Luminescent Metal Complexes. Part 5.[1] Luminescence Properties of Ring-substituted 1,10-Phenanthroline Tris-complexes of Ruthenium(II)

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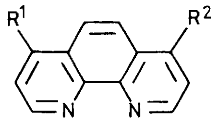
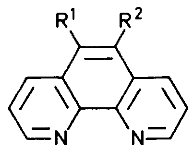
The absorption characteristics, emission spectra, luminescent quantum yields, and lifetimes are reported for 24 ruthenium(II) tris-1,10-phenanthroline complexes in EtOH–MeOH solution. Quantum yields fall between 0.019 and 0.403, the highest values being recorded for complexes substituted at the 4,7-sites with aryl groups. Incorporation of these derivatives into poly(vinyl chloride) film raises the quantum yields leading to values ranging from 0.40 to 0.75.

In earlier papers[2,3] we gave reasons for investigating ruthenium(II) tris-chelates of 2,2′-bipyridyls (bipy) and 1,10-phenanthrolines (phen) as dyes for possible use in luminescent solar collectors (LSC).[2,4,5] The spectroscopic properties of the parent unsubstituted complexes have been extensively investigated over the last two decades.[6–8] There is strong absorption down to 500 nm, a large energy separation (apparent Stokes shift) between the $d \longrightarrow \pi^*$ charge-transfer absorption band and the formally spin-forbidden emission band, and moderate quantum efficiency of luminescence φ_m at least at low temperature. The series is particularly attractive because of the possibility of tuning these properties to the requirements of LSCs through the introduction of substituents onto the ligands. We have therefore undertaken the synthesis and spectroscopic evaluation of a large number of derivatives. In Parts 1[3] and 2[9] we reported solution-phase results for 27 complexes within the $Ru(bipy)_3^{2+}$ series. It was shown that substituents have a rather small effect on the apparent Stokes shift but play a major role in controlling the value of φ_m. This results from their effects on both the radiative and non-radiative rate constants, effects which we were largely able to delineate on the basis of a simple three-state model.[9] Values for φ_m ranged from 0.002 to 0.306, the highest being for the complex with 4,4′-diphenyl-2,2′-bipyridyl.[3] Quantum yields were raised significantly when the complexes were incorporated into plastic films.

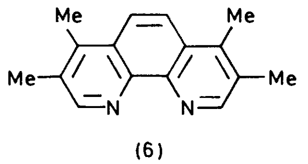
The present paper reports our complementary investigation of ruthenium(II) tris-chelates derived from the phen ligands (**1**)—(**24**). Because of the high φ_m value obtained for the complex of the phenyl-substituted bipy ligand, an essential feature for LSC application, and the reported high φ_m for $Ru(4,7\text{-diphenyl-phen})_3^{2+}$ as a glass at 77 K,[10] we have incorporated into the study a large number of complexes of mono- and di-aryl-substituted phen ligands.



(1) $R^1 = R^2 = H$
(2) $R^1 = Me, R^2 = H$
(4) $R^1 = R^2 = Me$
(7) $R^1 = Cl, R^2 = H$
(9) $R^1 = R^2 = Cl$
(11) $R^1 = Ph, R^2 = H$
(12) $R^1 = p\text{-}CH_3C_6H_4, R^2 = H$
(13) $R^1 = p\text{-}C_6H_5C_6H_4, R^2 = H$
(14) $R^1 = p\text{-}BrC_6H_4, R^2 = H$
(15) $R^1 = p\text{-}MeOC_6H_4, R^2 = H$
(16) $R^1 = R^2 = Ph$



(3) $R^1 = Me, R^2 = H$
(5) $R^1 = R^2 = Me$
(8) $R^1 = Cl, R^2 = H$
(10) $R^1 = Ph, R^2 = H$



(6)

