Optically Active Co-ordination Compounds. Part XXXIV.[1] Modification of Reaction Pathways in 1,10-Phenanthroline and its Derivatives by Metal Ions

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The reactivity of some derivatives of 1,10-phenanthroline, both free, and in the presence of some metal ions (Ru^{II}, Fe^{II}, Co^{III}, and Co^{II}), provides clear evidence for metal ion alteration of reaction profile in situations where more than one reaction is possible. The optical activity of the Ru^{II} complexes is discussed. The conversion, by hydroxide ion, of 1,10-phenanthroline-5,6-dione to 4,5-diazafluoren-9-one is shown to follow the expected benzilic acid pathway: the ultimate formation of the ketone is rationalised in terms of its exceptional stability, also evident in the behaviour of the ligands in the mass spectrometer.

SINCE the production of the first co-ordination complex of 1,10-phenanthroline, $[Fe(phen)_3](ClO_4)_2$, by Blau,[2] this ligand, together with many of its derivatives, has been studied [3] in co-ordination chemistry to an extent equalled only by one or two others. In particular, complexes of phenanthroline have long been the subject of intense kinetic scrutiny. Remarkably, despite scattered remarks regarding possible complications in the kinetics of substitutions or redox reactions at the metal ions in such complexes, caused by reactions of the ligand itself, there have been few attempts to examine its reactivity in the presence and absence of metal ions.

Indeed, few studies of the reactions of co-ordinated ligands have included a parallel study, or account, of the reactions of the free ligand. There are some exceptions to this, *e.g.* Jones and his students [4-8] have examined the reactivity towards electrophilic substitution of several organic compounds, mostly anilines, 8-hydroxyquinoline, and phenols, in the presence of metal ions. The minor changes in reactivity on complexation were not compatible with a valence bond interpretation of the co-ordinate bond. However, for most of the systems which they investigated, the metal ion was not bonded directly to an atom in the aromatic ring, and the observations relate more to a π-bonded system than a σ-bonded one.

An early study on reactions of the phenanthroline ligand was by Kuznetsov,[9] on the coupling of diazobenzene with $[Fe(phen)_3]^{2+}$, a reaction which does not occur in the free ligand. Later, the nitration of $[Co(phen)_3]^{3+}$ was found [10] to be about one hundred times faster than that of the free ligand. Recently, we discovered [11] that the nitration of phenanthroline in $[Co(en)_2(phen)]^{3+}$ occurs in a few seconds, even with relatively dilute (8M) nitric acid. During this reaction, some oxidation of phenanthroline to the diketone, 1,10-phenanthroline-5,6-dione (called quin here) also occurred, especially in the presence of bromide ions. This observation led to a reaction in which $(+)$-$[Co(phen)_3]^{3+}$ was quickly and quantitatively converted to $(+)$-$[Co(quin)_3]^{3+}$ without loss of optical activity. The production and isolation of this highly reactive new ligand provided the impetus for the present work.

We wished to evaluate the pathways of reaction adopted by some phenanthroline derivatives, under identical sets of conditions, when the organic compound is in the free and complexed state. By doing so we hope to cast further light on the factors which affect ligand reactivity on complexation.

Reductions

Reduction of aromatic nitro-groups to the primary amino-group is amply documented [12,13] and usually achieved by the use of a metal–acid couple, *e.g.* most commonly Fe–HCl or Sn–HCl. Such reductions in aqueous media at near neutral pH are uncommon, although cobalt-catalysed reductions of nitrobenzene using borohydride are known.[14]

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[1] Part XXXIII, L. S. Dollimore, R. D. Gillard, and I. H. Mather, *J.C.S. Dalton*, 1974, 518.

[2] F. Blau, *Monatsh.*, 1898, **19**, 647.

[3] W. R. McWhinnie and J. D. Miller, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 135; E. D. McKenzie, *Co-ordination Chem. Rev.*, 1971, **6**, 187.

[4] M. M, Jones, D. G. Lambert, and N. K. Chanla, *J. Amer. Chem. Soc.*, 1967, **89**, 557.

[5] N. K. Chanla and M. M. Jones, *Inorg. Chem.*, 1964, **3**, 1549.

[6] J. E. Hix and M. M. Jones, *Inorg. Nuclear Chem. Letters*, 1964, **26**, 781.

[7] M. M. Jones and K. E. Maguire, *J. Amer. Chem. Soc.*, 1963, **85**, 154.

[8] R. L. Jetton and M. M. Jones, *Inorg. Chem.*, 1962, **1**, 309.

[9] V. I. Kuznetsov, *Zhur. obshchei Khim.*, 1950, **20**, 807.

[10] A. F. Richards, J. H. Ridd, and M. L. Tobe, *Chem. and Ind.*, 1963, 1727.

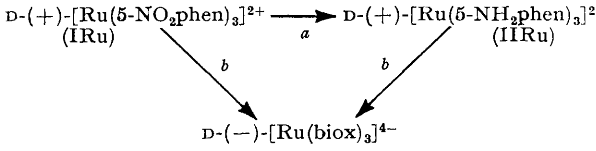
[11] R. D. Gillard, R. E. E. Hill, and R. Maskill, *J. Chem. Soc.* (*A*), 1970, 1447.

[12] S. Patai, ' Chemistry of the Nitro and Nitroso Group,' Interscience, 1969, chs. 1—3.

[13] P. A. S. Smith, ' Open Chain Nitrogen Compounds,' vol. 2, Benjamin, 1965, p. 422 and elsewhere.

[14] A. A. Vlcek and A. Rusina, *Proc. Chem. Soc.*, 1961, **161**; A. E. Brearley, H. Gott, H. A. O. Hill, M. O'Riordan, J. M. Pratt, and R. J. P. Williams, *J. Chem. Soc.* (*A*), 1971, **612**.

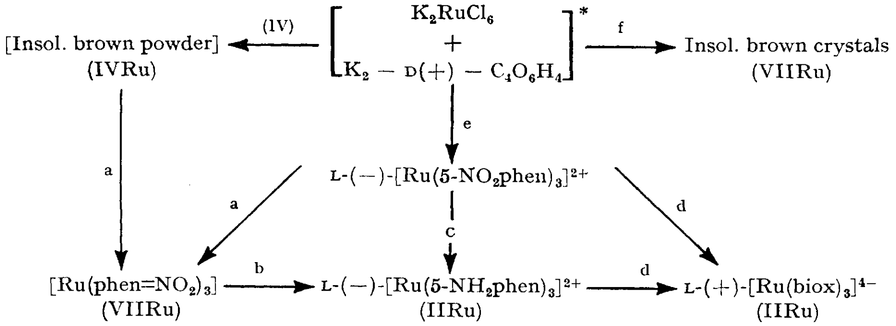
5-Nitro-1,10-phenanthroline, both free (I) * or as the D-(+)-enantiomer of its tris complex with ruthenium(II), (IRu) * is reduced quickly and smoothly to the 5-amino-compound (II) or (IIRu) using Sn–HCl reducing agent. There is a substantial loss of optical activity in the resulting (IIRu), D-(+)-$[Ru(5\text{-}NH_2phen)_3]^{2+}$: this is demonstrated by comparing the chiroptical properties of the two samples of D-(–)-$[Ru(biox)_3]^{4-}$ (IIIRu), produced by oxidizing the parent nitro-complex (IRu) or amino-product (IIRu) with alkaline permanganate.



[a] Sn–HCl. [b] $KMnO_4$–OH.

Chiroptical spectra of these complexes and others are discussed in Appendix 1 to this paper.

Reduction of the Free Ligand with Sodium Borohydride.—The novel reduction of free 5-nitro-1,10-phenanthroline by borohydride occurs readily in neutral or alkaline aqueous media, and yields, depending on the pH and temperature, several products, some unidentified: these may include products of reduction of the heterocyclic ring. However, by defining one set of conditions (see Experimental section) we isolated and identified three reduced species: 5-amino-1,10-phenanthroline (II), *NN'*-bis(1,10-phenanthrolin-5-yl)hydrazine (IV), and 5,5'-azo-1,10-phenanthroline (V). Their characterisation by i.r. spectra, mass spectrometry, and analysis, is given in detail in the Experimental section.



* See ref. 16 for details of this stereoselective complexation in the presence of potassium (+) tartrate; a, $NaBH_4$; b, HCl (after 30 min); c, Sn–HCl; d, $KMnO_4$–OH^-; e, 5-NO_2phen; f, 5-NH_2phen

SCHEME 1

To throw more light on the nature of (IV), 5-[^{15}N]-nitro-1,10-phenanthroline was prepared by the ready nitration of co-ordinated 1,10-phenanthroline discussed later under oxidation (see p. 1220). Labelled (IV) now showed i.r. absorption at 952 cm^{-1}, shifted from 965 cm^{-1}. Simple (reduced mass) calculation indicates that the shift is consistent with either C–N or N–O. In general, N–O bands in this region are more intense and rather broad: we therefore favour assignment of the band *ca.* 955 cm^{-1} to C–N. The shift of the band at 940 cm^{-1} for 5-amino-1,10-phenanthroline on salt formation would also favour this assignment.

