} = 1.04 and Q_{rev}/Q_{for} = 0.92 for a 1-hr experiment, where n_{app} is the number of faradays per mole of chelate and Q_{for} and Q_{rev} are the number of coulombs consumed in the forward and reverse electrolysis, respectively. The oxidized product in solution is bright green and is unstable to air overnight; however, under vacuum, it is stable for several days. The product, after exposure to air, was again the orange $Ru(bipy)_3{}^{2+}$ species as confirmed by its visible spectrum. Because of following chemical reactions, coulometric reductions gave values of n_{app} which varied depending on the duration of the experiment. In most cases n_{app} was much greater than 1.00, and the current decayed to a value higher than the initial residual cur-

---

(9) G. Morgan and F. Burstall, *J. Chem. Soc.*, 1649 (1937).

(10) W. A. Embry and G. H. Ayres, *Anal. Chem.*, **40**, 1499 (1968).

(11) T. Osa and T. Kuwana, *J. Electroanal. Chem.*, **22**, 389 (1969).

(12) L. R. Faulkner and A. J. Bard, *J. Amer. Chem. Soc.*, **90**, 6284 (1968).

(13) L. R. Faulkner and R. Bezman, *J. Amer. Chem. Soc.*, **94**, 6317 (1972).

(14) J. T. Maloy, K. B. Prater, and A. J. Bard, *J. Amer. Chem. Soc.*, **93**, 5959 (1971).

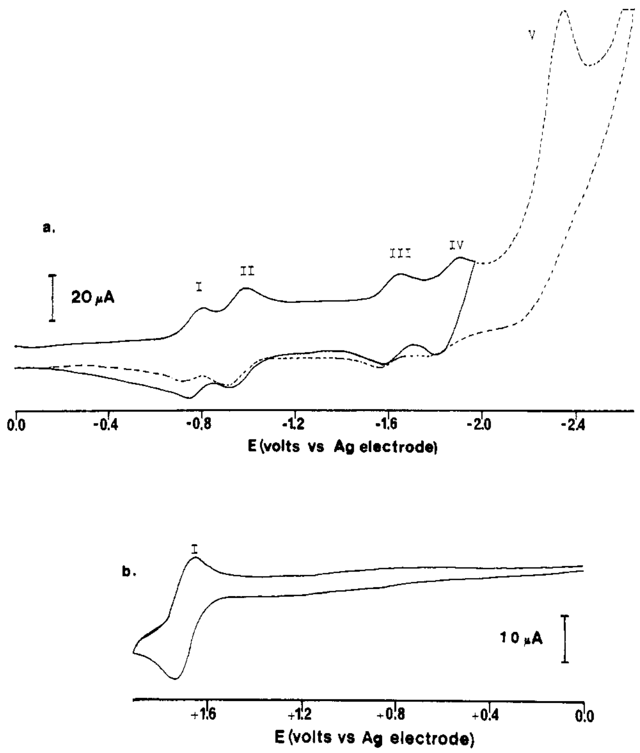


Figure 2. Cyclic voltammogram of 1 m*M* $Ru(TPTZ)_2(ClO_4)_3$/CH_3CN/0.1 *M* $TBABF_4$ at a Pt disk microelectrode: (a) scan from 0.0 to −2.6 V, scan rate = 200 mV/sec; (b) scan from 0.0 to +1.8 V, scan rate = 200 mV/sec.

rent. The coulometric results show that the oxidation of the $Ru(bipy)_3^{2+}$ is a one-electron process leading to the formation of a stable form, which we denote R^{3+}.

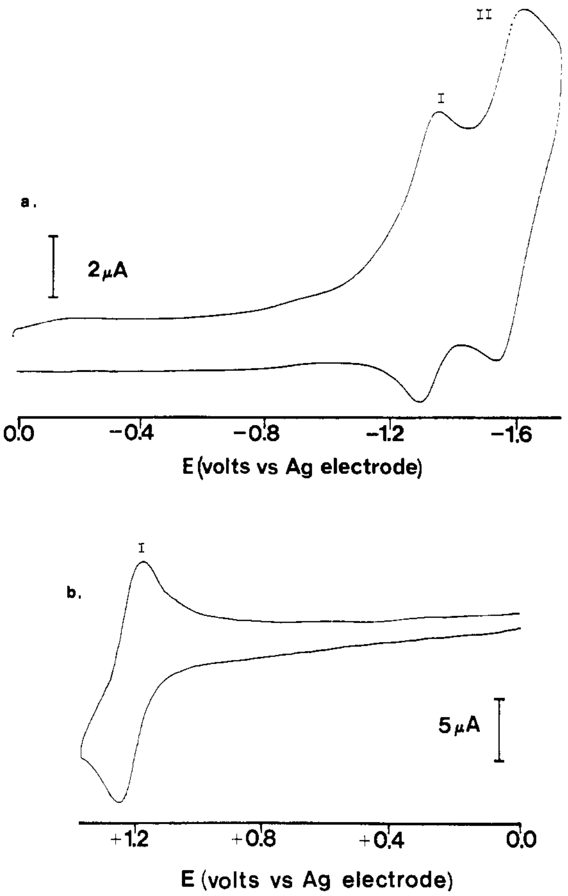


Figure 3. Cyclic voltammogram of 1 m*M* $Ru(terpy)_2(ClO_4)_2$/CH_3CN/0.1 *M* $TBABF_4$ at a Pt disk microelectrode: (a) scan from 0.0 to −1.8 V, scan rate = 200 mV/sec; (b) scan from 0.0 to +1.4 V, scan rate = 200 mV/sec.