Results and Discussion

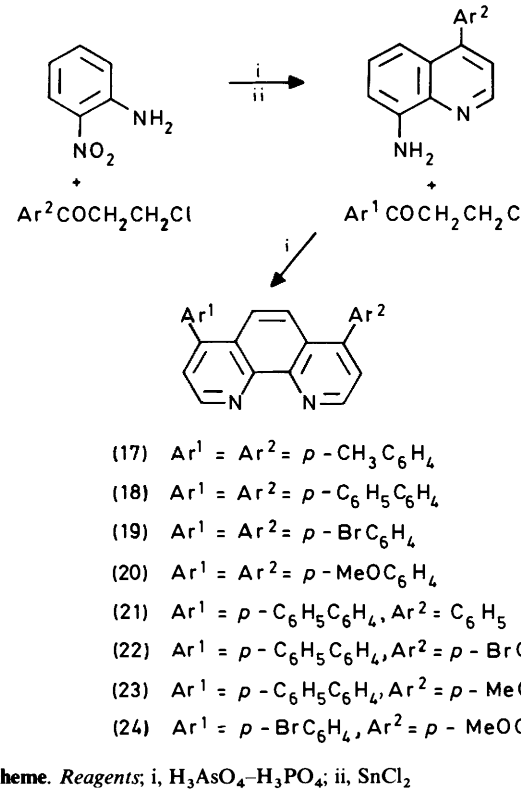
Preparation of Materials.—Ligands (**1**)—(**6**), (**8**), (**10**), and (**16**) were obtained as commercial samples. The 4-chloro and 4,7-dichloro derivatives (**7**) and (**9**) were obtained *via* the corresponding tautomerically mobile hydroxy derivatives according to the method of Snyder and Freier.[11] The series of 4-aryl-1,10-phenanthrolines (**11**)—(**15**) was prepared by the reactions of 8-aminoquinoline with the appropriate aryl β-chloroethyl ketones using the Yale modification of the Skraup reaction[12] after the work of Case's group.[13] 4,7-Diaryl derivatives (**17**)—(**24**) were obtained *via* sequential Skraup reactions, a pathway which provided access to both symmetrically and unsymmetrically substituted derivatives (Scheme). The ruthenium(II) tris-chelates were prepared using either potassium aquapentachlororuthenate essentially using the procedure of Anderson and Seddon,[14] or ruthenium trichloride in ethanol (Table 1). No attempts were made to separate the *meridional* and *facial* stereoisomers which are expected for the complexes of unsymmetrically substituted ligands.

Absorption and Emission Spectra.—The absorption band in the visible spectrum of $Ru(phen)_3^{2+}$ has been assigned to the metal $d \longrightarrow \pi^*$ transitions[15] whereas the emission occurs from the formally spin-forbidden counterpart of these transitions.[8] This leads to a large energy separation between the absorption and emission bands (the apparent Stokes shift) and this meets one of the requirements for application in an LSC.[2,4,5] The

Table 1. Preparation of ruthenium(II) tris-1,10-phenanthroline complexes $Ru(phen)_3{}^{2+}X_2{}^-$