Chemical evidence supports the suggested hydrazo-structure for (IV). Hydroxide treatment gives a mixture containing compounds (II) and (V), identified by i.r. and mass spectrum, which showed the *m/e* for 5-NH_2phen (195) and for 5,5'-azo-1,10-phenanthroline [386 and much more intense than for the same *m/e* value for compound (IV)]. Such dismutation of hydrazo-compounds with base to give azo- and amino-compounds is very well known.[13,15] Further, as an analogy, we find that when 6-nitroquinoline was treated with sodium borohydride at 80° in neutral water, 6,6-hydrazoquinoline is indeed formed. It was identified by analysis and its mass spectrum, which could readily be interpreted by reference to the fragmentation pattern of hydrazobenzene.

The production of hydrazo-compounds on reducing aromatic nitro-compounds is not unexpected, although the very mild aqueous conditions used here represent an interesting extension of the versatile reducing properties of borohydride. Particularly striking is the production (unfortunately in low yield) of the primary amine. We know of few other examples[14] of the reduction of aromatic nitro-compounds under such mild conditions.

These studies on the free ligand were undertaken for comparison with products of reduction by the same agent, borohydride, of metal complexes of 5-nitrophenanthroline, specifically of Fe^{II} and Ru^{II}.

Co-ordinated 5-Nitro-1,10-phenanthroline.—Treatment of (–)-$[Ru(5\text{-}NO_2phen)_3]^{2+}$ (IRu) with sodium boro-

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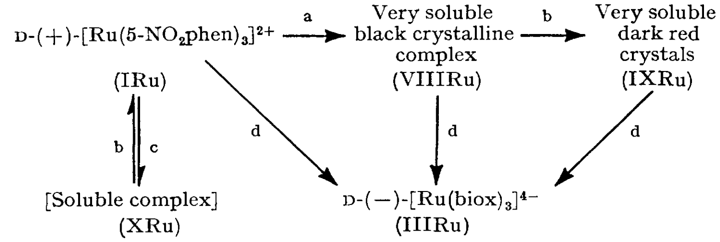
* The symbols in upper case Roman numerals denote the ligands derived from 1,10-phenanthroline. In this paper this symbol is given an obvious extension for its tris complex with ruthenium(II) (*e.g.* XVRu), with iron(II) (*e.g.* IIFe), with cobalt(III) (*e.g.* $XVCo^{III}$), and with cobalt(II) (*e.g.* $XVCo^{II}$). For ligands like 5-nitrophenanthroline (I), where there is no two-fold element of symmetry bisecting the chelate plane, there are two possible geometric isomers of $[ML_3]^{n+}$, one with a three-fold axis and the other without. We have made no attempt to distinguish them. Biox signifies the 2,2'-bipyridyl-3,3'-dicarboxylate anion. In (IIIRu), the bonding to ruthenium is through heterocyclic nitrogen.

[15] M. J. Namkung and T. L. Flecter, *Chem. Comm.*, 1969, **18**, 1052.

hydride in water, pH 7, gives a moderate yield of L-(−)-[Ru(5-NH$_2$phen)$_3$]$^{2+}$ (IIRu), of reduced optical purity (see Scheme 1). The 5-aminophenanthroline complex (IIRu) was identified by comparison with an authentic sample obtained † by Sn–HCl reduction of [Ru(5-NO$_2$phen)$_3$]$^{2+}$. I.r., circular dichroism (see Figure 7 in Appendix I), and electronic spectra matched perfectly, and elemental analysis was satisfactory.

Formation of the alleged polymer is always confined to the latter half of the reaction when much of the material is present as [Ru(5-NH$_2$phen)$_3$]$^{2+}$. The polymer could arise from a three-dimensional network of hydrazo-bridged co-ordinated phenanthroline ligands. This is partially supported by the finding of a similar polymeric material [(IVRu) in Scheme 1] from the reaction of 5,5′-hydrazophenanthroline (IV) with the Ru^{II}(+)-tartrate system. The reduction was not simplified by use of [Ru(phen)$_2$(5-NO$_2$phen)]$^{2+}$; precipitation of a polymeric substance occurs very rapidly here.

When resolved [Ru(5-NO$_2$phen)$_3$]$^{2+}$ (IRu) is treated with hydroxide ion (Scheme 2), the electronic spectrum changes (Figure 6 in Appendix 1) and, either at ambient temperature in 12 h, or in 20 min at 100°, a new complex (VIIIRu) is formed: its properties are given in the Experimental section. When the reaction is carried out on a larger (0·5 g) scale at the higher temperature, ammonia is formed in fair yield.



The reactions of hydroxide ion with co-ordinated 5-nitrophenanthroline; a, OH$^-$, 100°, 20 min; b, H$^+$; c, OH$^-$; d, KMnO$_4$–OH$^-$

SCHEME 2

The much faster oxidation, by alkaline KMnO$_4$, of [Ru(5-NO$_2$phen)$_3$]$^{2+}$ relative to [Ru(phen)$_3$]$^{2+}$, is clearly due to the basic conditions, which convert the 5-nitrophenanthroline complex to a more readily oxidisable species [presumably (XRu)].

The production of (IIIRu) from (VIIIRu) and (IXRu), [with optical activity lower than in samples of (IIIRu) obtained from (IRu)] indicates that the phenanthroline skeleton is maintained. The yield of (VIIIRu), based on the subsequent yield from it of (IIIRu), is not less than 80%.

Of greatest significance is the appearance of an electronic absorption centred at 340 nm with diminution of intensity of the π–π* short wavelength band of phenanthroline. This change is very similar, except that the intensity of the new band is less, to that found on borohydride addition to (IRu), where the disappearance of the aromatic (π–π*) band at 267 nm is accompanied by the contemporaneous appearance of a broad but intense band *ca.* 330 nm. The lower intensity in the hydroxide reaction may be due to an equilibrium between (XRu) and (IRu); the π–π* short wavelength band of 5-nitrophenanthroline is more evident here than in the borohydride case. Maximum intensity of the band at 340 nm in (XRu) is achieved only with very high base concentration, whereas as little as two equivalents of borohydride gave rise to complete formation of the anion (VIIRu). Whereas the reaction with hydroxide ion is reversible on protonation (provided this be done quickly), acidification of the borohydride intermediate (VIIRu) yields an optically active complex with spectroscopic properties very different from those of (IRu) or the fully reduced product (IIRu) (see Figures 5—7, Appendix I). Whereas the new absorption band at 340 nm for (VIIRu) (from borohydride) shows no Cotton effect (suggesting an uncoupling from the central helical absorptions), the initial species from L(−)-[Ru(5-NO$_2$phen)$_3$]$^{2+}$ and hydroxide shows enhanced optical activity (Figure 6). Burgess and Prince studied [17] the kinetics of dissociation of [Fe(5-NO$_2$phen)$_3$]$^{2+}$ (IFe) with hydroxide ion. The rate was much enhanced compared with other phenanthroline complexes [because of this we were not able to carry out the reaction to ammonia with (IFe)], and some curious anomalies occurred in the electronic spectrum of (IFe) in basic solutions: for example, the band at 528 nm was less intense than in neutral solution. We find the reverse of this effect, *i.e.* there is some increase in optical density in the band of [Ru(5-NO$_2$phen)$_3$]$^{2+}$ at 470 nm (Figure 6, Appendix I). Although the u.v. region for (IFe) was not discussed, a weak band was found at 328 nm for the free ligand in basic solution.

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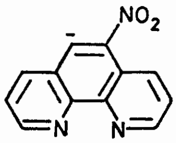
† While [Fe(5-NH$_2$phen)$_3$]$^{2+}$ could be made straightforwardly from ferrous sulphate and the free ligand, efforts to prepare the ruthenium analogue by the Bailar route [16] led to a rather insoluble complex (i-IIRu), which did not exhibit the considerable variability of electronic spectrum with pH found for (IIRu), and which was not optically active. (i-IIRu) did, however, analyse closely for the structure [Ru(phen=NH$_2$)$_2$]$_n$(ClO$_4$)$_{2n}$ in which bonding to ruthenium is envisaged as occurring through the amino-groups as well as the aza-nitrogens: this would explain the lack of response to pH change (see also comments in Appendix I, Figure 7).

[16] R. D. Gillard, R. E. E. Hill, and R. Maskill, *J. Chem. Soc.* (*A*), 1970, 707.

[17] J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1965, 4697.

The intermediacy of a deprotonated species was proposed:



based on work [18] in which deprotonation of *m*-dinitrobenzene by hydroxide ions was demonstrated, and on a finding that there was no analogous behaviour in complexes of 5-nitro-6-methylphenanthroline. This latter piece of evidence was said to favour the view of unique deprotonation at the 6-position. In fact, it is equally consistent with ' *aci*-nitrate ' [X=N(O)OH] formation, or the intervention of a dihydrophenanthroline,[19] or the stabilisation of a Meisenheimer adduct. Recent work suggests [20] that attack by hydroxide ion on the 2-position of certain co-ordinated phenanthrolines may occur, giving such spectroscopic changes as we note here.

Nitration of Trisphenanthrolineruthenium(II).—Nitration of D-(+)-$[Ru(phen)_3]^{2+}$ occurs more readily, using a concentrated sulphuric acid–sodium nitrate mixture, than for $[Co(phen)_3]^{3+}$. Complete conversion is achieved in 30 min at 100°. The intense colour changes occurring during the process suggest involvement of Ru^{III} species, but on pouring the mixture into water only the yellow Ru^{II} complex precipitates. Some accompanying oxidation to (VIRu) occurs, and the optical purity is reduced. The quinone impurity can be removed by extracting with alkali, but this further reduces the optical purity. There is, therefore, a substantial difference in the rates of nitration for 1,10-phenanthroline when free and when complexed as reported [10] for $[Co(phen)_3]^{3+}$ by Richards, Ridd, and Tobe.