Table II. Cyclic Voltammetry Results for $Ru(bipy)_3^{2+}$ [a]

	Oxidation			Reduction								
	I			I			II			III		
Scan rate	E_{pa} = +1.354 V			E_{pc} = −1.332 V			E_{pc} = −1.517 V			E_{pc} = −1.764 V		
(*V*), V/sec	$i_p/(V^{1/2}C)$	i_{pc}/i_{pa}	ΔE_p	$i_p/(V^{1/2}C)$	i_{pa}/i_{pc}	ΔE_p	$i_p/(V^{1/2}C)^b$	i_{pa}/i_{pc}	ΔE_p	$i_p/(V^{1/2}C)^b$	i_{pa}/i_{pc}	ΔE_p
0.02	3.2	1.0	60	3.3	0.96	59	3.4	0.96	65	3.7	0.98	68
0.05	3.4	0.99	62	3.8	0.98	56	3.4	0.98	70	3.6	0.97	66
0.10	3.1	1.0	61	4.3	0.98	62	3.5	0.93	64	3.3	1.0	65
0.20	3.4	1.0	64	4.8	0.98	60	3.5	0.93	66	3.7	0.96	60
0.50	3.2	0.98	55	3.9	0.97	61						
1.0	3.4	0.99	70	4.2		58						
2.0	4.1	1.0	68	4.2		65						
5.0	3.2		75	4.0		60						
10.0	3.0		55	3.8		72						
20.0	3.3		62	4.1		78						

[a] The solution was 1.27 m*M* $Ru(bipy)_3(ClO_4)_3$ and 0.1 *M* $TBABF_4$ in CH_3CN at 25°. i_{pc} = peak cathodic current, E_{pc} = cathodic peak potential, i_{pa} = peak anodic current, E_{pa} = anodic peak potential, $\Delta E_p = |E_{pc} - E_{pa}|$, C = concentration of chelate. [b] Peak currents for second and third waves measured from extrapolated decreasing current of preceding wave.

Table III. Cyclic Voltammetry Results for $Ru(terpy)_2^{2+}$ [a]

	Oxidation			Reductions					
Scan	I			I			II		
rate	E_{pa} = +1.28 V			E_{pc} = −1.43 V			E_{pc} = −1.70 V		
(*V*), mV/sec	$i_p/$ $(V^{1/2}C)$	$i_{pc}/$ i_{pa}	ΔE_p, mV	$i_p/$ $(V^{1/2}C)$	$i_{pa}/$ i_{pc}	ΔE_p	$i_p/$ $(V^{1/2}C)$	$i_{pa}/$ i_{pc}	ΔE_p
20	3.2	1.0	60	3.2	0.89	64	3.0	0.82	94
50	3.3	0.98	65	3.2	0.89	61	3.4	0.78	85
100	3.3	1.1	64	3.3	0.93	59	3.6	0.80	80
200	3.3	1.1	65	3.5	0.90	50	3.7	0.92	82
500	3.2	1.1	59	3.4	0.91	50	3.7	0.90	81

[a] Solution was 1.05 m*M* $Ru(terpy)_2(ClO_4)_2$ and 0.1 *M* $TBABF_4$ in CH_3CN; see Table II for notation.

Since the $i_p/(V^{1/2}C)$ values for the first three reduction processes are near that for the oxidation (considering corrections for residual current, preceding waves, and double layer charging), these processes are probably one-electron reductions, leading to the R^+, R^0, and R^- species. Similar comparisons for the other complexes show that all other waves probably are one-electron transfers. The fourth reduction wave of the bipyridyl complex shows no reversal current at scan rates less than 20 V/sec and has a peak current which corresponds to a 2.7-electron process; however, at scan rates greater than 20 V/sec the process becomes a one-elec-

Table IV. Cyclic Voltammetry Results for Ru(TPTZ)$_2^{3+}$ [a]

	Oxidation			Reduction											
	I			I			II			III			IV		
	E_{pa} = +1.52 V			E_{pc} = −0.84 V			E_{pc} = −1.00 V			E_{pc} = −1.66 V			E_{pc} = −1.91 V		
Scan rate (V), V/sec	$i_p/(V^{1/2}C)$	i_{pc}/i_{pa}	ΔE_p	$i_p/(V^{1/2}C)$	i_{pa}/i_{pc}	ΔE_p	$i_p/(V^{1/2}C)$	i_{pa}/i_{pc}	ΔE_p	$i_p/(V^{1/2}C)$	i_{pa}/i_{pc}	ΔE_p	$i_p/(V^{1/2}C)$	i_{pa}/i_{pc}	ΔE_p
0.02	2.3	0.73	70	2.4	1.0	98	2.7	1.00	94	2.9	1.0	80	2.8	1.0	94
0.05	2.5	0.77	72	2.3	1.0	80	2.8	0.99	81	2.8	1.0	84	3.0	1.0	90
0.10	2.4	0.79	73	2.2	0.99	71	2.9	1.00	83	3.0	1.0	76	3.1	1.0	87
0.20	2.0	0.83	68	2.2	0.9	70	2.8	1.00	70	2.9	1.0	72	3.1	1.0	83
0.50				2.4		83	2.9	1.00	89			78			110
1.0				2.2		91									
2.0				2.3		74									
5.0				2.2		72									
10.0				2.2		72									
20.0				2.0		71									

[a] The solution was 1.44 mM Ru(TPTZ)$_2$(ClO$_4$)$_3$ and 0.1 M TBABF$_4$ in CH$_3$CN; see Table II for notation.