			Preparation				Analytical data (%)							
							Found				Requires			
Compd.	Phen substituent	X^-	Time (h)	Yield (%)	Purification	Formula	C	H	N	Cl	C	H	N	Cl
(25)	None	Cl	0.25	77	from H_2O	$C_{36}H_{24}Cl_2N_6Ru{\cdot}6H_2O$	52.5	4.1	10.1	8.9	52.7	4.4	10.2	8.6
(26)	4-Methyl	I	0.5	37	H_2O wash	$C_{39}H_{30}I_2N_6Ru{\cdot}2H_2O$	47.9	3.4	8.5		48.1	3.5	8.6	
(27)	5-Methyl	Cl	0.5	77	H_2O wash	$C_{39}H_{30}Cl_2N_6Ru{\cdot}2H_2O$	59.0	4.2	10.5	8.8	59.2	4.3	10.6	9.0
(28)	4,7-Dimethyl	Cl	72[a]	55	H_2O wash	$C_{42}H_{36}I_2N_6Ru{\cdot}2.5H_2O$	48.9	3.6	7.9		49.1	4.0	8.2	
(29)	5,6-Dimethyl	I	0.5	71	H_2O wash	$C_{42}H_{36}I_2N_6Ru{\cdot}3H_2O$	48.6	3.7	8.2		48.8	4.1	8.1	
(30)	3,4,7,8,-Tetramethyl	Cl	72[a]	39	from EtOH	$C_{48}H_{48}I_2N_6Ru{\cdot}1.5H_2O$	52.9	4.7	7.3		52.9	4.7	7.7	
(31)	4-Chloro	I	0.25	62	H_2O wash	$C_{36}H_{21}Cl_3I_2N_6Ru{\cdot}3H_2O$	41.2	2.4	7.8	10.1	41.1	2.6	8.0	10.1
(32)	5-Chloro	Cl	0.5	77	H_2O wash	$C_{36}H_{21}Cl_5N_6Ru{\cdot}3H_2O$	49.3	3.4	9.5	20.2	49.7	3.1	9.7	20.4
(33)	4,7-Dichloro	I	0.25	69	H_2O wash	$C_{36}H_{18}Cl_6I_2N_6Ru{\cdot}H_2O$	38.7	1.9	7.5		38.5	1.8	7.5	
(34)	5-Phenyl	I	0.5	64	from H_2O–EtOH	$C_{54}H_{36}I_2N_6Ru{\cdot}3H_2O$	54.8	3.2	7.1		55.1	3.6	7.1	
(35)	4-Phenyl	Cl	0.5	56	H_2O wash	$C_{54}H_{36}Cl_2N_6Ru{\cdot}6H_2O$	61.4	4.4	7.8	7.2	61.8	4.6	8.0	6.8
(36)	4-Tolyl	Cl	0.5	75	H_2O wash	$C_{57}H_{42}Cl_2N_6Ru{\cdot}6H_2O$	62.5	4.9	7.4	6.8	62.7	5.0	7.7	6.5
(37)	4-*p*-Biphenylyl	Cl	0.5	83	H_2O wash	$C_{72}H_{48}Cl_2N_6Ru{\cdot}5H_2O$	69.0	4.6	6.6	5.8	68.7	4.7	6.7	5.6
(38)	4-*p*-Bromophenyl	Cl	0.5	75	H_2O wash	$C_{54}H_{33}Br_3Cl_2N_6Ru{\cdot}6H_2O$	50.3	3.4	6.4		50.4	3.5	6.5	
(39)	4-*p*-Methoxyphenyl	Cl	0.5	67	H_2O wash	$C_{57}H_{42}Cl_2N_6O_3Ru{\cdot}6H_2O$	60.5	4.7	7.0	6.1	60.1	4.7	7.4	6.2
(40)	4,7-Diphenyl	Cl	0.5	71	H_2O wash	$C_{72}H_{48}Cl_2N_6Ru{\cdot}4H_2O$	69.7	4.8	6.7	5.6	69.7	4.6	6.8	5.7
(41)	4,7-Ditolyl	Cl	1.25	83	H_2O wash	$C_{78}H_{60}Cl_2N_6Ru{\cdot}6H_2O$	68.8	5.0	5.8	4.9	68.8	5.3	6.2	5.2
(42)	4,7-Bis(biphenylyl)	Cl	2	85	H_2O wash	$C_{108}H_{72}Cl_2N_6Ru{\cdot}3H_2O$	76.2	4.5	5.0	4.3	76.3	4.3	5.0	4.2
(43)	4,7-Bis-(*p*-bromophenyl)	Cl	4	89	*b*	$C_{72}H_{42}Br_6Cl_2N_6Ru{\cdot}4H_2O$	50.7	2.9	4.6		50.5	2.9	4.9	
(44)	4,7-Bis-(*p*-methoxyphenyl)	Cl	1	94	from H_2O–EtOH	$C_{78}H_{60}Cl_2N_6O_6Ru{\cdot}4H_2O$	66.0	4.6	5.9		65.9	4.8	5.5	
(45)	4-*p*-Biphenylyl-7-phenyl	Cl	2	86	H_2O wash	$C_{90}H_{60}Cl_2N_6Ru{\cdot}3H_2O$	74.7	4.9	5.5	4.7	74.5	4.6	5.8	4.9
(46)	4-*p*-Biphenylyl-7-*p*-bromophenyl	Cl	3	95	H_2O wash	$C_{90}H_{57}Br_3Cl_2N_6Ru{\cdot}4H_2O$	63.6	3.8	5.1		64.0	3.8	5.0	
(47)	4-*p*-Biphenylyl-7-*p*-methoxyphenyl	Cl	12	88	H_2O wash	$C_{93}H_{66}Cl_2N_6O_3Ru{\cdot}5H_2O$	70.6	4.7	5.3	4.8	70.8	4.8	5.3	4.5
(48)	4-*p*-Bromophenyl-7-*p*-methoxyphenyl	Cl	3	83	from H_2O–EtOH	$C_{75}H_{51}Br_3Cl_2N_6O_3Ru{\cdot}5H_2O$	57.0	3.7	5.3		56.8	3.9	5.3	

[a] In ethanol, see Experimental section. [b] Chromatography over Al_2O_3, CH_3CN as eluant.



Scheme. *Reagents*; i, H_3AsO_4–H_3PO_4; ii, $SnCl_2$

detailed photophysics of $Ru(phen)_3{}^{2+}$, and indeed of ruthenium(II) polypyridine complexes in general, is a subject of continuing interest.[6,7]

