Equilibria in Complexes of *N*-Heterocyclic Molecules. Part 19.† Reactions of Tris(2,2′-bipyridyl)-, Tris(1,10-phenanthroline)-, and Bis(2,2′-bipyridyl)dicyano-ruthenium(III) in Aqueous Solution

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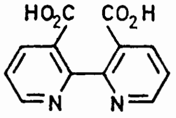
The reactions of $[Ru(bipy)_3]^{3+}$, $[Ru(phen)_3]^{3+}$, and $[Ru(bipy)_2(CN)_2]^+$ in aqueous solution have been followed (bipy = 2,2′-bipyridyl, phen = 1,10-phenanthroline). Neither $[Ru(bipy)_3]^{3+}$ nor $[Ru(phen)_3]^{3+}$ racemizes or dissociates in aqueous solution, contrary to earlier reports. Both react to form new species which appear to be covalently hydrated. Further reaction takes place at the ligand with $[Ru(phen)_3]^{3+}$, but the formation of the new species is at least initially reversible. The reaction to form new purple compounds, one of which can be isolated, is completely reversible in the case of $[Ru(bipy)_3]^{3+}$, and with retention of optical configuration. The series of reactions described fits the known reactions involving the tervalent complexes when they are reduced and a mechanism for the known formation of H_2O_2 is provided. The CN groups in $[Ru(bipy)_2(CN)_2]^+$ react in aqueous solution to yield $[Ru(bipy)_2(OH_2)_2]^{3+}$ by a series of complex steps. Solid $Ru(bipy)_2(SCN)_2{\cdot}4H_2O$ can be isolated from such reaction mixtures following reduction and addition of $[SCN]^-$ ion.

It has generally been assumed that the behaviour of the $[Ru(bipy)_3]^{3+}$ and $[Ru(phen)_3]^{3+}$ ions ‡ in solution closely parallels that of the corresponding iron(III) compounds. Basolo and Pearson,[1] citing the earlier work of Dwyer and Gyarfas,[2-4] state that the optically active ruthenium(III) cations rapidly racemize in solution at room temperature. However, upon re-examination of these earlier results, it is apparent that this claim is unfounded. In the case of $[Ru(bipy)_3]^{3+}$, made by the oxidation of the corresponding optically active ruthenium(II) species in 0.5 mol dm^{-3} H_2SO_4 with Ce^{IV}, Dwyer and Gyarfas [2] found that reduction by the addition of iron(II) sulphate crystals to the solution yielded the starting material with the sign and magnitude of its optical activity *unchanged*. It was therefore concluded that during the time of the measurement no racemization had occurred. A similar result to this was also found [3] for the oxidation and subsequent reduction of optically active $[Ru(phen)_3]^{2+}$ in 3 mol dm^{-3} H_2SO_4. Unless the reactions in this case were carried out quickly, however, activity was said [4] to be lost rapidly at 20 °C. The instability of the blue $[Ru(phen)_3]^{3+}$ cation had previously been noted by Dwyer *et al.*[5] in the course of their study of the redox potential of the Ru^{II}–Ru^{III} couple in aqueous sulphuric acid solutions. Unlike the corresponding bipy system, $[Ru(phen)_3]^{3+}$ was found to be unstable in all the acid concentrations studied, the blue oxidized form apparently undergoing self-reduction. The reaction was said [5] to be most pronounced at the lower acid concentrations and it was proposed that the reaction occurring was the oxidation of the co-ordinated phenanthroline ligands to yield 2,2′-bipyridyl-3,3′-dicarboxylic acid (1).