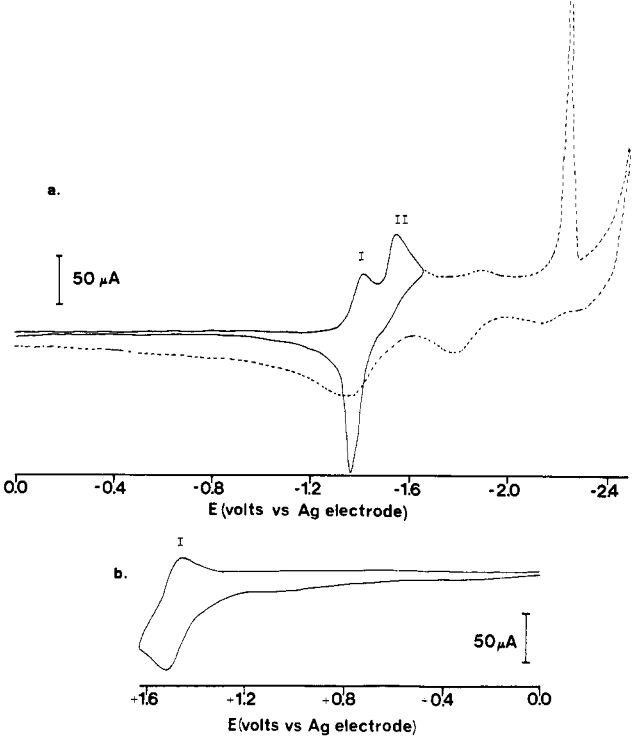


Figure 4. Cyclic voltammogram of 1 mM Ru(o-phen)$_3$(ClO$_4$)$_2$/CH$_3$CN/0.1 M TBABF$_4$ at a Pt disk microelectrode: (a) (—) scan from 0.0 to −1.7 V, scan rate = 200 mV/sec; (- - -), scan from 0.0 to −2.5 V, scan rate = 200 mV/sec; (b) scan from 0.0 to +1.65 V, scan rate = 200 mV/sec.

tron transfer and displays some reversal current (Figure 1 insert). In DMF, where the background for the cathodic range is more negative than that for acetonitrile, close to reversible fourth waves were obtained at 200 V/sec. This behavior can be ascribed to the addition of four electrons to R^{2+} followed by liberation of one or more ligands and simultaneous reduction of the liberated bipyridine (the free ligand is reduced at this potential). At the higher scan rates, oxidation of R^{2-} species before loss of ligands is observed.

Simultaneous electrochemistry and esr studies have been made on this complex and show paramagnetic species produced for the oxidation, first, third, and fourth reductions. The spectra of the oxidation and first and third reductions were broad singlets, while the fourth reduction yields a spectra with some hyperfine structure superimposed on a singlet.[15]

Since the ecl of the mixed system of 10-methylphenothiazine (10-MP) and Ru(bipy)$_3^{2+}$ was studied, a brief investigation of the electrochemistry of 10-MP was undertaken. 10-MP oxidizes in two one-electron steps. The first oxidation is a Nernstian process with E_{pa} at +0.83 V *vs.* sce, which is close to the value in DMF, +0.82.[16] The character of the second oxidation of 10-MP depends on the conditions of the medium, such as the amount of water present in the solvent, etc.[17] In our mixed system the second oxidation occurs simultaneously with the oxidation of R^{2+} to R^{3+}. Billon's data indicate that the difference in the two oxidation peak potentials for 10-MP is 600 mV, which is the difference noted between the first oxidation of 10-MP and the oxidation of Ru(bipy)$_3^{2+}$. 10-MP is not reducible in this medium at the Pt-disk electrode up to potentials of −2.5 V *vs.* sce.

Spectroscopic Data. The luminescence spectrum of Ru(bipy)$_3$(ClO$_4$)$_2$ in acetonitrile solution at room temperature is shown in Figure 5a. The only maximum of emission occurs at 607 nm, which is very similar to the data of Lytle and Hercules.[18] Similar emission behavior, though of lower intensity, has been obtained when the oxygen in the solution has not been removed by the usual freeze–pump–thaw technique as expected, since O$_2$ is an effective triplet quencher.[19]

The luminescence of Ru(o-phen)$_3$(ClO$_4$)$_2$ and Ru(terpy)$_2$(ClO$_4$)$_2$ has been reported by Veening and Brandt[20] and Crosby and coworkers.[21,22] Published emission spectra[21,22] for Ru(o-phen)$_3$Cl$_2$ and Ru(terpy)$_2$I$_2$ in EMPA rigid glass at 77°K show four maxima in the 580–720 nm range, where the two shorter wavelength maxima are of higher intensity than the lower energy ones. In our studies in deoxygenated aceto-

---

[15] D. K. Boyd and A. J. Bard, unpublished experiments, University of Texas, 1972.

[16] L. R. Faulkner, H. Tachikawa, and A. J. Bard, *J. Amer. Chem. Soc.*, **94**, 691 (1972).

[17] J. P. Billon, *Ann. Chim. (Paris)*, 7, 183 (1962).

[18] F. E. Lytle and D. M. Hercules, *Photochem. Photobiol.*, **13**, 123 (1971).

[19] J. B. Birks, "Photophysics of Aromatic Molecules," Wiley, New York, N. Y., 1970, p 206.

[20] H. Veening and W. W. Brandt, *Anal. Chem.*, **32**, 1426 (1960).