Data obtained in the present investigation for the positions of the charge-transfer absorption bands, the extinction coefficient, and the position of the emission band are listed in Table 2. Values refer to solutions in EtOH–MeOH (4:1) and typical spectra are shown in Figure 1. Two distinct absorption bands are normally apparent which distinguishes the spectra from those obtained under the same conditions for the $Ru(bipy)_3{}^{2+}$ series where the lower wavelength transition appeared as a shoulder.[3] The emission spectra for all the phen complexes show an unsymmetrical band, *cf.* Figure 1. The structure apparent in spectra obtained for members of the series in glasses at 77 K[8,16,17] is thus lost under the present conditions of measurement. Because of the broadness of the emission band the $\lambda_{max.}$ values are considered to be only reliable to ±5 nm. Absorption and emission data for aqueous solutions of eight of the present complexes have been published by Sutin and his co-workers.[18] Less wide ranging studies have been reported by Nakamaru's group[19] and by Miller and Prince.[20] Where comparisons are possible, the present absorption and emission data show a satisfactory agreement with those obtained elsewhere; as in Sutin's study,[18] the values obtained for the extinction coefficient of the charge-transfer band, ε_s, are somewhat larger than those reported by Miller and Prince.[20]

The unsubstituted parent compound (**25**) absorbs at 420 and 445 nm. These band positions are relatively insensitive to methyl substitution as noted elsewhere[16-18] but compound (**30**) is of interest in providing the sole example wherein the lower

Table 2. Spectroscopic properties of ruthenium(II) tris-1,10-phenanthroline complexes in EtOH–MeOH (4:1 v/v) at 20 °C

Compd.	$\lambda_{\text{max.}}^{(abs)}$/ nm	$\varepsilon \times 10^{-4}$/ l mol^{-1} cm^{-1} [a]	$\lambda_{\text{max.}}^{(em)}$/ nm	φ_m [b]	τ_m/μs	$10^2\ k_R$/ μs^{-1}	$10^2\ k_N$/ μs^{-1}
(**25**)	420 445	2.00	595	0.019	0.45	4.2	217.8
(**26**)	424, 445	2.20	602	0.054	0.80	6.8	119.2
(**27**)	424, 445	2.10	597	0.061	0.85	7.2	110.4
(**28**)	428, 448	2.27	600	0.059	0.85	6.9	110.7
(**29**)	430, 450	1.98	598	0.143	2.50	5.7	34.3
(**30**)	422, 439	2.33	595	0.032	0.48	6.7	201.6
(**31**)	426, 450	1.81	630	0.037	1.78	2.1	54.1
(**32**)	425, 446	1.79	604	0.035	0.67	5.2	144.1
(**33**)	436, 456	2.06	668	0.028	1.55	1.8	62.7
(**34**)	424, 448	2.17	597	0.033	1.15	2.9	84.1
(**35**)	430, 450	2.21	605	0.109	4.00	2.7	22.3
(**36**)	430, 453	2.36	605	0.117	3.50	3.3	25.3
(**37**)	432, 454	2.87	612	0.184	4.90	3.8	16.6
(**38**)	432, 452	2.53	615	0.136	4.10	3.3	21.1
(**39**)	432, 452	2.53	615	0.130	3.25	4.0	26.8
(**40**)	438, 463	2.86	618	0.366	6.40	5.7	9.9
(**41**)	442, 464	2.74	618	0.280	6.43	4.4	11.2
(**42**)	441, 465	3.63	620	0.360	7.20	5.0	8.9
(**43**)	442, 464	3.30	623	0.403	5.95	6.8	10.0
(**44**)	442, 468	3.79	615	0.387	6.10	6.3	10.1
(**45**)	438, 465	3.37	618	0.330	6.10	5.4	11.0
(**46**)	440, 465	3.10	623	0.310	6.00	5.2	11.5
(**47**)	445, 468	3.48	620	0.305	6.05	5.0	11.5
(**48**)	438, 464	2.55	625	0.237	5.95	4.0	12.8

[a] Extinction coefficient for the longer wavelength charge-transfer band.
[b] Measured relative to a solution of rhodamine B as standard, $\varphi = 0.73$.[3]

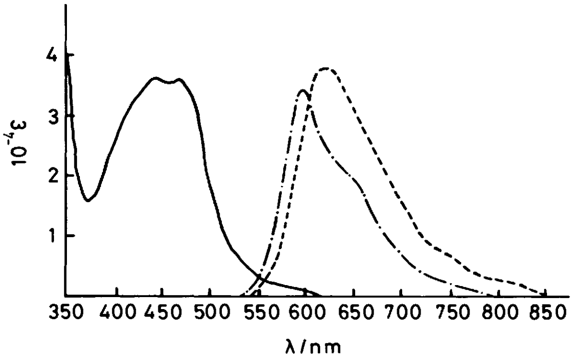


Figure 1. The absorption (——) and emission (– – –) spectra for complex (**42**) as a solution in EtOH–MeOH (4:1 v/v) and the emission spectrum (· — · —) of (**42**) in poly(vinyl chloride) film, approximate concentration 3×10^{-5}M

energy transition is to shorter wavelength than that of the parent. This apparently is a consequence of methyl substitution β to the ring nitrogens: a similar blue shift upon β-methyl substitution was observed in the $Ru(bipy)_3{}^{2+}$ series.[3] 5-Chloro and 5-phenyl substituents give rise to a small bathochromic shift but the absorption bands are shifted further to the red when aryl groups are introduced at the 4- and 4,7-positions. Introduction of aryl groups is accompanied by the expected increase in ε_s.[21]