(1)

We have recently been interested [6-8] in the way solvation affects the racemization and dissociation of phen and bipy complexes in aqueous solution and more particularly in the role that covalently hydrated and related species [9,10] play in these reactions. In the course of these studies we have had occasion to follow the rates of racemization of $[Ru(phen)_3]^{3+}$ and $[Ru(bipy)_3]^{3+}$ under the same conditions used in previous studies [7,8] of the analogous iron(III) compounds. We found that, as expected, $[Ru(phen)_3]^{3+}$ and $[Ru(bipy)_3]^{3+}$ neither racemize nor dissociate in 100% H_2SO_4 solution. When we attempted to follow the rate of racemization of optically active $[Ru(phen)_3]^{3+}$ in chlorine-saturated aqueous solution a rather surprising reaction was found to occur. The compound does not racemize and a new optically active compound is produced. This compound maintains its optical activity indefinitely in chlorine-saturated aqueous solution. On prolonged standing it was also found that $[Ru(bipy)_3]^{3+}$ reacts to form new optically active species which also retain optical activity indefinitely. It is therefore evident that no racemization reactions take place in either of the two systems, a result in marked contrast to that obtained for the corresponding iron(III) compounds. It was decided to undertake an investigation of these reactions, the results of which are presented below.

EXPERIMENTAL

Optically active $[Ru(phen)_3][ClO_4]_2{\cdot}2H_2O$ and $[Ru(bipy)_3][ClO_4]_2{\cdot}2H_2O$ were obtained using the method of Dwyer and Gyarfas.[2,4] Alternatively, they may be formed directly using the Bailar asymmetric synthesis.[11] However, this latter method gives, using D-(+)-tartrate, Δ-$[Ru(phen)_3]^{2+}$ and Δ-$[Ru(bipy)_3]^{2+}$ only in 35 and 60% optical purity, respectively.[12] The compound $[Ru(bipy)_2(CN)_2]^+$ was prepared according to the method of Schilt.[13,14] To effect oxidation of the compounds in aqueous solution, either chlorine gas (B.D.H. Laboratory Reagent, 99% pure) or solid cerium(IV) nitrate hexahydrate was used.

Infrared spectra were recorded with a Perkin-Elmer 257 grating spectrophotometer using either KBr discs or Nujol mulls calibrated against polystyrene. Circular-dichroism spectra were obtained with a Jobin-Yvon (C.N.R.S.-Roussel-Jouan) Dichrographe III. Electronic spectra were

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† Part 18 is ref. 33.

‡ bipy = 2,2′-Bipyridyl, phen = 1,10-phenanthroline.

recorded with a Beckman DK2A ratio-recording spectrophotometer and ^{1}H n.m.r. spectra with a 90 MHz Perkin-Elmer R32 spectrometer at 35 °C using either $SiMe_4$ or $Na[Me_3Si(CH_2)_3SO_3]$ as internal standards. E.s.r. spectral measurements were made using a Varian 109 spectrometer.

RESULTS AND DISCUSSION

(*a*) $[Ru(bipy)_3]^{n+}$.—When *orange* solutions of $[Ru(bipy)_3]^{2+}$ are oxidized with either Ce^{IV} or Cl_2, *green* solutions of $[Ru(bipy)_3]^{3+}$ are initially obtained. On standing, however, these *green* solutions, if maintained under an atmosphere of Cl_2 undergo a colour change passing from *green* to *purple*. The purple solution has $\lambda_{max.}$ in the visible region of the electronic spectrum at 472 nm. If optically active $[Ru(bipy)_3]^{2+}$ is used initially, optical activity is maintained throughout the reactions. These can indeed be most easily followed by the changes observed in optical activity. The c.d. spectra of $[Ru(bipy)_3]^{2+}$ and the green $[Ru(bipy)_3]^{3+}$ and purple compounds prepared from the former by oxidation are shown in Figure 1. It is seen that, apart from the changes in the visible region of the spectrum, the magnitude of the 'exciton' band in the u.v. region decreases on reaction of the green $[Ru(bipy)_3]^{3+}$ ion to form the purple species. It has been shown that such changes can be directly related either to a decrease in the number of aromatic di-imine ligands involved in the exciton coupling,[15-17] or to changes in the configuration of the ligands themselves.[6,8,10,12,18] On prolonged standing in aqueous solution under a chlorine atmosphere the purple compound maintains its optical activity at room temperature.