Oxidation to D-(+)-$[Ru(quin)_3]^{2+}$.—The conversion of D-(+)-$[Co(phen)_3]^{2+}$ to D-(+)-$[Co(quin)_3]^{2+}$ with a mixture of concentrated sulphuric and nitric acid, and sodium bromide at 100° has been reported.[11] D-(+)-$[Ru(phen)_3]^{2+}$ under the same conditions affords good yields * of D-(+)-(VIRu). Little or no optical activity is lost in the process, as found in the Co^{III} case: reaction of $NaIO_4$ with D-(+)-(VIRu) quantitatively yields a species with spectroscopic properties identical to those of D-(−)-$[(IIIRu)]^{4-}$ but which we have not yet formally identified (this degradation is in complete contrast to the $[Co(quin)_3]^{3+}$ case which will be discussed later). Comparison of the optical purity of this compound with that of the same product obtained from $KMnO_4$ oxidation of the pure D-(+)-$[Ru(phen)_3]^{2+}$ shows that they are very similar.

There is no comparable reaction of the free ligand.

Reactions of 1,10-*Phenanthroline*-5,6-*quinone*.—The preparation of 1,10-phenanthroline-5,6-quinone (VI) from $[Co(phen)_3]^{3+}$, and from the sodium borohydride reduction product of 5-nitrophenanthroline, has already been described.[11] Both syntheses represent a considerable improvement on the method given by Smith and Cagle,[21] and probably on a recent route [22] through nitration, reduction, and oxidation. This compound is the structural analogue of phenanthrenequinone, but the chemical properties of the two are exceedingly dissimilar. Smith and Inglett first reported [23] the unusual conversion of the quinone (VI), by base at 100°, to the ketone (XI). They described this as a decarbonmonoxidation, comparing it with the decarbonmonoxidation of oxalyl esters and polycarbonyl compounds. (Their comments are ambiguous; while they imply loss of a CO unit as the gaseous molecule,† there is no reference in the paper to its detection. It may be that their description implies no more than a stoicheiometric loss of a CO unit.)

We reinvestigated the formation of 4,5-diazafluoren-9-one (XI) from 1,10-phenanthroline-5,6-quinone, (VI). Since both represent new ligands of potential interest, their chemical reactivity was investigated in the presence and absence of some metal ions.

The Reaction of 1,10-*Phenanthroline*-5,6-*quinone with Hydroxide Ion and Molecular Oxygen*.—Scheme 3 summarises the essential features of this reaction; details are given in the Experimental section. The system resembles in a general way the redox system of *p*-benzoquinone.[24] (XIV) is converted rapidly to (VI) with nitrating mixture, while the reverse reaction is achieved even more rapidly using hydrazine hydrochloride. (VI) is also oxidised quickly by hydrogen peroxide to (III).

Remarkably, (III) is also the sole product when (XIV), suspended in boiling, vigorously oxygenated, water is treated dropwise with 4M-hydroxide, allowing the brown colour which develops after each addition to discharge, until the solution finally remains colourless.

The Nature of Compound (XIV).—We assemble here evidence for our formulation of (XIV) as the ene-diol, 1,10-phenanthroline-5,6-diol. 1,10-Phenanthroline-5,6-diol has been made before, by Zacharias and Case [25] using a Skraup reaction to convert 8-amino-5,6-dimethoxyphenanthroline into 5,6-dimethoxyphenanthroline, which, treated with a hydrogen iodide–red phosphorus

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* F. P. Dwyer, E. Humpoletz, and R. S. Nyholm, *J. Proc. Roy. Soc. New South Wales*, 1946, **80**, 212 attributed the instability of trisphenanthrolineruthenium(III) complexes in weak acid to oxidation of ligand to 2,2′-bipyridyl-3,3′-dicarboxylic acid. Later, with H. A. McKenzie, Dwyer suggested that the iron complex behaved similarly (*ibid.*, 1947, **81**, 93).

† R. C. Elderfield (' Heterocyclic Compounds,' vol. 7, p. 354) also speaks of this as the first reaction in which CO is lost from a 1,2-diketone. A presumably similar reaction is the conversion (R. Cuisa and D. Buono, *Gazzetta*, 1950, **80**, 864) of 2-phenyl-4-carboxy-5,6-benzoquinoline by permanganate to 2-phenyl-4-carboxy-1-azafluorenone.

[18] R. J. Pollitt and B. C. Saunders, *Proc. Chem. Soc.*, 1962, 176.

[19] W. Traber and P. Karrer, *Helv. Chim. Acta*, 1958, **41**, 2066.

[20] R. D. Gillard and J. R. Lyons, *J.C.S. Chem. Comm.*, 1973, 585.

[21] G. F. Smith and F. W. Cagle, *J. Org. Chem.*, 1947, **12**, 781.

[22] J. E. Dickeson and L. A. Summers, *Austral. J. Chem.*, 1970, **23**, 1023.

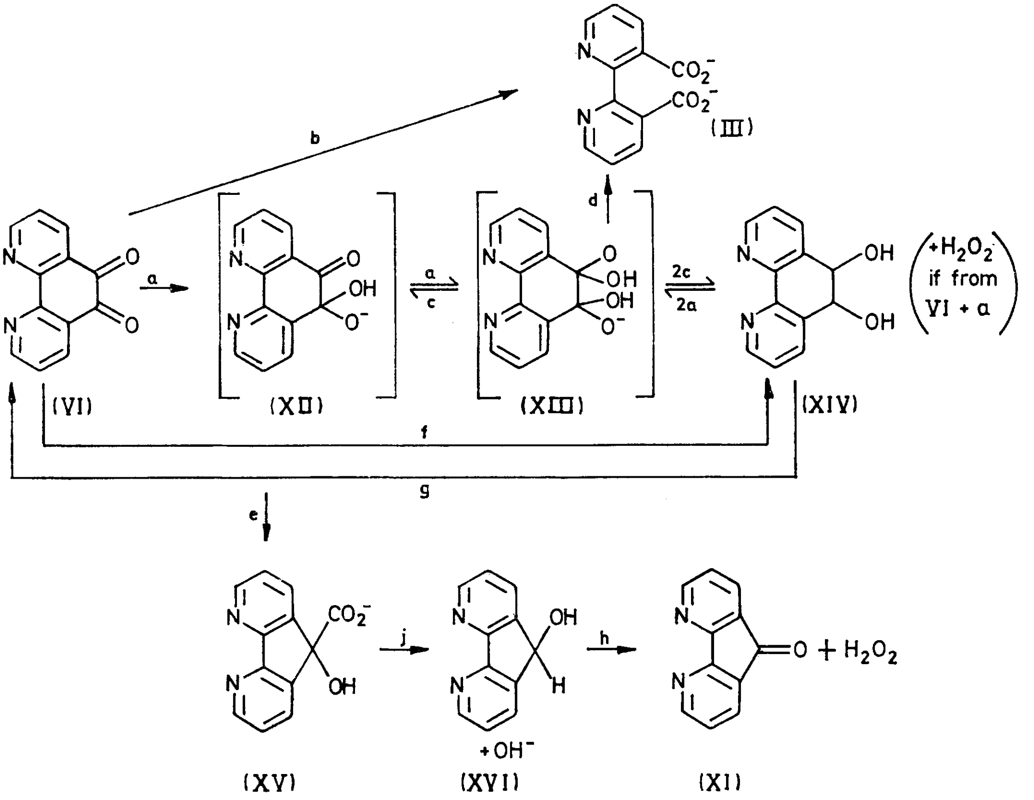
[23] G. F. Smith and G. E. Inglett, *J. Amer. Chem. Soc.*, 1950, **72**, 842.

[24] L. F. Fieser and M. Fieser, ' Text Book of Advanced Organic Chemistry,' Reinhold, p. 851.

[25] D. E. Zacharias and F. H. Case, *J. Org. Chem.*, **1962**, **27**, 3878.

mixture, gave (XIV). They report an m.p. of 390° and details of the extinction coefficients for four absorptions in the range 212—294 nm in acid solution, all of which match our own measurements exactly. Although they measured an extinction coefficient in 0·1M-hydroxide for a band at 228 nm, they seem not to have further studied the remarkable properties of this compound.* Buehler has provided an excellent review [27] on the properties of ene-diols, some salient features of which are reproduced here. Almost all heterocyclic ene-diols, of the form $R^1{\cdot}C(OH){:}C(OH){\cdot}R^2$, are yellow or orange. (XIV) is yellow and the hydrochloride salt is brick red. The stability of ene-diols appears to depend on two factors (i) conjugative effects, and (ii) steric hindrance from *ortho*-substituents. The steric effect is closely allied to the ease of oxidation by air, which occurs most readily when there is little steric hindrance. Further stabilisation is achieved through chelation, *e.g.* in 1,2-di-(2-pyridyl)ethylene-1,2-diol. Further, such hydrogen bonding gives rise to absorption in the visible region. Intermolecular hydrogen bonding is a distinct possibility for (XIV) and would help to explain the very high m.p. (XIV) has a weak shoulder (400 nm) on the band at 294 nm. The benzoin–enediol equilibrium is expected to favour benzoin in acid conditions: this is *not* found for heterocyclic enediols, or for (XIV). Many enediols will decolourise iodine or cupric acetate solutions: (XIV) is no exception; it also gives a positive result in the characteristic test with 1,2-dinitrobenzene (*i.e.* a violet colouration in alkaline solution).