The emission maximum in the parent unsubstituted compound is observed at 595 nm. All but (**30**) emit to longer wavelength, the largest shift in the band being observed in the 4,7-dichloro derivative (**33**). Where comparisons are possible with data for the correspondingly substituted derivatives in the $Ru(bipy)_3{}^{2+}$ series,[3] it appears that the substituent effects on $\lambda_{\text{max.}}$(emission) are qualitatively similar. Furthermore, the energy separation between the absorption and emission bands, the apparent Stokes shift, in the two series are also comparable. This is illustrated by the following values of Δν in kK (figures for the corresponding 4- or 4,4′-disubstituted bipy-complexes are shown in italics): (**25**) 5.7, *6.3*; (**28**) 5.7, *6.4*; (**31**) 6.3, *6.4*; (**33**) 6.9, *6.6*; (**40**) 5.4, *5.4*.

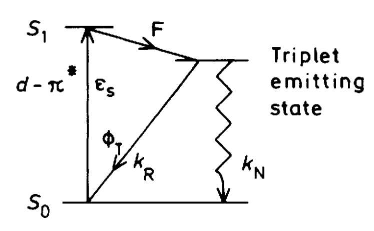


Figure 2. Schematic representation of the three-state model

Luminescent Lifetimes and Quantum Efficiencies.—Lifetimes, τ_m, and φ_m values (Table 2) of deoxygenated solutions (EtOH–MeOH, 4:1 v/v) were measured using apparatus and procedures described previously.[3] For the measurements of τ_m, deoxygenation of the solution was achieved using freeze–pump–thaw cycles.[3] This method was used during preliminary measurements of φ_m but initial indications that this led to higher values of φ_m relative to those obtained for solutions deoxygenated by nitrogen bubbling were not substantiated. The latter method subsequently became the preferred procedure for preparing deoxygenated solutions. Sutin and his co-workers[18] obtained luminescent lifetimes for (**25**), (**27**)—(**30**), (**32**), (**34**), and (**40**) as solutions in water. The present set of values (for EtOH–MeOH) are lower for all but the phenyl-substituted derivatives, *i.e.* (**34**) and (**40**). That the emission parameters are sensitive to the solvent is consistent with φ_m data obtained for the parent complex (**25**) by Nakamura's group.[19] They report values of 0.049 in water and 0.015 in EtOH. The present value of 0.019 is in satisfactory agreement with the latter figure. However, their values for the 4,7-diphenyl derivative (**40**) in EtOH (0.13 and 0.22 depending upon the standard) are somewhat lower than the 0.366 obtained here.

It is apparent from the present data that solution-phase lifetimes and luminescence yields are particularly dependent upon the type and site of the substituent. The 5,6-dimethyl derivative (**29**) and complexes bearing aryl groups in the 4- and 4,7-positions have markedly longer lifetimes and higher quantum yields. γ-Phenyl substitution gave rise to a similar but less pronounced effect in the $Ru(bipy)_3{}^{2+}$ series.[3,9] [Compare τ_m and φ_m values for the parent unsubstituted complex (**25**) 0.45 μs, 0.019 and the 4,7-diphenyl derivative (**40**) 6.40 μs, 0.366 with those for $Ru(bipy)_3{}^{2+}$ 1.15 μs, 0.089 and Ru(4,4′-diphenylbipy)$_3{}^{2+}$ 1.95 μs, 0.306]. Substituents attached to the pendant phenyl groups also have an effect upon τ_m and φ_m. However, trends observed in the 4-aryl series are not reproduced in the 4,7-diaryl compounds.

k_R and k_N Values.—In our previous study[9] of the electronic processes of the $Ru(bipy)_3{}^{2+}$ series of complexes we utilised a simple three-state model (Figure 2). The term *F* is the fractional intersystem crossing probability, φ_T is the quantum efficiency of triplet emission, and k_R and k_N are the radiative and non-radiative transition rate constants from the triplet manifold. Under conditions where oxygen and self-quenching are absent we can write $\varphi_m = \varphi_T F = k_R \tau_m F$. Calculation of k_R [and hence k_N from the relationship $\tau_m = (k_R + k_N)^{-1}$] requires a knowledge of the value of *F*.