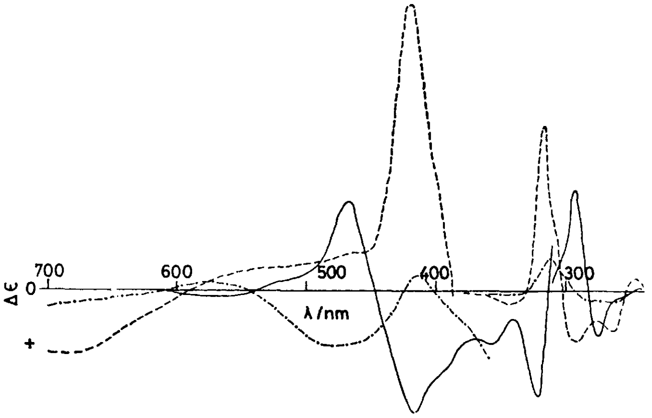

FIGURE 1 C.d. spectra of the bipy complexes in aqueous solution: (——) Δ-$[Ru(bipy)_3]^{2+}$, visible c.d. × 1, u.v. c.d. × 0.1; (– – – –) Δ-$[Ru(bipy)_3]^{3+}$, visible c.d. × 25, u.v. c.d. × 0.25; (— · — · —) Δ-purple compound, same scale as $[Ru(bipy)_3]^{3+}$

These findings must be placed in context of the $a(H^+)$ and $a(H_2O)$ of the solution in which the oxidation from Ru^{II} is carried out. It is found that in 100% H_2SO_4 where $a(H_2O) = 0$ no reactions to form purple compounds occur and the green $[Ru(bipy)_3]^{3+}$ ion maintains its optical activity indefinitely. Reaction to form the purple species is slow in reasonably concentrated H_2SO_4 and is fastest in chlorine water (pH *ca.* 3). Detailed kinetic studies have not yet been carried out. In all cases, racemization is *not* observed and these results contradict earlier statements.[1] Confusion may have arisen if the reaction had been observed with optical-rotatory techniques. At the sodium D and Hg green lines the rotation of the purple species is small and may have been obscured with the use of less sensitive instruments than now available.

The results contrast with those found[7,8] for the reaction of the corresponding $[Fe(bipy)_3]^{3+}$ ion in aqueous acid solution. In this case racemization occurs, then dissociation of the ligands, although in 100% H_2SO_4 the compound is stable indefinitely as well. The results are generally in agreement with the general increase in stability of complexes with di-imine ligands of metals in the iron triad on proceeding down the group,[1] and the much greater stability of the $[Ru(bipy)_3]^{3+}$ compound towards racemization and dissociation permits the observation of this new reaction.

An optically active purple product from the oxidation of orange $[Ru(bipy)_3]^{2+}$ in chlorine water or in chlorine-saturated H_2SO_4 solution where $a(H_2O) \neq 0$ can be isolated as a solid perchlorate salt (Found: C, 39.8; H, 3.2; N, 9.3. Calc. for the stoicheiometric ratio $Ru : bipy : ClO_4 : H_2O = 1 : 3 : 3 : 1$, C = 40.6; H = 3.1; N = 9.4%). Empirically, the compound is thus $Ru(bipy)_3(ClO_4)_3{\cdot}H_2O$. Aside from the electronic and c.d. spectral evidence alone, it was possible to establish that this compound is not simply a dimorph of green $[Ru(bipy)_3][ClO_4]_3$ which contains the six-co-ordinate $[Ru(bipy)_3]^{3+}$ cation.