Further evidence for the structure (XIV) comes from i.r. spectroscopy: for the neutral molecule, a strong hydrogen-bonded O–H is centred *ca.* 3000 cm^{-1}. An intense band at 1620 cm^{-1} which is shifted to 1600 cm^{-1} in the hydrochloride salt, is, we believe, due to a *cis*-substituted ethylenic double bond.



SCHEME 3 Reaction of (VI) with oxygen and hydroxide ion; a, OH$^-$; b, O_2^{2-}; c, H$^+$; d, O_2, trace OH$^-$; e, O_2, excess of OH$^-$; f, $N_2H_6Cl_2$; g, HNO_3–H_2SO_4; h, O_2; j, $- CO_2 + H_2O$

Oxidation of Compound (XIV).—The oxidation of (XIV) to (III) is not unexpected: 1,2-di-(2-pyridyl)ethylene-1,2-diol gives [27] pyridine-2-carboxylic acid when treated with dioxygen in the presence of $FeCl_3$ or with hydrogen peroxide. However, Weissberger, LuValle, and Thomas have studied [28] the reaction of a number of α-ketols with dioxygen, concluding that the normal reaction gives the corresponding diketone and peroxide. We find peroxide formation, established [29] by the luminol test, in the production of (XIV) and of (XI), as shown

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* 4,7-Phenanthroline-5,6-diol has also been prepared [26] by Druey and Schmidt by Raney nickel reduction of the 5,6-dione: no comment was made on redox reactions for this diol either.

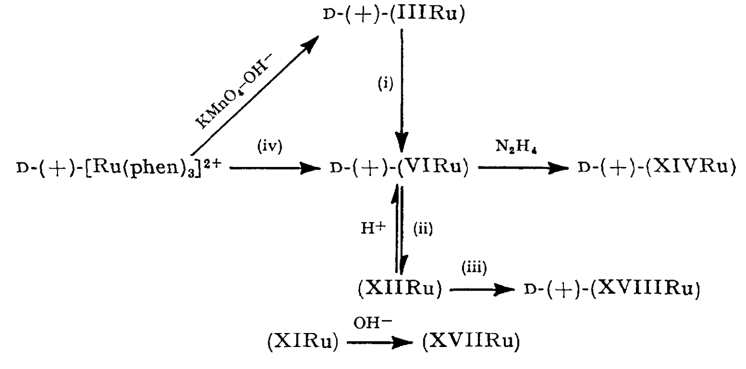
[26] J. Druey and P. Schmidt, *Helv. Chim. Acta*, 1950, **33**, 1080.

[27] C. A. Buehler, *Chem. Rev.*, 1964, **64**, 7.

[28] A. Weissberger, J. E. LuValle, and D. S. Thomas, *J. Amer. Chem. Soc.*, 1943, **65**, 1934.

[29] R. D. Gillard and A. Spencer, *J. Chem. Soc.* (*A*), 1970, 1761.

in Scheme 3. The work embodied in Scheme 3 shows that (XI) is produced from (VI) *via* (XII), (XV), and (XVI), a route which is essentially the same as that known [30] for phenanthrenequinone, *i.e.* a benzilic acid rearrangement followed by decarboxylation (which in the present case is spontaneous) and concurrent oxidation, all occurring in solution. It is very likely, therefore, that all of the phenanthroline-1,2-diketones which have been converted to the azafluorene in this way (these are [26] the 4,5-, 1,8-, 1,5-, and 1,7-phenanthroline-5,6-diones) proceed *via* a benzilic acid rearrangement. Phenanthrenequinone reacts only as far as the benzilic acid. To obtain fluorenone this acid must be strongly heated in air or oxygen. The heterocyclic analogue is remarkable, therefore, for its spontaneous decarboxylation. The oxidation must also proceed very rapidly in solution. The driving force for these reactions is presumably obtained from the very great stability of (XI), strikingly demonstrated through mass spectrometry, and discussed in Appendix 2.



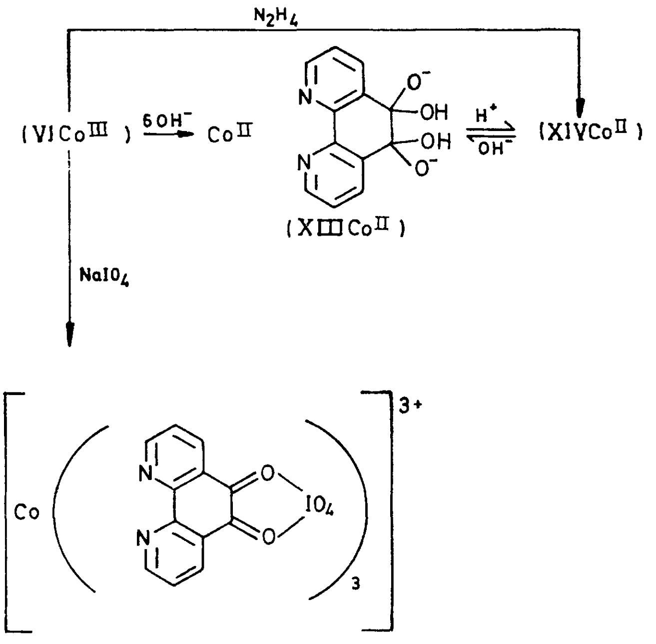
SCHEME 4 Reactions of complexes of ruthenium(II): (i) concentrated base followed by sodium perchlorate; (ii) very dilute base; (iii) dilute base, heat; (iv) H_2SO_4, NaBr, HNO_3

Influence of Metal Ions.—The reactions studied are summarised in Schemes 4 and 5.

There is a striking contrast in reactivity for the ligands attached to cobalt and to ruthenium(II). The reactivity in the presence of Co^{II} much more closely resembles that of the free ligand. The conversion of (XIRu) to (XVIIIRu) is unique: there is no comparable reaction of the free ligand.

The formation of some of the complexes in Schemes 4 and 5 is of interest. When Smith originally prepared the ligands (III) and (VI) [23,31] he attempted to make their Fe^{II} complexes, but obtaining no colouration with either ligand, concluded that complex formation had not occurred.

In a similar way, Dickeson and Summers could not make a cupric complex [22] of the quinone. However, James, Parris, and Williams report [32] on the stability of the iron(II) complex * of (III). They also found no colour (they place the expected charge transfer absorption in the u.v. region). We have not examined the case for iron(II) further. It is possible to prepare ($VICo^{III}$) directly from cobalt(II) chloride, but the oxidation of $[Co(phen)_3]^{3+}$ is much better. Our attempts to prepare the fluorenone complex ($XICo^{III}$) from cobalt(II) chloride and from sodium tris(carbonato)-cobaltate(III) were unsuccessful. We have not attempted to make, directly, a cobalt complex of (III). In contrast, all of the Ru^{II} complexes, except (XIRu), form very easily; (XIVRu) we could make only as shown in the



SCHEME 5 Reactions of complexes of cobalt-(II) and -(III)

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* This complex, in the ferric form, is also a product of the reaction of molecular oxygen with $[Fe(phen)_3]^{2+}$ according to Williams.[33]

[30] J. F. Eastham and S. Selman, *Quart. Rev.*, 1960, 221.

[31] G. F. Smith and F. P. Richter, 'Phenanthroline and Substituted Phenanthroline Indicators,' Chemical Company, Columbus, Ohio, 1944.

[32] B. R. James, M. Parris, and R. J. P. Williams, *J. Chem. Soc.*, 1961, 4635.

[33] R. J. P. Williams, *Fed. Proc.*, 1961, **20**, 5.

Scheme, from (VIRu) and hydrazine. This difficulty * is most likely the result of competition from the enol oxygens in complexation under the direct conditions.

Reactions of the Complexes of Ruthenium(II) *with Base.*—Treatment of (VIRu) with base proceeds in two clear stages: its mode of reaction depends on the hydroxide ion concentration. When the solid complex is added to a large excess of 4M-sodium hydroxide solution it dissolves almost instantly giving a red-orange solution. Immediate reacidification regenerates (VIRu) *i.e.*

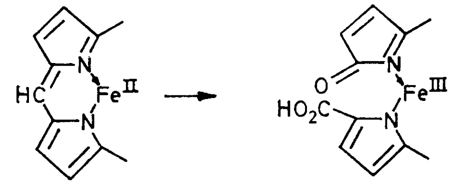
$$(\text{VIRu}) \underset{\text{H}^+}{\overset{\text{OH}^-}{\rightleftharpoons}} (\text{XIIRu})$$

(Soluble complex) †

If (VIRu) is allowed to stand, in air, in the hydroxide solution, the colour soon darkens, especially if heated, and the product is essentially (IIIRu). The optical purity of (IIIRu) so prepared is some 30% lower than that of the parent complex (see Figure 4, Appendix 1).