The normal assumption is that *F* is unity and indeed Demas and Crosby[22] have confirmed this value for the $Ru(bipy)_3{}^{2+}$ complex primarily on the basis of the observation that φ_m is

Table 3. Spectroscopic properties of ruthenium(II) tris-4,7-diaryl-1,10-phenanthroline complexes in poly(vinyl chloride) film at 20 °C

Compound	Substituent	$\lambda_{max.}^{(abs)}$/nm	$\lambda_{max.}^{(em)}$/nm	φ_m	$\tau_m/\mu s$	$10^2\ k_R/\mu s^{-1}$	$10^2\ k_N/\mu s^{-1}$
(40)	4,7-Diphenyl	438, 468	595	0.75	6.9	10.9	3.6
(41)	4,7-Ditolyl	434, 468	595	0.50	6.1	8.2	8.2
(42)	4,7-Bis-(*p*-biphenylyl)	440, 470	598	0.40	6.8	5.9	8.8
(44)	4,7-Bis-(*p*-methoxyphenyl)	436, 474	598	0.40	6.2	6.5	9.6
(45)	4-*p*-Biphenylyl-7-phenyl	438, 470	593	0.49	7.0	7.0	7.3
(46)	4-*p*-Biphenylyl-7-*p*-bromophenyl	436, 468	595	0.60	6.6	9.1	6.1
(47)	4-*p*-Biphenylyl-7-*p*-methoxyphenyl	436, 470	597	0.46	6.9	6.7	7.8
(48)	4-*p*-Bromophenyl-7-*p*-methoxyphenyl	436, 470	597	0.54	5.7	9.5	8.0

independent of the wavelength of excitation. For **(25)** in aqueous solution, energy-transfer experiments[23] have given a value of *ca.* 0.6 but a more recent electron-transfer study[24] has raised this value to *ca.* 1.0. Sriram and Hoffman[7] investigated the lifetime and emission intensity of the complex in mixtures of H_2O and D_2O and assigned values of 0.84 in water and 1.0 in D_2O. At the present time, and in the absence of data to the contrary, we assume that for EtOH–MeOH solution F is unity throughout the series, enabling us to equate φ_m with φ_T and hence to calculate k_R and k_N. Results of such a calculation appear in Table 2.

The principal features of the k_R and k_N values within the series are the small variations within the former and much greater variations in the latter. This was also manifested within the data for the Ru(bipy)$_3{}^{2+}$ compounds[9] but the contrast was less apparent. To some extent this can be attributed to the different range of substituents investigated in the present series.

In the Ru(bipy)$_3{}^{2+}$ series, k_N values for complexes bearing $+M$, $-I$, and methyl substituents in the 4,4′-positions were shown to be a function of the emission energy.[9] This is a manifestation of the energy-gap law, *i.e.*, as the energy between the emitting state and the ground state becomes smaller, so non-radiative processes become more important in the decay of the excited state. However, complexes bearing other types of substituents, or substituent in other positions, did not follow the same function. Thus Ru(4,4′-diphenylbipy)$_3{}^{2+}$ had a lower k_N than that predicted on the basis of the energy-gap correlation.

For the series of complexes reported here, with the exception of **(33)**, there is rather little variation in the position of $\lambda_{max.}$(emission) whereas values of k_N vary between 9×10^{-2} and $220 \times 10^{-2}\ \mu s^{-1}$. Clearly the energy-gap law does not hold. The 4-aryl substituted complexes **(35)**—**(39)** have k_N values significantly lower than for all the non-aryl substituted compounds, as well as that of the 5-phenyl derivative **(34)**. 4,7-Diaryl derivatives have k_N values which are lower still.

Measurements of Poly(vinyl Chloride) Film.—As part of the programme of evaluation of these materials, eight of the 4,7-diaryl-substituted compounds were incorporated into poly(vinyl chloride) (PVC) film. Table 3 lists the absorption and emission data and the k_R and k_N values calculated on the same basis as that for the solution-phase results. The concentrations of the materials in the film, *ca.* 3×10^{-5}M, are not known sufficiently accurately to justify evaluation of extinction coefficients.

Comparison of the data in Tables 2 and 3 shows that the wavelengths of the absorption maxima are little changed whereas the emission maximum undergoes a significant blue shift on changing from fluid to a plastic medium: the latter is well illustrated by inspection of the emission spectra for **(42)** in Figure 1. It is evident, therefore, that the apparent Stokes shift is much reduced in the plastic medium compared with the alcoholic solution. The radiative and non-radiative rate constants are also changed for the majority of the complexes in Table 3. The former is raised and the latter is lowered leading to an enhancement of the quantum yield. These results show that solvent relaxation is having a significant effect on the energy and rate constants of the emitting state. Such a solvent-relaxation effect is not unexpected for this class of compound. The excited charge-transfer states involve considerable charge separation and hence the creation of a polarity difference between the ground and excited states. Recent evidence shows that there is localisation on one ligand of the transferred electron for a time sufficiently long for Raman scattering from the localised state to be observed.[25] This implies the creation of a large transient dipole moment. Hence optical excitation will take the complex to an unrelaxed state and emission will occur from the relaxed state. In a rigid medium of low dielectric constant relaxation will be reduced leading to a smaller Stokes shift. This in turn implies weaker electron-vibration coupling which, together with a larger energy gap for a blue-shifted transition, results in a lower value for k_N.