While the i.r. spectra of the purple compound and of $[Ru(bipy)_3]Cl_2{\cdot}6H_2O$ are similar in most respects, there are some significant differences. The ligand bands of the latter compound are found at 770 and 730 cm^{-1}. For the purple compound these bands are shifted to slightly lower wavenumber (663 and 625 cm^{-1} respectively) and in addition, there is an extra ligand band which appears at 627 cm^{-1}. The band at 1 390 cm^{-1} is not present for the purple solid and there is some variation in the intensities of the C=N and C=C stretching frequencies at *ca.* 1 400 cm^{-1}. For $[Ru(bipy)_3]Cl_2{\cdot}6H_2O$ the order of decreasing intensity of the three bands are 1 454, 1 413, and 1 437, while for the purple compound the order is 1 439, 1 457, and 1 415 cm^{-1}.

The reaction to form the new purple compound is completely reversible. When purple $Ru(bipy)_3(ClO_4)_3{\cdot}H_2O$ prepared from optically active $[Ru(bipy)_3]^{2+}$ is dissolved in water the spectrum of the orange solution corresponds to that of authentic $[Ru(bipy)_3]^{2+}$ of the same chirality. Optical configuration is thus retained in all the steps. The ^{1}H n.m.r. spectrum of the orange solution formed corresponds exactly to that of authentic $[Ru(bipy)_3]^{2+}$ in D_2O. The spectrum of purple $Ru(bipy)_3(ClO_4)_3{\cdot}H_2O$ was recorded in a wide variety of solvents and compared to that of $[Ru(bipy)_3]^{2+}$ in the same solvents. In most organic solvents and in Na[OD] + D_2O (pD *ca.* 12) and DCl + D_2O (pD *ca.* 2) the purple solid yields $[Ru(bipy)_3]^{2+}$ quantitatively. However, in CF_3CO_2D the purple compound has signals at

8.9, 8.05, 6.95, and 6.2 p.p.m. compared with those of $[Ru(bipy)_3]^{2+}$ at 7.8 and 6.1 p.p.m. Unfortunately, the spectra are broad and interpretation is not possible. It is evident that the purple ruthenium(III) compound has been reduced to Ru^{II}, but that the ligands are not equivalent to those in $[Ru(bipy)_3]^{2+}$. After a while, reaction takes place to yield different, but as yet unidentified, species in each case. After 1 week, solutions of the purple compound have broad signals at 8.0, 7.5, and 6.8 p.p.m. compared with $[Ru(bipy)_3]^{2+}$ at 8.0, 6.9, and 6.8 p.p.m.