[21] D. M. Klassen and G. A. Crosby, *J. Chem. Phys.*, **48**, 1853 (1968).

[22] G. A. Crosby, W. C. Perkins, and D. M. Klassen, *J. Chem. Phys.*, **43**, 1498 (1965).

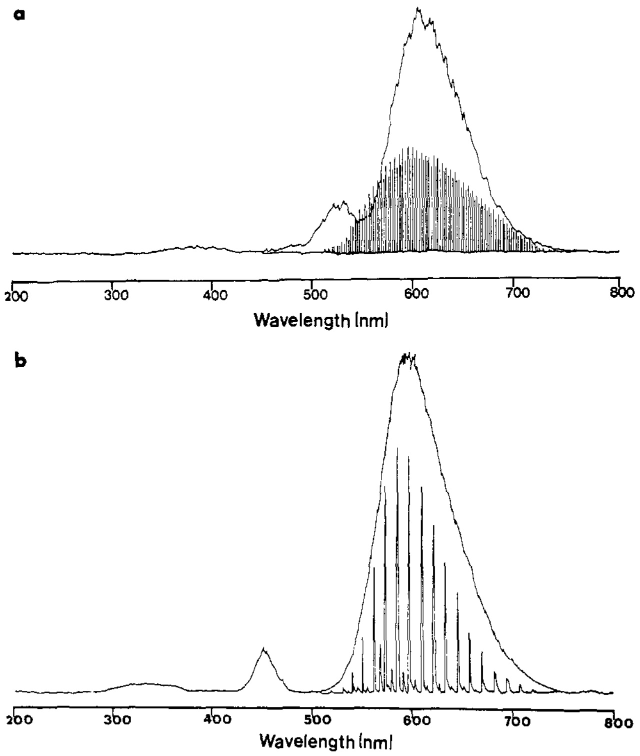


Figure 5. Ecl and luminescence spectra of (a) bipy chelate and (b) *o*-phen chelate from 450 to 800 nm. The spiked spectra is ecl. The solution for ecl was 1 m*M* complex/degassed CH_3CN/0.1 *M* $TBABF_4$ and that for luminescence was the same, except without supporting electrolyte: (a) $Ru(bipy)_3(ClO_4)_2$, excitation at 500 nm; (b) $Ru(o\text{-phen})_3(ClO_4)_2$, excitation at 475 nm.

nitrile solutions, $Ru(o\text{-phen})_3{}^{2+}$ (Figure 5b) showed one emission maximum at 590 nm and $Ru(terpy)_2{}^{2+}$ and $Ru(TPTZ)_2{}^{3+}$ displayed no emission at room temperature.

Ecl at Stationary Working Electrodes. Application of cyclic square waves at a frequency of 0.2 Hz between potentials for formation of R^{3+} and R^+ in the $Ru(bipy)_3(ClO_4)_2$ system at a platinum wire electode results in intense orange emission, easily visible to the nondark adapted eye (Figure 5a). The intensity of this emission is at least as intense as the ecl observed with rubrene solutions at similar concentrations (1 m*M*). The emission extends from roughly 520 to 770 nm with the maximum located at 610 nm, nearly identical with the phosphorescence emission. The taller spikes correspond to stepping the voltage in a positive direction (R^{3+} production), while the smaller spikes correspond to stepping in a negative direction (R^+ production). Upon close examination, a shoulder at 630 nm is observed. The close proximity of the main emission at 610 nm makes a thorough analysis of the longer wavelength emission very difficult. This shoulder is not observed in the photoexcitation spectrum in solution, but it occurs at the identical location of the second emission band of $Ru(bipy)_3(ClO_4)_2$ in rigid glass at 77°K.[4,21]

The ecl intensity at 610 nm (0.2 Hz) in acetonitrile is quite constant with time; however, in DMF the intensity decays to a very low level after the first few pulses. Ecl emission is also observed when higher cyclic frequencies are used between the same potentials. Applying the same pulsing technique between potentials for the formation of R^{3+} and either R^0 or R^-, similar spectra of much higher intensity are obtained. The relative ecl intensity for the different generation conditions are in the following ratios for generation of R^{3+} and the following reduced forms: $R^+:R^0:R^- = 1:4:11$. Similarly, intense ecl is obtained by varying the potential between the first oxidation wave and the fourth reduction wave; however, these conditions cause some dark brown or black unidentified substance to precipitate out on the electrode surface. Ecl emission is also obtained from a nondegassed $Ru(bipy)_3(ClO_4)_2$–acetonitrile system; however, the intensity of this emission is only 1% of an oxygen free sample.

Three additional experiments were done to investigate various other phenomena related to the ruthenium–bipyridine complex system. The original description of this ecl involved pulse experiments with the dichloride salt of $Ru(bipy)_3{}^{2+}$ rather than the perchlorate salt. The electrochemistry of this system is similar to that of $Ru(bipy)_3(ClO_4)_2$, except that an irreversible oxidation at about +1.16 V is observed; this is attributed to oxidation of chloride ions, since LiCl in acetonitrile shows a similar oxidation at that potential. Application of the cyclic square wave technique to this compound yields similar ecl emission spectra as the perchlorate salt, with the difference that the ratio of the relative intensities of ecl maxima for stepping to potentials of the first three reduction waves is 1:2.5:2.9 and that the total luminescence intensities are much lower. Ecl resulting from the pulsing between the oxidation of Cl^- and any of the first three reductions of $Ru(bipy)_3{}^{2+}$ yields very low intensity luminescence.