Treatment of (VIRu) in dilute solution with 8—10 equivalents of hydroxide ion also reveals an initial pre-equilibrium step reversible with acid: heating the solution in air gives rise to a species which is similar to, but not exclusively (IIIRu) [the sole product of base treatment of (XIRu)] and (IIIRu). In base, (VIRu) exhibits a strong charge-transfer band at 304 nm, while (XVIIRu) has a very similar band at 292 nm. The product of attack by dilute hydroxide on (VIRu) has a band at 295 nm rather broader than those at 304 (IIIRu) and 292 (XVIIRu) (see Figure 4, Appendix 1). The dilute conditions probably give some benzilic acid rearrangement of the complexed quinone of (VIRu) producing (XIRu) which further reacts rapidly with the base, in known manner, forming (XVIIRu). This is in remarkable contrast to the free-ligand reactivity where the very dilute conditions favour formation of (III); the concentrated alkali gives only (XI), *i.e.* reversal of effects operates in respect of free ligand and its ruthenium complex.

The conversion of (XIRu) (to (XVIIRu) deserves special comment. The free ligand (XI) (Scheme 3) is not attacked by hydroxide even on boiling for an hour. (XVIIRu) is produced from (XIRu) within the time of mixing the reagents. The new complex was identified by chemical analysis and i.r. spectrum [which showed (i) a strong carboxylate absorption at 1605 cm^{-1}, slightly different in position to that in (IIIRu), (ii) some significant differences from (IIIRu) in the 700—800 cm^{-1} region, (iii) the characteristic bands of a complexed bipyridyl]. Purification was effected by elution on Sephadex G10; (XVIIRu) eluted rather more slowly than (IIIRu), though still very much faster than cationic complexes of ruthenium. The reaction of (XIRu) with base resembles the case reported [33] by Williams in which a haemoglobin is oxidised by molecular oxygen to choleglobin:



There is, of course, no change of oxidation state of the metal ion in our system.

The complex (XIVRu) was prepared by treating (VIRu) with hydrazine hydrochloride. The reduction appears to be slower than that of the free ligand. (XIVRu) reacts with base in exactly the same way as (VIRu) under the dilute conditions.

Reactions of Cobalt Complexes: a Comparison.—Reactions of the cobalt complexes are given in Scheme 5. (VICo^{III}), the complex analogous to (VIRu) above, reacts with six or more equivalents of base to give (XIIICo^{II}), a black crystalline complex. This, on acidification is found to give exclusively (XIVCo^{II}), which is also the product from (VICo^{III}) and hydrazine hydrochloride. Basification regenerates (XIIICo^{II}). The complex (XIVCo^{II}) has a magnetic moment of 4·4 B.M., and analysis confirms the changed oxidation state, Co^{II}. The electronic spectrum of (XIIICo^{II}) is unremarkable but the i.r. spectrum is unusual; it shows a very broad and intense absorption from 3500 cm^{-1} declining in strength to 2500 cm^{-1} and then a very intense band, very broad, centred at 1600 cm^{-1}. For this reason we believe that this complex is as designated in the Scheme. Chemical analysis fits well for the tetrapotassium salt. The stabilisation by metal ions of intermediates where two hydroxyl groups are attached to a single carbon has been reported [34] for hydrated *trans*-dichlorotetrakis[(4-formyl)pyridine]rhodium(III) chloride. Further, such a structure (XIIICo^{II}) fits in with our Scheme 3 very well.

The reactivity for complexes of cobalt clearly differs from that for ruthenium. It is likely that the ability of cobalt to change oxidation state is bound up in this difference. The great reluctance of the cobalt complexes to evoke fission of the 5,6-bond of the co-ordinated phenanthroline derivative is demonstrated by comparing the reactions of (VIRu) and (VICo^{III}) with sodium periodate: D-(+)-(VICo^{III}) forms a stable ester with

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* The rather variable complexing ability of these ligands for cobalt and ruthenium may be related to two factors, ionic size and ligand distortion. Ligand distortion in (III) is likely to result from steric interaction of the 3,3′-carboxylate groups: in (VI) and (XI) it derives from the modification of the 5,6-position in phenanthroline. In all three cases, the heterocyclic nitrogen atoms are expected to be non-coplanar. The smaller Co^{2+} and Co^{3+} cations are expected to be affected by this distortion more than the larger Ru^{II} ions. The relative ease of removal with EDTA of (VI) from VICo^{III} contrasted with the removal of phenanthroline or 5-nitrophenanthroline from [Co(phen)$_3$]$^{3+}$ or from (ICo^{III}) respectively is consistent with this suggestion which implies a much reduced stability for (VICo^{III}).

† The nature of this soluble complex which is in reversible equilibrium with (VIRu) and is designated as (XIIRu) in Scheme 4 is discussed in the light of the findings of reactivity in the presence of Co^{II} as metal ion in the next section.

[34] R. D. Gillard and B. T. Heaton, *J. Chem. Soc.* (*A*), 1968, 1405.

TABLE 1

Preparation of enantiomeric ruthenium(II) complexes *via* the Bailar–Liu–Liu synthesis

	Ligand	Optical purity (%) of ruthenium(II) complex
	1,10-Phenanthroline	35 [a] L-(—)-hand
	2,2′-Bipyridyl	60 [a] L-(—)-hand
(III)	2,2′-Bipyridyl-3,3′-dicarboxylic acid	5 [c] L-(+)
	5-Nitro-1,10-phenanthroline	30 [b] L-(—)
(XIV)	1,10-Phenanthroline-5,6-diol	0·0 [d]
(VI)	1,10-Phenanthroline-5,6-dione	5 [b] L
(XI)	4,5-Diazofluoren-9-one	0·0
(II)	5-Amino-1,10-phenanthroline	0·0 [e]

[a] Reference to literature values. [b] By conversion to (IIIRu). [c] Prepared from tris(1,10-phenanthroline)ruthenium-(III) of known purity. [d] Complex not identified. [e] Complex not $[Ru(5\text{-}NH_2phen)_3]^{2+}$ by this route, perhaps (i-IIRu).

periodate (there is considerable intensification of the negative 468 nm and positive 390 nm c.d. bands).

The Bailar–Liu–Liu Asymmetric Synthesis.—With the increasing number of new phenanthroline ligands available we extended our investigations of the Bailar–Liu–Liu asymmetric synthesis.[35] It was shown earlier[16] that the predominant enantiomer found for the Ru^{II} complexes of phenanthroline and the 5-nitro-derivative was the L-(—)-form.

There appears to be a correlation between the optical purity of the complex produced and the nature of the 5,6-bond in the phenanthroline derivative. The effect of altering the 5,6-bond, either by reducing it or changing it entirely [in (XI)], or of steric hindrance, clearly reduces

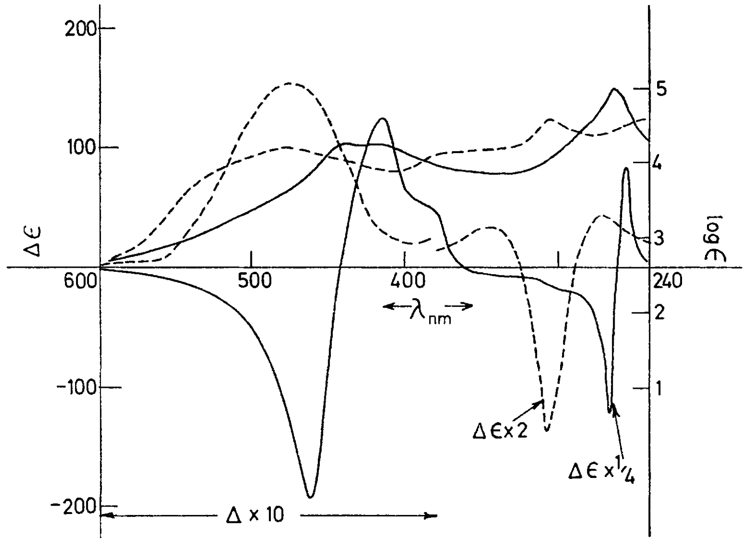

FIGURE 1 Reaction of L-(—)-$[Ru(phen)_3](ClO_4)_2$ with potassium permanganate; solid lines represent the electronic and c.d. spectra of starting material and the dashed lines the electronic and c.d. spectra of the product L-(—)-$[Ru(biox)_3]^{4-}$

TABLE 2

First charge-transfer band (nm) of complexes, or ligand electronic transition, occurring in the u.v. region

	Compound	Symbol	0·05M Acid	Neutral	0·05M Base	ε [a]
(1)	1,10-Phenanthroline (phen)		272	265	264	3·33
(2)	$Ru(phen)_3(ClO_4)_2$		262	262	262	12·4
(3)	5-Nitrophenanthroline ($5\text{-}NO_2phen$)	(I)	277	267	267	2·48
(4)	$Ru(5\text{-}NO_2phen)_3(ClO_4)_2$	(IRu)	266	265	269	7·21
(5)	5-Aminophenanthroline ($5\text{-}NH_2phen$)	(II)	296	281	280	2·19
(6)	$Ru(5\text{-}NH_2phen)_3(ClO_4)_2$	(IIRu)	263	272	274	5·69
(7)	2,2′-Bipyridyl (bipy)		301	281	281	1·67
(8)	$Ru(bipy)_3(ClO_4)_2$		286	286	286	6·16
(9)	2,2′-Bipyridyl-3,3′-dicarboxylic acid (biox)	(III)	267	270	271	0·853
(10)	$K_4[Ru(biox)_3]$	(IIIRu)	301	304	305	4·24
(11)	1,10-Phenanthroline-5,6-dione (quin)	(VI)	315	295		1·57
(12)	$Ru(quin)_3(ClO_4)_2$	(VIRu)	295	295		4·58
(13)	4,5-Diazafluoren-9-one (diazone)	(XI)	320, 329	306, 320	319, 305	1·24
(14)	$Ru(diazone)_3(ClO_4)_2$	(XIRu)	298	298		4·79
(15)	1,10-Phenanthroline-5,6-diol (phendiol)	(XIV)	295	256		3·53
(16)	$Ru(phendiol)_3(ClO_4)_2$	(XIVRu)	275	275		
(17)	$Co(quin)_3(ClO_4)_2$	($XICo^{III}$)	320	321		2·77
(18)	$Co(phendiol)(ClO_4)_2$	($XIVCo^{II}$)	295	285		7·10
(19)	$Ru(bipy\text{-}3\text{-}ox)_3Na$ [b]	(XVIIRu)	291	293	294	5·01
(20)	9-Aminophenanthrene		252	250		4·45

[a] Measured in acid unless otherwise stated, all values in $10^4\ l\ mol^{-1}\ cm^{-1}$. [b] bipy-3-ox = 2,2′-Bipyridyl-3-carboxylic acid.