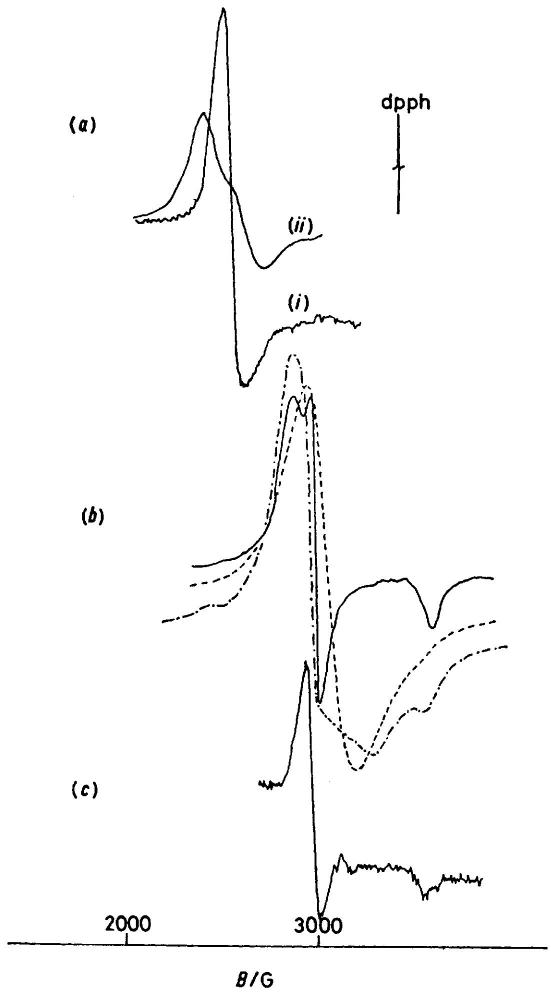

FIGURE 2 E.s.r. spectra of the complexes: (*a*) $[Ru(bipy)_3]^{3+}$, (*i*) frozen chlorine-water solution, gain 2×10^3, modulation 5G, microwave (m.w.) frequency, and power 9.105 and 10 mW, (*ii*) $Ru(bipy)_3(PF_6)_3$ powder, gain 1.25×10^2, modulation 1G, m.w. frequency, and power 9.109 and 10 mW, (*b*) (———) purple solution from (*a*) (*i*) frozen, gain 2×10^3, modulation 5G, m.w. frequency, and power 9.105 and 10 mW, (—·—·—) $Ru(bipy)_3(ClO_4)\cdot H_2O$ powder, gain 2×10^2, modulation 4G, m.w. frequency, and power 9.105 and 10 mW, (– – – –) purple compound (powder) obtained by heating solutions, settings as for last spectrum; (*c*) frozen chlorine-water solution of initial purple solution of $[Ru(phen)_3]^{3+}$, gain 5×10^3, modulation 10 G, m.w. frequency, and power 9.117 and 10 mW

The e.s.r. spectra of d^5 tris(di-imine) complexes of Fe^{III}, Ru^{III}, and Os^{III} have been recorded[19] and are characterized by a strong absorption corresponding to *g ca.* 2.6 and a very weak and variable absorption corresponding to *g* 0—1.14. Similar results were found (Figure 2) when chlorine gas was bubbled through an orange solution of $[Ru(bipy)_3]^{2+}$ and green $[Ru(bipy)_3]^{3+}$ was formed. However, if chlorine gas is continually bubbled through the solution until it becomes purple two new strong absorptions develop at *g ca.* 2.3. The purple solid $Ru(bipy)_2(ClO_4)_3\cdot H_2O$ isolated from such solutions shows no absorption at *g ca.* 2.6 and a strong broad absorption at *g ca.* 2.3. The spectrum is shown in Figure 2. Apart from a small absorption at $g_{\parallel}$ 1.8 no other signals are observed, even up to 8 000 G.*

It was found necessary to store the purple solution under a chlorine atmosphere for at least 2 weeks before all traces of the absorption at *g ca.* 2.6, corresponding to green $[Ru(bipy)_3]^{3+}$, disappeared. If the solution is heated during the initial stages of reaction with chlorine water a second purple compound can be isolated. This compound is unidentified as yet and is the subject of further study. It is possible that some of this second compound may be present in the solution, thus giving rise to the two peaks observed in the e.s.r. spectrum. However, it has been recently reported[20] that in frozen solution $[Ru(salen)(PPh_3)Cl]$ [salen = *NN'*-ethylenebis-(salicylideneiminate)] gives a very similar spectrum with g_1 2.24, g_2 2.13, and g_3 1.93. The magnetic and e.s.r. properties were interpreted in terms of a ligand field of rhombic symmetry.

In the case of the corresponding reaction with $[Ru(phen)_3]^{3+}$, absorptions at *g* 2.3 and 1.8 are observed for the initial purple compound formed. This spectrum is also shown in Figure 2. It has previously been found that the *g* values of low-spin d^5 compounds may vary significantly with solvent.[21] Jørgensen[22] has correlated changes in the electronic spectra in different solvents with both changing dielectric constant of the medium and changes in metal–ligand bond lengths. Lowering the dielectric constant produced a shift to lower wavenumbers in the spectrum. Such effects make interpretation of the e.s.r. spectrum more difficult. However, one possible explanation for the spectral changes observed upon formation of the purple compounds in solution is that there is a loss of symmetry in the co-ordination sphere.

The problem remains then that the purple compound is equivalent to neither $[Ru(bipy)_3]^{3+}$ nor $[Ru(bipy)_3]^{2+}$ but is derived from the former and easily reacts under very mild conditions to give the latter. Furthermore, these interconversions, the spectral results, and the stoicheiometry of the purple compound all suggest a formulation similar in most respects to the conventional tris compounds. It is possible to envisage two stereochemistries which fit the above results.