A second experiment, involving 1 m*M* $Ru(bipy)_3Cl_2$ in a 1 : 1 benzene/acetonitrile solution (0.2 *M* $TBABF_4$) that was pulsed between the appropriate peak potentials, resulted in an ecl intensity at the maximum that was substantially greater than the acetonitrile alone case but still only about 30–40% of the $Ru(bipy)_3(ClO_4)_2$/acetonitrile ecl intensity.

Ecl emission has been observed from mixed systems where the second component in the system has been 10-methylphenothiazine. With the 10-MP/$Ru(bipy)_3(ClO_4)_3$ or (Cl^- salt), pulsing the solution between 10-MP oxidation peaks potential and the various E_{pc}'s of the metal chelate yields the same ecl emission as recorded from $Ru(bipy)_3{}^{2+}$ alone. The intensity of the emission from this mixed system is comparable to the ecl intensity from ruthenium complex. Here, again, the taller peaks correspond to the anodic pulse (oxidation of 10-MP).

Using the pulsed ecl technique with the $Ru(o\text{-phen})_3(ClO_4)_2$, $Ru(terpy)_2(ClO_4)_2$, and $Ru(TPTZ)_2(ClO_4)_3$ system gave either much lower emission than the bipyridine counterpart or none at all. $Ru(o\text{-phen})_3(ClO_4)_2$ pulsed at a frequency of 0.2 Hz between the first oxidation (R^{3+} production) and the first or second reduction results in low level ecl with a maximum at 590 nm, not far from the phosphorescence maximum. The more intense ecl spikes results on the oxidation half-cycle pulse (Figure 5b). Employing the same technique, low level ecl was obtained from $Ru(terpy)_2(ClO_4)_2$ when the solution was pulsed between the first oxidation and the first reduction. This luminescence extends from 550 to 750 nm with the maximum at 660 nm. The larger ecl spikes occurred on the reduction pulse and the smaller spikes on the oxidation pulse. Intensity *vs.* time studies at 50 Hz show that this low-level emission increases somewhat with time. When the solution is pulsed at 0.2 Hz between the oxidation and the second reduction, similar ecl emission is observed except that the higher ecl spikes are obtained on the oxidation pulse. No ecl emission could be obtained from $Ru(TPTZ)_2(ClO_4)_3$ in acetonitrile.

Ecl at the RRDE. Experiments at the RRDE were undertaken to confirm the cyclic voltammetric experiments and to obtain steady state ecl for determination of the overall ecl efficiency, ϕ_{ecl}, defined as photons emitted per redox reaction step. The RRDE techniques generally followed previous practice,[14,23] and the absolute calibration of the photodiode has been described elsewhere.[24] Initial experiments involved measurement of the disk current, i_d, and the ring current, i_r, at different potentials and rotation rates, ω. A typical scan of i_d *vs.* E_d (Figure 6) for $Ru(bipy)_3^{2+}$ shows the three reduction waves of essentially equal height. Similarly a scan to positive potentials shows the oxidation wave. Evidence for the stability of the electrogenerated species was obtained by determination of the collection efficiency, N (where $N = |i_r/i_d|$), for generation of a species at the disk electrode and collection of this species at the ring electrode. Typical values, given in Table V, are close to the theoretical value for total collection of the disk-generated species at an electrode of this geometry ($N = 0.54$). The initial disk current, i_d, values for the three reduction processes are in the ratio 1:2:3; however, i_d *vs.* t studies (at constant E_d and E_r) reveal that after approximately 30 sec, the disk current, derived from the second or third reduction process ($E_d = -1.60$ or -1.90 V, respectively), increases with time, while the ring current remains constant. The slope of this plot also increases with time. By the same method, the i_d and i_r for the one-electron oxidation and for the one-electron reduction processes of $Ru(bipy)_3^{2+}$ are constant for at least 7 min.

Table V. RRDE Collection Efficiencies, N_k,[a] for $Ru(bipy)_3^{2+}$

Rotation rate (ω), radians/sec	Oxidation I $E_d = +1.48$ V $E_r = 0.00$ V[c]	Reductions I $E_d = -1.37$ V $E_r = 0.00$ V	Reductions II[b] $E_d = -1.60$ V $E_r = 0.00$ V	Reductions III[b] $E_d = -1.90$ V $E_r = 0.00$ V
66	0.47	0.50	0.51	0.52
132	0.51	0.52	0.52	0.51
198	0.51	0.52	0.51	0.52
264	0.53	0.53	0.51	0.52
330	0.54	0.53	0.52	0.51

[a] N_k = ring current/disk current, for the disk potential set for the designated process and the potential of the ring adjusted to one where $Ru(bipy)^{2+}$ is produced. [b] These values were recorded by stepping the disk from 0.0 V *vs.* sce to the potential of the process studied and quickly measuring i_d and i_r because of the time dependence of i_d for the second and third reductions. [c] All potentials *vs.* sce.

The generation of ecl at the RRDE was accomplished by holding the ring at a potential where one reactant was generated (*e.g.*, at +1.48 V where R^{3+} is produced) and adjusting the disk to potentials where the other reactant is generated (*e.g.*, at -1.37 V, R^+; at -1.60 V, R^0; or at -1.90 V, R^-). The intensity of the ring of light was determined with the photodiode. For example, the ecl with $E_r = +1.48$ V and E_d scanned from 0 to more negative values is shown in Figure 6. The relative intensities at the three reduction waves are in the ratio 1:2:3, directly proportional to the total disk current. When the disk is held at +1.48 V and the ring scanned to negative potentials, the ecl intensity remains constant, as expected, since with the geometry of the RRDE employed here i_r is much larger than i_d for the same electrode reaction. The intensity of emission for any of the combinations of E_r and E_d remained steady for at least 7 min, even under conditions where i_d and i_r are changing. After numerous voltammetric and ecl experiments on a given solution, the RRDE voltammograms still exhibited nearly the same i_d and $E_{1/2}$ values as the fresh solution.