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[35] C. F. Liu, N. C. Liu, and J. C. Bailar, *Inorg. Chem.*, 1964, **3**, 1085.

the optical activity [see (III), (VI), and (XI)]. It is possible that this derives from a loss in coplanarity of the heterocyclic rings which is caused by steric hindrance, or by 5,6-bond alteration. This lack of planarity then gives rise to an unfavourable geometry for complexation; *i.e.* after initial one-ended attachment of the ligand to the metal, the second stage of attachment, normally very fast, is slower. If the one-ended state were to occur for a significant time, ligand scrambling is likely, leading to a racemic product.

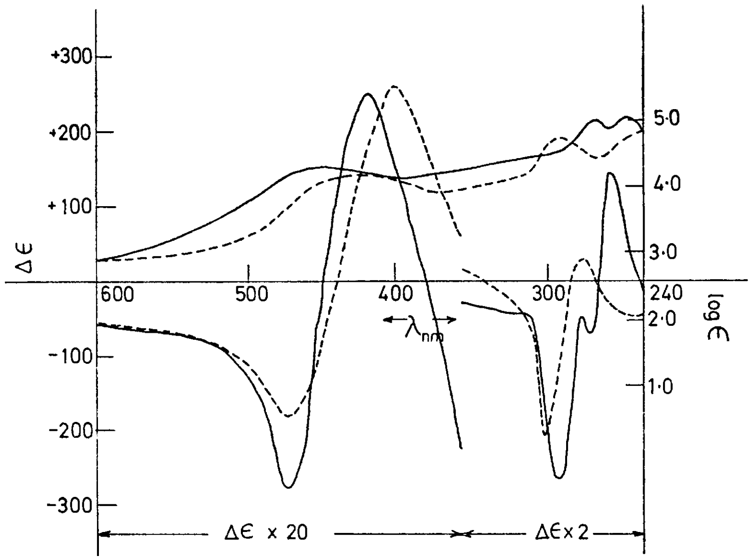


FIGURE 2 The solid lines represent the electronic and c.d. spectra of L-(−)-(VIRu), L-(−)-$[Ru(quin)_3](ClO_4)_2$, and the dashed lines the corresponding spectra of L-(−)-(XIVRu)

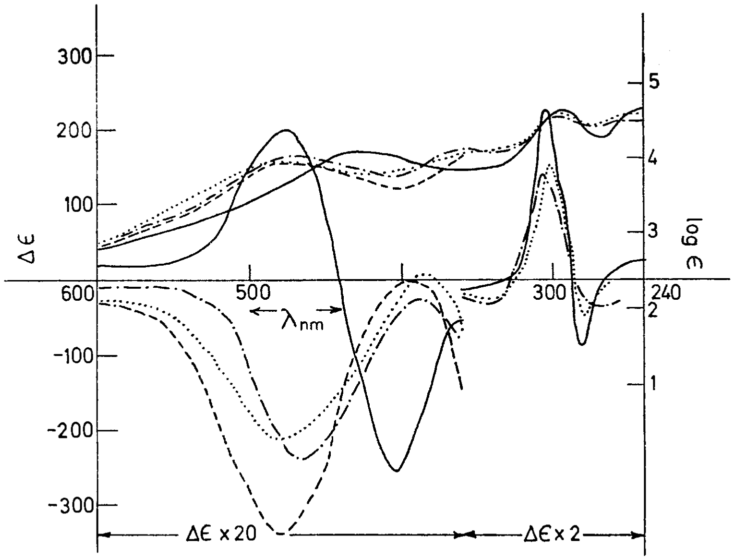


FIGURE 3 The reactions of the tris complex D-(+)-$[Ru(quin)_3](ClO_4)_2$, D-(+)-(VIRu), with (a) sodium periodate and (b) concentrated hydroxide: (——) represents the spectra (electronic and c.d.) of D-(+)-(VIRu); (a), (– – – –) treated with $NaIO_4$; (b), (····) the spectra of the product of treating (VIRu) with concentrated base, chromatographing on Sephadex G10, and then acidifying; (— · — · —) the spectra of the same product, in basic solution

CONCLUSION

The work embodied in this paper has revealed an unsuspected reactivity in almost any kind of phenanthroline derivative when complexed to a metal. If there is present in the ligand a source of strain, the metal complex of the ligand will, as a primary requirement, react in such a way as to remove this strain first. There may or may not be an associated change in the metal oxidation state.

We regard our observations as circumstantial evidence for the influence of this ligand reactivity in kinetic studies involving metal complexes of heterocyclic nitrogen ligands, and wish to stress the importance of characterizing products in such systems.

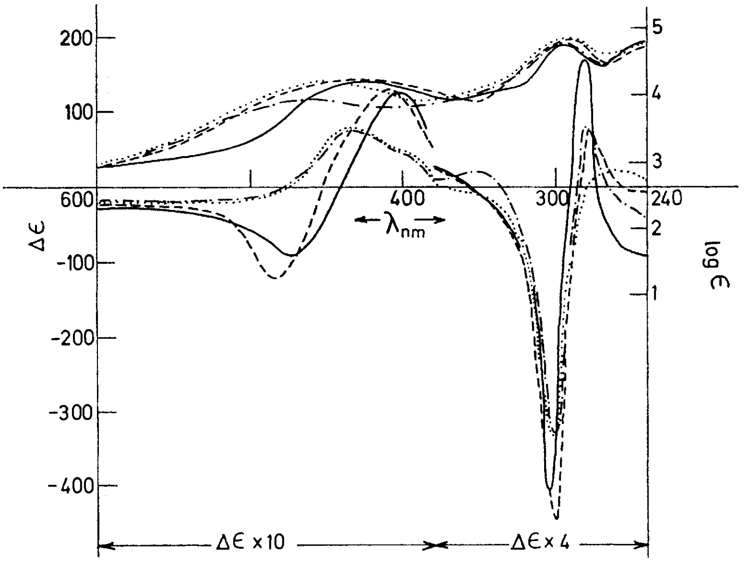


FIGURE 4 The reaction of L-(–)-[Ru(quin)$_3$]$^{2+}$, L-(–)-(VIRu), with hydroxide ion: (——) represents the spectra of L-(–)-(VI-Ru), as its perchlorate; the lines (– – – –; · · · ·; — · — · —) represent the spectra of the products of respectively adding to L-(–)-(VIRu) a cold solution of KOH, heating this solution to 80°, and finally of making the solution acid

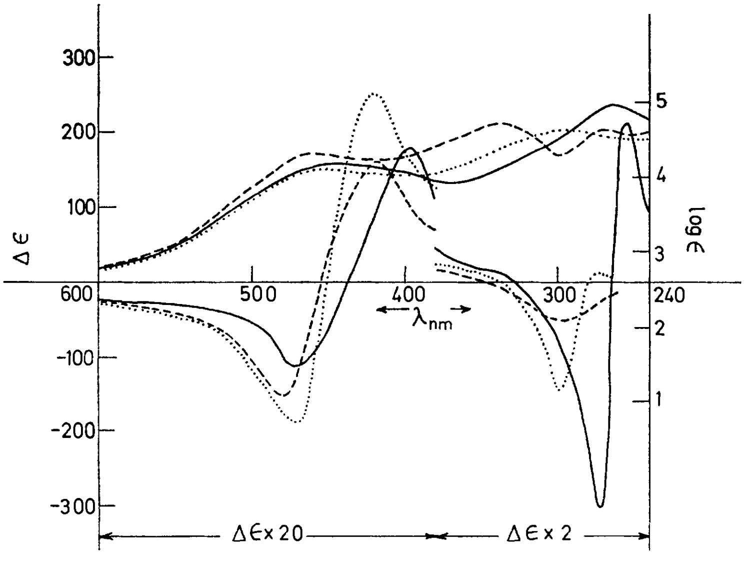


FIGURE 5 The reduction of L-(–)-(IRu) perchlorate with sodium borohydride: the full line (——) represents the circular dichroism and electronic absorption spectrum of L-(IRu), (– – – –) represents the spectra obtained on treating it with NaBH$_4$ in cold solution, and (· · · ·) the properties of the latter solution made acid after 20 min

APPENDIX 1

Electronic Spectroscopy.—The electronic spectra of most of the ligands and metal complexes discussed in this paper, including c.d. studies on the resolved complexes, are given here. Where possible the measurements were made in acidic, neutral, and alkaline aqueous media in order to discover possible ligand reactivities. Some interesting shifts of the first short wavelength charge-transfer bands occurring in the u.v. in complexes and of the $n \longrightarrow \pi^*$ transitions for the ketonic ligands are noted. Extinction coefficients were determined for all the compounds for the first absorptions appearing in the u.v. region, usually in a faintly acidic medium. Table 2 assembles the results which are entirely in line with expectation, *i.e.*, ligands which are capable of interacting with protons or hydroxide ions show wavelength shifts with pH. The most surprising result is that of (IRu) and this has been amply discussed earlier (p. 1219).