The first of these contains a unidentate bipy ligand as shown in (2). Such a structure has recently been proposed[23] for an iridium(III) compound, isostructural with (2). Such species have also been proposed[24,25] for reactions involving $[Ru(bipy)_3]^{2+}$, but attempts to

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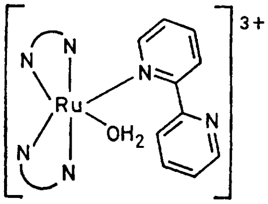
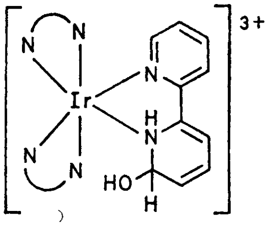
* Throughout this paper: $1\ G = 10^{-4}\ T$.

isolate them have been unsuccessful.[24,26] A compound containing this configuration could be trapped as purple $Ru(bipy)_3(ClO_4)_3\cdot H_2O$ when precipitated as the perchlorate salt. The compound is itself unstable in moist air forming green $Ru(bipy)_3(ClO_4)_3\cdot nH_2O$ slowly. When dissolved in inert solvents, it is possible that the free nitrogen atom of the unbonded pyridyl nucleus reco-ordinates to the Ru atom. The compound may then be reduced to the ruthenium(II) state either by the water molecule originally present in the purple solid or by residual water in the organic solvents used. It is already known [27-30] that this reaction takes place with a number of tris complexes of phen and bipy with Ru^{III}, Os^{III}, and Fe^{III}. In concentrated CF_3CO_2D the free nitrogen would be unable to co-ordinate to Ru although such behaviour was, however, *not* noted in DCl solution.



(2)

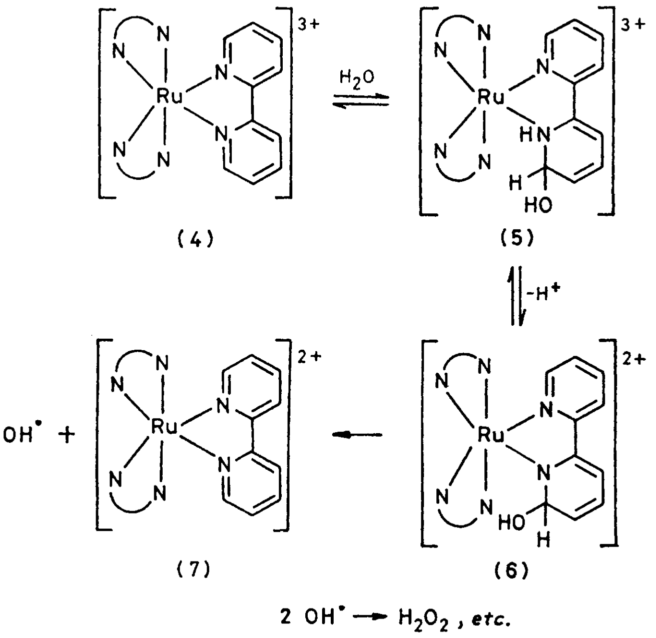
The evidence for unidentate bipy in the iridium(III) species is not convincing. The studies [23] merely show that the compound synthesized is not equivalent to the normal six-co-ordinate $[Ir(bipy)_3]^{3+}$ ion and that any reaction of this latter species to produce the new one is slow in aqueous solution. The photochemical evidence [23-25] in such systems for these compounds containing unidentate bipy is even more questionable in the light of the finding that fluorescence from free bipy [31] and phen [32] only occurs when the ligand is covalently hydrated. Indeed, we have recently been able to show [33] that the iridium(III) complex of Watts *et al.*[23] does contain a covalently hydrated bipy molecule and that unidentate bipy is not present in the compound. The second possible formulation for purple $Ru(bipy)_3(ClO_4)_3\cdot H_2O$ is thus a covalent hydrate of the parent ruthenium(III) complex, of the type shown in (3).