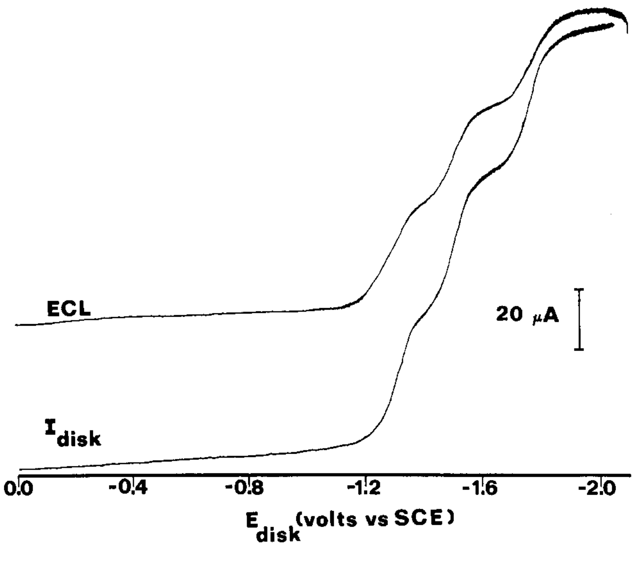


Figure 6. Ecl intensity and disk current, I_d, *vs.* disk potential, E_d, for $Ru(bipy)_3^{2+}$ in CH_3CN.

The ϕ_{ecl} was determined by adjusting E_r and E_d to appropriate values and determining the ecl intensity incident on the photodiode. This is corrected for geometric factors and frequency[24] to yield the total emission, I, in photons/sec. The disk current (corrected for any residual current), i_d, in the limit of a fast redox reaction, represents the number of annihilations, so that[14,23]

$$\phi_{ecl} = nFI/i_d \tag{1}$$

Values of ϕ_{ecl} at different rotation rates are shown in Figure 7. The efficiency of this system (5–6%) is relatively high compared with most other systems exhibiting ecl.[24] Because of the relatively low ecl intensities of the other Ru chelate systems, RRDE studies of them were not undertaken.

Discussion

The cyclic voltammetry results for the $Ru(bipy)_3^{2+}$ system demonstrate the existence of species R^+, R^0, and R^- with "effective" ruthenium oxidation states of *I*, 0, and $-I$. For very fast scan rates evidence is obtained for the R^{2-} species [Ru($-$II)]. Previous reports of low

---

(23) J. T. Maloy and A. J. Bard, *J. Amer. Chem. Soc.*, **93**, 5968 (1971).

(24) A. J. Bard, C. P. Keszthelyi, H. Tachikawa, and N. E. Tokel, "Chemiluminescence and Bioluminescence," D. M. Hercules, J. Lee, and M. J. Cormier, Ed., Plenum Press, New York, N. Y., 1973.

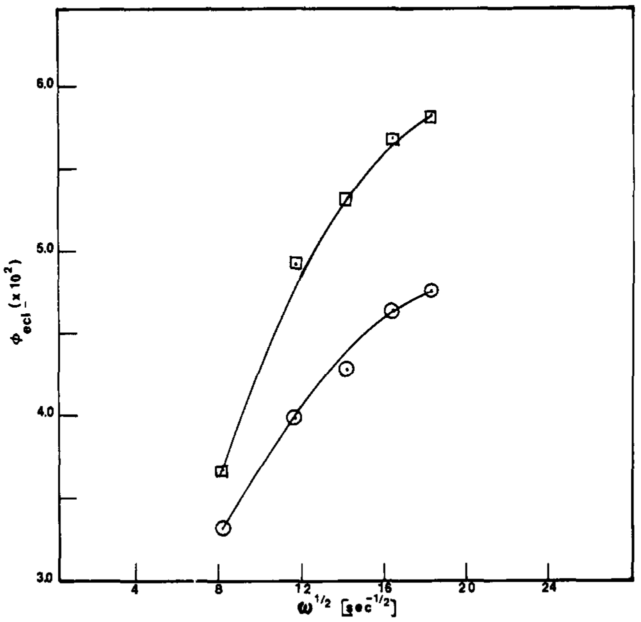


Figure 7. ϕ_{ecl} *vs.* $\omega^{1/2}$ for 1 m*M* Ru(bipy)$_3$(ClO$_4$)$_2$/degassed CH$_3$CN/0.1 *M* TBABF$_4$: -⊙-, $E_d = -1.37$ V, $E_r = +1.48$ V; -⊡-, $E_d = +1.48$ V, $E_r = -1.37$ V.

oxidation states of ruthenium have appeared.[25] The R^{2-} species is unstable, however, and probably liberates bipyridine, which is reducible to the anion radical at these potentials and leads to the multielectron wave at slower scan rates. Similar liberation of ligand upon electrochemical reduction in aprotic solvents has been observed by Tanaka and coworkers[26] for the bipyridyl complexes of Co(II), Mn(II), Ni(II), and Fe(II). Coulometric reductions demonstrate that these lower oxidation state species undergo slow decomposition which prevents their isolation. The oxidized species, R^{3+}, however, is very stable. The best description of the electrochemical processes can probably be given in terms of the molecular orbital (MO) diagram for the system. The MO diagram for the d^6 chelate assuming octahedral symmetry is shown in Figure 8a. In the R^{2+} state all orbitals through the t$_{2g}$(π) are occupied.