Experimental

Materials.—1,10-Phenanthroline, 4-methyl-, 5-methyl-, 4,7-dimethyl-, 5,6-dimethyl-, 3,4,7,8-tetramethyl-, 5-chloro-, 5-phenyl-, and 4,7-diphenyl-1,10-phenanthrolines were obtained from commercial suppliers. The following were prepared essentially *via* literature procedures: 4-chloro-1,10-phenanthroline[11] **(7)**, m.p. 158—162 °C (lit.,[26] 163—165 °C), 4,7-dichloro-1,10-phenanthroline[11] **(19)**, m.p. 249—251 °C (lit.,[11] 249—250 °C), 4-phenyl-1,10-phenanthroline[13a] **(11)**, m.p. 103—104 °C (lit.,[13a] 105—106 °C), 4-tolyl-1,10-phenanthroline[13b] **(12)**, m.p. 166—167 °C (lit.,[13b] 169—170 °C), 4-*p*-biphenylyl-1,10-phenanthroline[13b] **(13)**, m.p. 189—192 °C (lit.,[13b] 192.5—193.5 °C), 4,7-ditolyl-1,10-phenanthroline[13b] **(17)**, m.p. 181—183 °C (lit.,[13b] 184—185 °C), 4,7-bis-(*p*-biphenylyl)-1,10-phenanthroline[13b] **(18)**, m.p. 297 °C (lit.,[13b] 291—292 °C), 4,7-bis-(*p*-methoxyphenyl)-1,10-phenanthroline[13] **(20)**, m.p. 203—207 °C (lit.,[13b] 208—209 °C).

4-p-*Bromophenyl*-1,10-*phenanthroline* **(14)**. To a well stirred solution of 8-aminoquinoline (3.61 g), 75% arsenic acid (9.46 g), and phosphoric acid (25 ml) at 100 °C was added *p*-bromophenyl β-chloroethyl ketone[27] (8.66 g) at such a rate that the temperature did not exceed 120 °C. The temperature was raised to 140 °C for 1.5 h. The mixture was cooled and poured onto ice and the resulting solution made alkaline (30% aqueous KOH). The mixture was cooled at 0 °C overnight. The precipitate was collected, washed with water, and extracted with boiling toluene (700 ml). To the extract was added CH_2Cl_2 (200 ml) and the combined solution dried ($MgSO_4$). The solvent was evaporated and the residue recrystallised from toluene to afford 4-p-*bromophenyl*-1,10-*phenanthroline* as pale brown microcrystals (4.8 g, 57%), m.p. 218—219 °C (Found: C, 64.5; H, 3.3; N, 8.0; Br, 23.9. $C_{18}H_{11}BrN_2$ requires C, 64.5; H, 3.3; N, 8.4; Br, 23.8%).

4,7-*Bis*-(p-*bromophenyl*)-1,10-*phenanthroline* **(19)**. (i) 4-*p*-Bromophenyl-8-nitroquinoline. *o*-Nitroaniline (8.4 g), arsenic acid (21.7 g), orthophosphoric acid (60 ml), and *p*-bromophenyl β-chloroethyl ketone (22.3 g) were treated as above to afford 4-p-*bromophenyl*-8-*nitroquinoline* as light yellow needles (11.2 g, 56%), m.p. 148—149 °C (from cyclohexane) (Found: C, 54.9; H, 2.75; N, 8.1; Br, 24.7. $C_{15}H_9BrN_2$ requires C, 54.7; H, 2.75; N, 8.5; Br, 24.3%).

(ii) 4-*p*-Bromophenyl-8-aminoquinoline. A solution of tin(II) chloride dihydrate (21.4 g) and 4-*p*-bromophenyl-8-nitroquinoline (10.3 g) in absolute EtOH (70 ml) was heated to reflux for 4 h. The solution was made alkaline with aqueous NaOH and the collected filtrate extracted with ether in a Soxhlet extractor. The ether was evaporated and 4-*p*-bromophenyl-8-aminoquinoline (4.1 g) used below without further purification.