(3)

One difficulty with this structure is that it is hard to understand why it should be comparatively stable in neat CF_3CO_2D solution. However, some reaction does take place (^1H n.m.r. studies show it is reduced to Ru^{II} at least) and it is most likely that some reaction intermediate on the route to $[Ru(bipy)_3]^{2+}$ is stabilized. One powerful piece of evidence is that the purple compound in concentrated H_2SO_4 yields green $[Ru(bipy)_3]^{3+}$ quantitatively. It would thus seem impossible then for the purple compound to contain unidentate bipy since it would be unable to reco-ordinate to Ru in concentrated H_2SO_4. The covalent hydrate formulation is also an attractive choice when viewed against the known covalent hydrates of free bipy,[31] phen,[32] and of $[Pt(bipy)(CN)_2]$.[34]

Such a compound also fits the known [27-30,35] reaction behaviour of $[M(bipy)_3]^{3+}$ (M = Fe, Ru, or Os) in aqueous solution. When these compounds are added to water reduction takes place to yield the metal(II) species. Ozone and H_2O_2 can be detected [27] although neither of these oxidize the bivalent cations at room temperature. A reaction scheme incorporating the covalently hydrated complex readily explains these observations, and is shown in (4)—(7). Further evidence for the covalent hydrate structure comes from the reactions involving the phen analogue in which the phen ligand cannot be unidentate.



(4) (5) (6) (7)

$$2\,OH^{\bullet} \longrightarrow H_2O_2\text{, etc.}$$

(*b*) $[Ru(phen)_3]^{n+}$.—It was noted in the introduction to this paper that when $[Ru(phen)_3]^{2+}$ is oxidized with Cl_2 or Ce^{IV} in aqueous solution, instead of racemization occurring, a new optically active species is produced, as is the case with $[Ru(bipy)_3]^{2+}$ under similar conditions. Initially *green* solutions of $[Ru(phen)_3]^{3+}$ are obtained which *quickly* turn *purple* at room temperature. If optically active $[Ru(phen)_3]^{3+}$ is used the purple solution obtained is optically active and thus the reaction parallels exactly that of the bipy complex, except that the reaction with phen is faster. The visible spectrum of the purple solution has λ_{max} at 498 nm and c.d. spectra of the appropriate compounds are shown in Figure 3. The reaction to form the purple compound is most rapid in water and does not proceed in concentrated H_2SO_4 where *neither* racemization nor dissociation is observed. The spectra of $[Ru(phen)_3]^{3+}$ were recorded in 7.0 mol dm^{-3} H_2SO_4 to eliminate interference due to the formation of the purple species since at this concentration the reaction to yield that compound is fairly slow.

Initially the reactions with $[Ru(phen)_3]^{2+}$ are reversible, the c.d. spectrum of the starting material being restored on addition of hydrazine or $[OH]^-$ to blue-green solutions of $[Ru(phen)_3]^{3+}$ and the purple compound as soon as it is formed. However, a complication in the reaction then ensues. Over 2 h the purple compound reacts to yield a new *mauve* complex in solution which is also optically active and whose c.d. spectrum is also shown in Figure 3. This reaction was noticed originally by Dwyer *et al.*[5] but we believe that the reaction they saw was most probably the formation of the initial purple compound since 'instability' was noted even in 3N H_2SO_4 where subsequent reactions are quite slow. They suggested that the compound formed was the tris complex of (1), due to oxidation of the phen ring. This suggests that attack by H_2O also occurs remote from the nitrogen atoms of the ligand. Tris(2,2′-bipyridyl-3,3′-dicarboxylic acid)ruthenium(II) has since been characterized[12] but the spectra obtained on reduction of solutions of the final mauve compound do not correspond to the published electronic and c.d. spectra. However, while the subsequent products have not been characterized, the initial reactions are analogous to those of the $[Ru(bipy)_3]^{2+}$ ion. Since phen cannot form unidentate complexes, these findings lend strong support to the covalent hydrate formulation of both species. As a final point, Watts *et al.*[23] suggested, as did the quoted authors,[36] that the structure of $PtCl(PEt_3)_2(phen)(BF_4)$ contains a stable unidentate phen ligand. This is not correct. The Pt^{II} atom is five-co-ordinate with non-equivalent Pt–N interactions in the solid state of 2.14(2) and 2.84(2) Å.