Using the treatment of lower oxidation states in tris(bipyridine) complexes by Hanazaki and Nagakura,[27] one can get a more detailed molecular orbital diagram of the highest occupied MO (HOMO, t$_{2g}$) and the lowest unoccupied MO (LUMO, t$_{1u}$). When the O_h symmetry is reduced to D_3, the actual microsymmetry of these complexes, the triply degenerate orbitals will be split into two orbitals, one which is doubly degenerate and one which is singly degenerate. This is represented in the left- and right-hand sides of Figure 8b.

When an electron is placed in the t$_{1u}$(π*), as in reduction, then this electron will repel those in the t$_{2g}$(4πd) orbital. This results in the reduction of the metal ionization potential and raises the orbital energies of the ligands to reduce their electron affinities, as shown in the center of Figure 8b. Using this diagram for the reductions of Ru^{2+}, the first electron would go into the a$_2$ orbital yielding a paramagnetic species. The second electron then pairs with the first on the a$_2$ orbital producing a diamagnetic species. The third electron enters the degenerate e$_g$ level, again yielding a paramagnetic species. Oxidation involves removal of an electron from the t$_{2g}$ level and produces a species which is paramagnetic. This explanation is consistent with the observed paramagnetism of the R^{3+}, R$^+$, and R$^-$ species.[15]

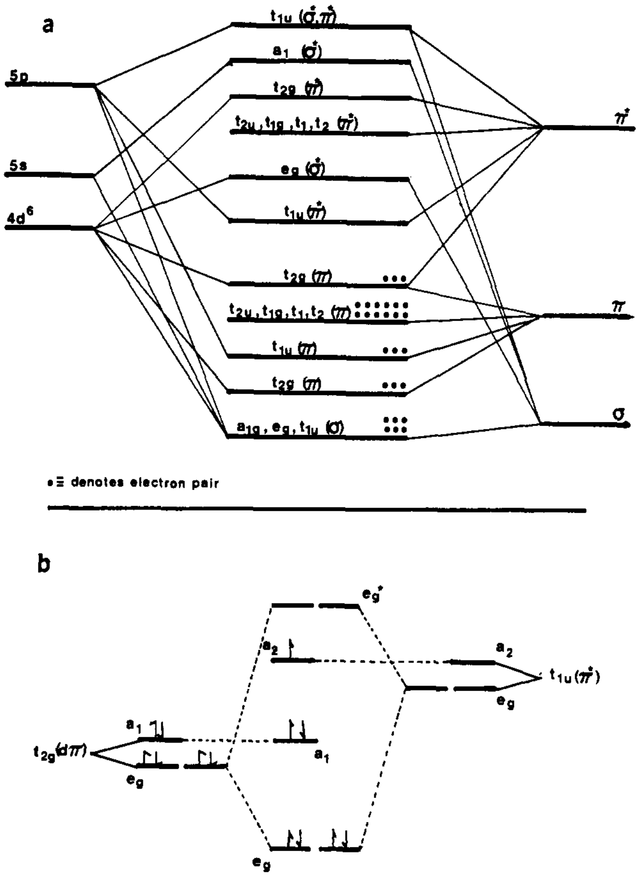


Figure 8. (a) Molecular orbital diagram for a complex with full σ and π bonding and octahedral microsymmetry. For Ru(bipy)$_3{}^{2+}$, six 4d electrons, 12 ligand σ electrons, and 36 ligand π electrons fill the levels through the t$_{2g}$(π) level. (b) Schematic of the interaction of the t$_{2g}$(π) and t$_{1u}$(π*) orbitals upon addition of an electron in a complex of D_3 microsymmetry.

A generally similar picture probably holds for the terpy and *o*-phen complexes. For the Ru(TPTZ)$_2{}^{3+}$ complex, however, the parent compound contains ruthenium in an effective III oxidation state.[10] The oxidation observed for it at +1.52 V then corresponds to Ru(IV); this species apparently is stable for at least a few seconds.

The ecl results from formation of excited triplet R^{2+} as a result of the redox reactions. The reaction

$$R^{3+} + R^{+} \longrightarrow {}^{3}(R^{2+})^{*} + R^{2+} \qquad (2)$$

is energy sufficient, since the triplet state energy is about 2.04 eV and the $\Delta G°$ for the reaction is -2.7 eV. The high ecl efficiency of this process can be attributed to the direct formation of an emitting excited state so that the triplet state suffers less quenching than for the case when triplet–triplet annihilation must precede luminescence. The ecl which arises when R^0 partici-

---

(25) (a) R. N. Goldberg and L. G. Hepler, *Chem. Rev.*, **68**, 231 (1968); (b) G. A. Heath and R. L. Martin, *Aust. J. Chem.*, **23**, 1721 (1970); (c) A. M. Bond, G. A. Heath, and R. L. Martin, *J. Electrochem. Soc.*, **117**, 1362 (170).

(26) (a) N. Tanaka and Y. Sato, *Bull. Chem. Soc. Jap.*, **41**, 2059 (1968); (b) *ibid.*, **41**, 2064 (1968); (c) *Inorg. Nucl. Chem. Lett.*, **4**, 487 (1968); (d) *ibid.*, **2**, 359 (1966); (e) *Electrochim. Acta*, **13**, 335 (1968).