(iii) 4,7-Bis-(*p*-bromophenyl)-1,10-phenanthroline (**19**). 4-*p*-Bromophenyl-8-aminoquinoline (2 g), arsenic acid (2.3 g), orthophosphoric acid (6 ml), and *p*-bromophenyl β-chloroethyl ketone (2.1 g) were treated together as above to afford 4,7-*bis*-(p-*bromophenyl*)-1,10-*phenanthroline* as a light brown amorphous powder (1.5 g, 64%), m.p. 142 °C (from cyclohexane) (Found: C, 58.5; H, 2.9; N, 5.4. $C_{24}H_{14}Br_2N_2$ requires C, 58.8; H, 2.9; N, 5.9%).

4-p-*Biphenylyl*-7-*phenyl*-1,10-*phenanthroline* (**21**). Using the above conditions 4-*p*-biphenylyl-8-aminoquinoline[13b] (1.1 g), arsenic acid (1.3 g), orthophosphoric acid (3.5 ml), and phenyl β-chloroethyl ketone (0.83 g) afforded 4-p-*biphenylyl*-7-*phenyl*-1,10-*phenanthroline* as light beige rhomboids (0.6 g, 40%), m.p. 265—267 °C (from toluene) (Found: C, 87.8; H, 5.0; N, 6.4. $C_{30}H_{20}N_2$ requires C, 88.2; H, 4.9; N, 6.8%).

4-p-*Biphenylyl*-7-p-*bromophenyl*-1,10-*phenanthroline* (**22**). Using the above conditions 4-*p*-biphenylyl-8-aminoquinoline (3.9 g), arsenic acid (12 g), orthophosphoric acid (13 ml), and *p*-bromophenyl β-chloroethyl ketone (4.34 g) afforded 4-p-*biphenylyl*-7-p-*bromophenyl*-1,10-*phenanthroline* as a yellow amorphous powder (1.8 g, 64%), m.p. 155—156 °C (Found: C, 73.8; H, 4.3; N, 5.3. $C_{30}H_{19}BrN_2$ requires C, 73.9; H, 3.9; N, 5.3%).

4-p-*Biphenylyl*-7-p-*methoxyphenyl*-1,10-*phenanthroline* (**23**). By the above procedure 4-*p*-biphenylyl-8-aminoquinoline (1.8 g), arsenic acid (2.3 g), orthophosphoric acid (6 ml), and *p*-methoxyphenyl β-chloroethyl ketone[28] (1.7 g) afforded 4-p-*biphenylyl*-7-p-*methoxy*-1,10-*phenanthroline* as a pale yellow amorphous solid (from cyclohexane) (0.4 g, 16%), m.p. 223—225 °C (Found: C, 84.5; H, 5.1; N, 6.0. $C_{31}H_{22}N_2O$ requires C, 84.8; H, 5.1; N, 6.4%).

4-p-*Bromophenyl*-7-p-*methoxyphenyl*-1,10-*phenanthroline* (**24**). By the above procedure, 4-*p*-bromophenyl-8-aminoquinoline (2 g), arsenic acid (2.3 g), orthophosphoric acid (6 ml), and *p*-methoxyphenyl β-chloroethyl ketone (1.67 g) afforded 4-p-*bromophenyl*-7-p-*methoxyphenyl*-1,10-*phenanthroline* as an amorphous powder (from cyclohexane) (0.89 g, 28%), m.p. 98 °C (Found: C, 65.7; H, 4.0; N, 5.9; Br, 17.0. $C_{25}H_{17}BrN_2O \cdot H_2O$ requires C, 65.5; H, 4.1; N, 6.1; Br, 17.4%).

Complexes.—In the general procedure, based on the work of Anderson and Seddon,[14] a solution of three equivalents of the ligand in dimethylformamide was added slowly to a hot aqueous solution of potassium aquapentachlororuthenate (1 equiv.) acidified with a few drops of 6N-HCl. The solution was refluxed until the colour changed from red to green (for reaction times see Table 1). In some instances further DMF was added during the reaction to redissolve precipitated ligand. Sodium hypophosphite was added and the solution heated further (2—12 h) until the solution was red. The complexes were isolated either as the chloride or iodide salts by precipitation with either concentrated HCl or KI solution respectively.

Two complexes (**28**) and (**30**) were prepared by treating three equiv. of ligand with ruthenium trichloride in refluxing ethanol for 72 h followed by precipitation as the chloride using concentrated HCl.

The procedure for incorporating materials into poly(vinyl chloride) film was as described elsewhere.[3]

Spectroscopic Measurements.—Instrumentation and procedures used for the measurment of absorption and emission parameters were as described earlier,[3] with the exception that standard nitrogen bubbling procedures were frequently used to deaerate solutions in place of freeze–pump–thaw cycles.

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