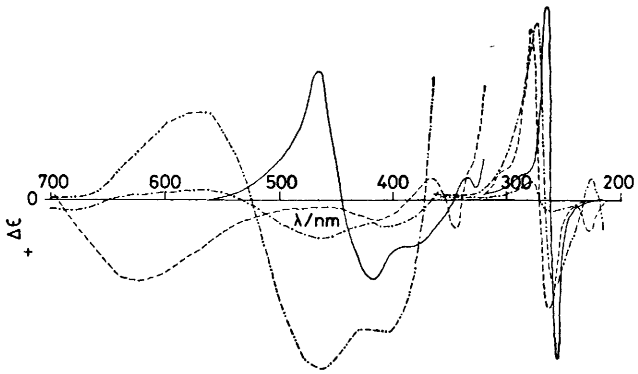


FIGURE 3 C.d. spectra of the phen complexes in aqueous solution: (——) Δ-$[Ru(phen)_3]^{2+}$, visible c.d. × 1, u.v. c.d. × 0.05; (– – – –) Δ-$[Ru(phen)_3]^{2+}$, visible c.d. × 3, u.v. c.d. × 0.2; (— · — · —) Δ-purple compound initially obtained, same scale as $[Ru(phen)_3]^{3+}$; (– – · · – – · ·) Δ-*final purple* compound after 14 h, visible c.d. × −2, u.v. c.d. × 0.3

(*c*) $[Ru(bipy)_2(CN)_2]^{n+}$.—Schilt[37] has examined the redox behaviour of the $[M(bipy)(CN)_2]^{n+}$ series of compounds for metals of the iron triad. It was shown to be possible to reversibly oxidize the iron(II) and osmium(II) compounds, but with $[Ru(bipy)_2(CN)_2]$ an entirely different set of reactions occur. For this compound, the solution, upon oxidation by Ce^{IV}, initially turns *green*, corresponding to the initial formation of $[Ru(bipy)_2(CN)_2]^+$, and then quickly reacts to give a *dark green* solution which turns *orange* and finally *red-brown*. These colour changes are irreversible. This experiment was repeated with $[Ru(bipy)_2(CN)_2]$ suspended in water and using Cl_2 as the oxidant. The same reactions as observed by Schilt[37] occurred.

While it appeared initially that this reaction might be akin to those involving $[Ru(bipy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$, it has been possible to show that the reaction involves the co-ordinated cyanide moieties. An aqueous solution of $[Ru(bipy)_2(CN)_2]^+$ was allowed to react in chlorine water to completion, then exposed to the air to remove the chlorine. To the resulting *red-brown* solution, the electronic spectrum of which corresponds closely to that observed[38] when $[Ru(bipy)_2(OH_2)_2]^{2+}$ is oxidized in solution, was added solid K[SCN]. A *deep green* compound immediately precipitated. This compound is $Ru(bipy)_2(SCN)_2 \cdot 4H_2O$ (Found: C, 44.2; H, 3.5; N, 13.8. Calc.; C, 43.9; H, 4.0; N, 14.0%). No ν(CN) (M–CN) stretch is observed in the product although the absorption at 2 110 cm^{-1} is typical of a metal-bonded thiocyanate group. The i.r. spectra of the product and of the starting material $Ru(bipy)_2(CN)_2 \cdot 3H_2O$ are virtually identical in all other aspects and so the reaction of this compound was not investigated further. The remarkable feature of this reaction is that it is not observed for the corresponding iron(III) and osmium(III) cations, which are quite stable at room temperature.

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