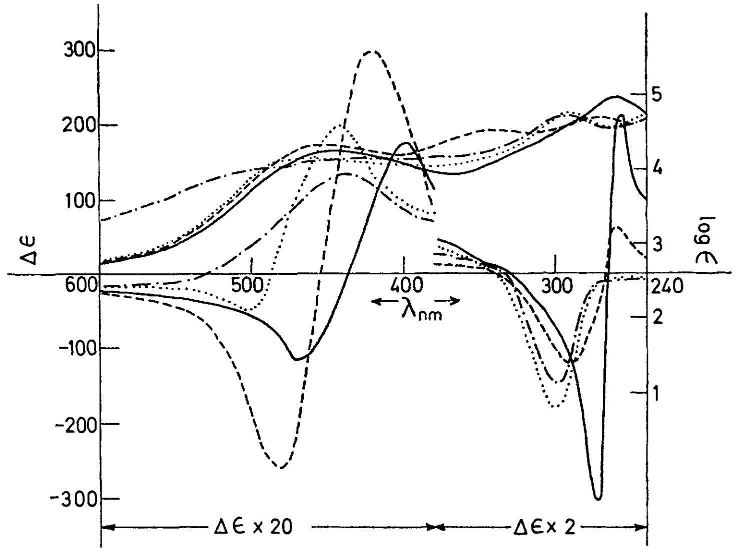


FIGURE 6 The reaction of L-(−)-(IRu) with OH^-. The full line (——) shows the spectra of L-(IRu), (– – – –) shows the spectra obtained on treating L-(−)-(IRu) perchlorate with hydroxide in the cold, (· · · ·) shows the spectra obtained by keeping the last at 80° for 30 min, and the lines (— · — · —) show the properties of the resultant solution after acidification

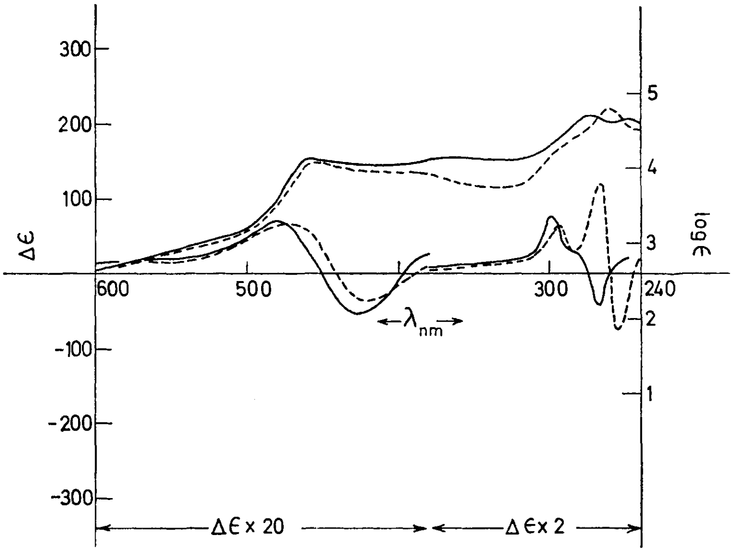


FIGURE 7 The dependence of the electronic spectrum of D-(+)-[Ru(5-NH_2phen)$_3$](ClO_4)$_2$, D-(+)-(IIRu), upon pH: (——) properties of the basic solution of the perchlorate; (– – – –) properties of the acid solution of the perchlorate

Optical Activity.—Table 3 summarises our results for the chemical interconversion of optically active phenanthroline complexes: certainly the largest number of these complexes to be correlated for absolute configurations so far.

With the exception of the complex of the bipyridyl derivative, the most important spectroscopic observation arising out of the above chemical conversions is that all of the c.d. spectra for, say, the L-hands, show the characteristic first negative then positive curves looking from long to short wavelength, in the visible, and then again in the u.v. region of the spectrum. Thus in spite of drastic changes at the 5,6-bond of phenanthroline, all our

TABLE 3

Chemical interconversion of optically active complexes of ruthenium(II)

Initial complex *	Reagents	New complex
L-(−)-Ru(phen)$_3^{2+}$	$KMnO_4$–OH^-	L-(+)-Ru(biox)Na_4
L-(−)-Ru(phen)$_3^{2+}$	H_2SO_4–NaBr–HNO_3	L-(−)Ru(quin)$_3^{2+}$
L-(−)-Ru(quin)$_3^{2+}$	N_2H_4,2HCl	L-(−)-Ru(phendiol)$_3^{2+}$
D-(+)-Ru(quin)$_3^{2+}$	$NaIO_4$, or OH^- conc.	D-(−)-Ru(biox)$_3Na_4$
L-(−)-Ru(phen)$_3^{2+}$	$NaNO_3$–H_2SO_4	L-(−)-Ru(5-NO_2phen)$_3^{2+}$
L-(−)-Ru(5-NO_2phen)$_3^{2+}$	Sn–HCl	L-(−)-Ru(5-NH_2phen)$_3^{2+}$

* Signs of rotation where given are for λ_{546}.

L-isomers exhibit negative then positive c.d. bands at longer wavelength.

It is intriguing to note that the profiles of visible c.d. and of the c.d. in the u.v. are very similar for a given compound; the u.v. maxima are more intense. Indeed, it is not unreasonable to suggest that the c.d. in the visible region of these compounds stems from coupling with the u.v. helical absorptions.

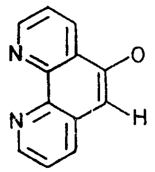
APPENDIX 2

Mass Spectrometry of Derivatives of 1,10-*Phenanthroline and Bipyridyl*.—Derivatives of phenanthroline and bipyridyl have not, so far as we know, been examined collectively by mass spectrometry. Some conclusions of the present work depended quite heavily on this technique, so that we have assembled a large body of information relating to derivatives of 1,10-phenanthroline, and to a lesser extent, 2,2′-bipyridyl. In particular, the remarkable stability of 4,5-diazafluoren-9-one is demonstrated.

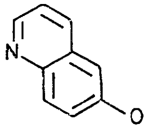
With few exceptions phenanthroline and bipyridyl derivatives (and 6-nitroquinoline) exhibit a parent ion corresponding to the molecular ion: most often this is the major peak, under the experimental conditions employed (70 and 30 eV; 8 kV ion volts, with a source pressure 10^{-6}—10^{-7} mm, and temperature 180—230 °C). 5-Nitrophenanthroline and 6-nitroquinoline comply with the known general property of nitroaromatics in which the first process in the ion chamber is:

$$\text{Ph-NO}_2 \xrightarrow{E} \text{Ph-ONO} \xrightarrow{E} \text{Ph-O} + \text{NO}$$

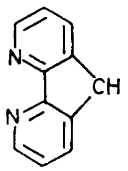
Loss of NO from the molecular ions yields peaks at 195 and 144 for the nitrophenanthroline and the nitroquinoline respectively. Direct loss of NO_2 also occurs giving masses 179 and 128 respectively. The 195 and 144 fragments are (i) and (ii). For phenanthroline loss of CO next occurs giving a strong and lone peak at 167, presumably (iii). This, and the 179 fragment (iv), lose one and two carbon atoms and their associated hydrogens to give bipyridyl fragments ranging from 154 to 152, the 152 peak being dominant. For pure phenanthroline, the 154 peak is favoured, corresponding to (phen—C_2H_2). The C_2H_2 fragment can be found at mass 26. Symmetrical cleavage of the bipyridyl fragments leads to masses 77—74, which arise from pyridine systems: the 77 peak is strongest for phenanthroline, being (pyridine —