(27) I. Hanazaki and S. Nagakura, *Bull. Chem. Soc. Jap.*, **44**, 2312 (1971).

pates in the redox reaction can be explained by the occurrence of the reaction

$$R^{3+} + R^0 \longrightarrow R^+ + {}^3(R^{2+})^* \qquad (3)$$

followed immediately by (2) forming additional excited triplet. Similarly, when R^- is the reactant, the reaction

$$R^{3+} + R^- \longrightarrow R^0 + {}^3(R^{2+})^* \qquad (4)$$

occurs first, followed by (3) and (2). For the RRDE electrode, where the flux of R^{3+} at the ring is greatly in excess of the flux at the disk for this same electrode process the occurrence of this sequence of reaction, when either R^+, R^0, or R^-, is generated at the disk, can explain the 1 :2 :3 ratio of emission intensities observed (Figure 6). This explanation requires that the efficiency of excited state formation is the same for all three redox processes 2–4 and that quenching of the triplet by the electrogenerated intermediates is probably negligible. An alternate explanation is that only a single redox step (2), (3), or (4) occurs but that the efficiency of formation of the excited state increases as the free energy of the redox step increases; the observed 1 :2 :3 ratio would then have to be coincidental. The observed ratios for single electrode ecl would be explained in a similar manner; theoretical simulation of a case such as this has not yet been accomplished.

Previous spectroscopic studies[4,5] have suggested that the observed emission for $Ru(bipy)_3{}^{2+}$ at 607 nm is derived from an excited triplet state. The photoexcited emissions in solution at room temperature, obtained by Lytle and Hercules[18] and the present work, differ from the spectra taken in rigid glass in that they only exhibit the shortest wavelength emission. In their paper, Klassen and Crosby[21] assign this emission band to 0–0 transition derived from the (d–π^*) transition. The longer wavelength emissions are assumed to be 0–1, 0–2, and 0–3 transitions from the same excited triplet state. However, the shoulder at 630 nm, noted in the ecl of $Ru(bipy)_3{}^{2+}$, does not appear in the solution phosphorescence. It appears unlikely that this shoulder represents a transition from triplet $Ru(bipy)_3{}^{2+}$; it perhaps is caused by a different conformation of the complex or by a species such as a dimer, formed during the redox reaction but not during photoexcitation.

Acknowledgment. The support of this research by the Army Research Office, Durham, and the National Science Foundation (NSF GP-31414X) is gratefully acknowledged. We thank Professor K. DeArmond for helpful comments on this work.

On the Pathway of Bridge–Terminal Ligand Exchange in Some Binuclear Metal Carbonyls. Bis(*pentahapto*cyclopentadienyldicarbonyliron) and Its Di(methyl isocyanide) Derivative and Bis(*pentahapto*cyclopentadienylcarbonylnitrosylmanganese)

R. D. Adams and F. A. Cotton*

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843.

Received February 26, 1973

Abstract: The previously reported proton (Bullitt, Cotton, and Marks) and carbon (Gansow, Burke, and Vernon) nmr data for $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ and new data reported here for $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(CNCH_3)_2$ are discussed in terms of possible pathways by which bridge and terminal ligands (CO and/or CH_3NC) can be interchanged. It is shown how all of the data can be understood using two assumptions: (1) bridges open and close only in pairs; (2) rotational barriers in unbridged tautomers contribute critically to activation energies when such rotations are necessary. It is further shown that simple one-for-one bridge–terminal interchanges are not only unnecessary to account for any of the observations but that their occurrence is incompatible with the data for $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(CNCH_3)_2$. The published results for rearrangements of $(\eta^5\text{-}C_5H_5)_2Mn_2(CO)_2(NO)_2$ (Marks and Kristoff) are also analyzed using the proposed mechanism.

In 1966 the idea was first proposed[1] that in a polynuclear metal carbonyl, the carbonyl ligands might be able to migrate from bridging to terminal positions and *vice versa*. At that time, the question of rate was not explicitly discussed since it was not relevant to the problem then under consideration.[2] In 1970 bridge–terminal site exchange was again proposed, with the explicit suggestion that it can be rapid and thus afford the basis for fluxional or other stereochemically nonrigid behavior in polynuclear metal carbonyls.[3–6] Specifically, it was shown that the cis

---

(1) F. A. Cotton, *Inorg. Chem.*, **5**, 1083 (1966).

(2) It has recently been shown that the most important one of the particular isomerization processes discussed in 1966 is indeed rapid, thus making $Rh_4(CO)_{12}$ a molecule with fluxional character as remarkable as that of bullvalene: *cf.* F. A. Cotton, L. Krucynski, B. L. Shapiro, and L. F. Johnson, *J. Amer. Chem. Soc.*, **94**, 6191 (1972).

(3) J. G. Bullitt, F. A. Cotton, and T. J. Marks, *J. Amer. Chem. Soc.*, **92**, 3155 (1970); *Inorg. Chem.*, **11**, 671 (1972).

(4) Although it was observed independently by two groups[5,6] that the ^{59}Co nmr spectrum of $Co_2(CO)_8$ in solution shows only a single signal, despite the fact that infrared studies[7] had shown that both bridged, $(CO_3)Co(\mu\text{-}CO)_2Co(CO)_3$, and nonbridged, $(CO)_4CoCo(CO)_4$, isomers are present, in neither case was the rapid interconversion of the two