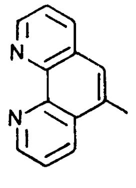
(i) 195



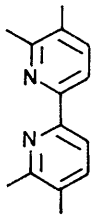
(ii) 144



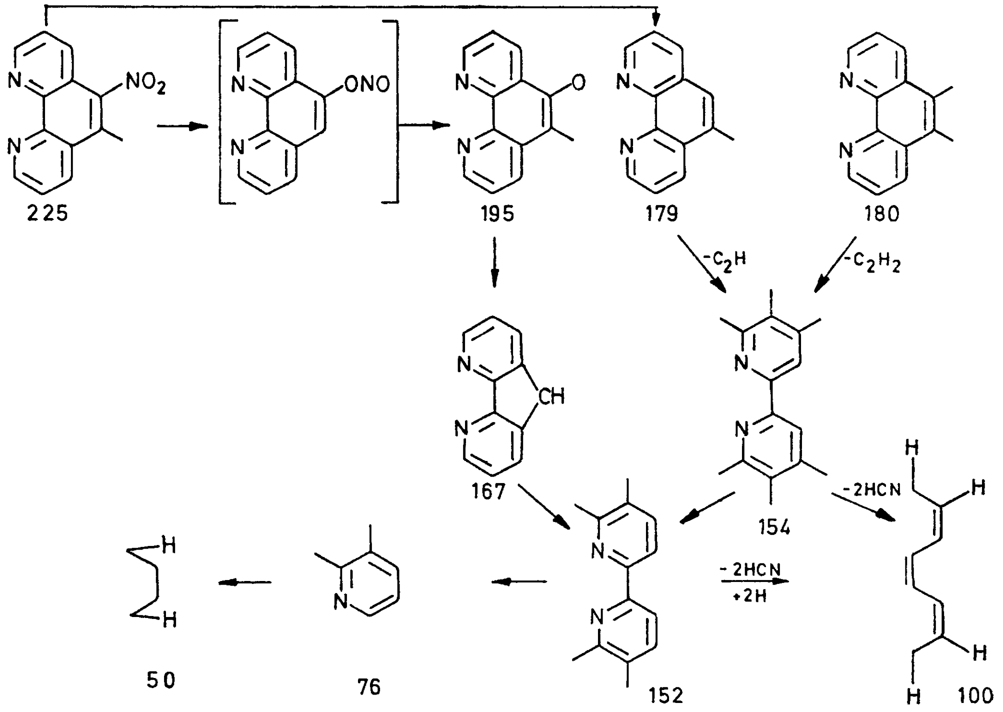
(iii) 167



(iv) 179



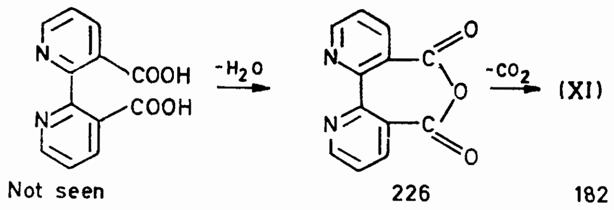
(v) 152



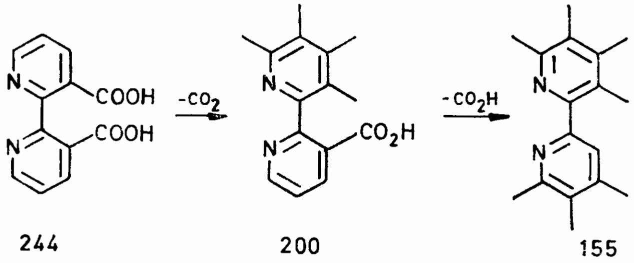
2H). There is also a pattern of fragments around mass 100: this represents simultaneous loss of 2HCN units from the bipyridyl fragments, a known feature[36] of heterocyclic compounds. For the same reason, a mass peak occurs at 50 or below due to HCN elimination from the pyridine fragments.

The fragmentation of bipyridyl is identical with the above pathway from mass 154; these pathways are summarised below.

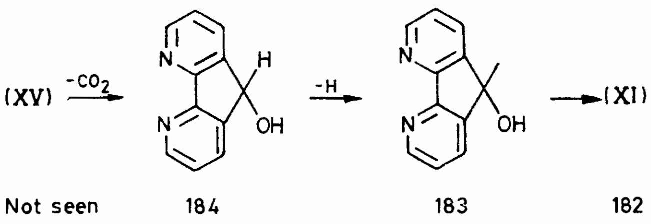
The fragmentation patterns of the following compounds have a common relationship in that they all form, partially or wholly, 4,5-diazafluoren-9-one before fragmenting further according to the pattern of this molecule. They are: (VI), (III), (XIV), (XV), and (XVI). The most significant observation is that of (III) forming, at least in part, the diaza-ketone in the ion chamber. The carboxylic acids (III) and (XV) do not show molecular ions. The principal peak for (III) is 226 (alone) and the next occurs at 200 and then 182 which is the molecular ion for the diaza-ketone. The pathway must be:



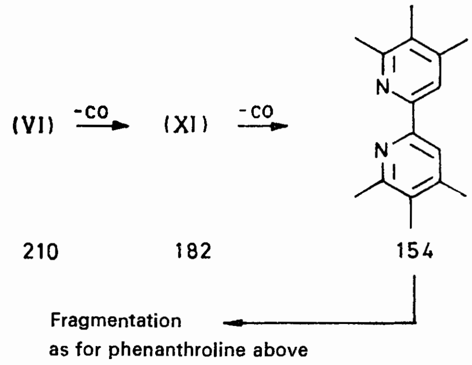
Also, (III) breaks down by a different route:



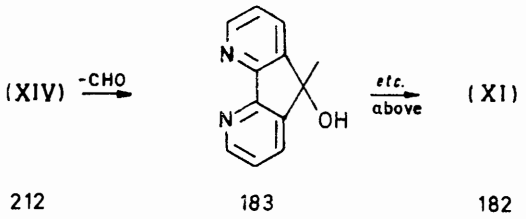
The 200 and 155 peaks are connected by a clear metastable at 120·5. Metastable states exclusive to the ketone are clearly evident in the ensuing fragmentation pattern. The breakdown of (XV) is simpler:



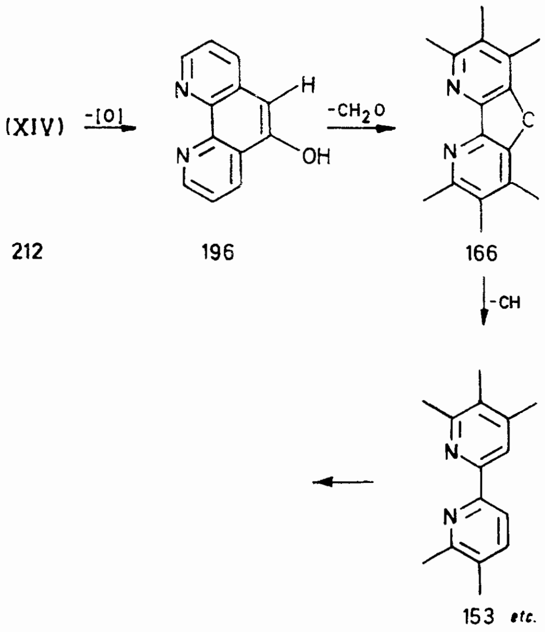
The presence of carbon dioxide at mass 44 is very evident in these two cases. Calculations from metastable states found at 130·5 and 105·5 in (VI) (and the ketone) clearly show an initial process:



(XIV) appears to adopt two pathways. One is:



The first stage was calculated from a metastable at 158·5 which relates the 212 and 183 peaks. Another metastable at 116·5 fits best for masses 166 and 139; it is very difficult to fit this into any pathway although it must be involved in the second one that (XIV) adopts which may be of the form:



The fragmentation pattern for 4,5-diazafluoren-9-one is shown to be:

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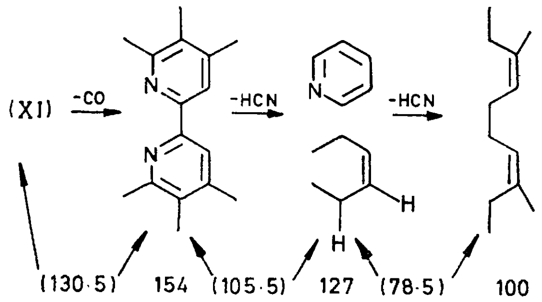
[36] M. S. Fortuin, Ph.D. Thesis, University of Newcastle-upon-Tyne, 1969.



The bracketed figures are metastable states. There is clearly also symmetrical cleavage of the bipyridyl (m = 154) to pyridine fragments at $m = 77$. That this ketone is a common factor in the fragmentation patterns of (III), (VI), (XIV), (XV), and (XVI) indicates a remarkable stability for the molecule. We have already mentioned its considerable chemical stability; the mass spectrometric evidence confirms this.

TABLE 4

Mass spectrometric results for phenanthroline and bipyridyl derivatives

Compound	Mol. Ion															
2,2′-Bipyridyl	156	129	104	78	64	51	39	27								
2,2′-Bipyridyl-3,3′-carboxylic acid		226	200	182	155	129	128	117	104	100	78	77	64	51	44	
1,10-Phenanthroline-5,6-dione	210	182	154	127	128	100	74 →	77	61 →	64	51 50	39	28			
Phenanthroline	179 180	154	125 →	129	99 →	102	90	74 →	77	63	50 51	39	26			
1,10-Phenanthroline-5,6-diol	212	196	183 182	166	153 →	156	139	127	129	112 113	106	101	74 ↷ 78	62 ↷ 65	50 51	44 28
4,5-Diazafluoren-9-one	182	154	127	99 →	101	91	74 →	78	63	50 51	39	27 28				
4,5-Diazafluoren-9-ol	184 →	182	167 168	153 →	155	140	126 →	129	104	98 →	103	86 ↷ 92	73 ↷ 79	61 ↷ 64	50 51	39 27
9-Hydroxy-4,5-diazafluorene-9-carboxylic acid		182 ↷ 184	167 168	153 →	156	140	126 ↷ 130	114	98 →	106	91 92	74 ↷ 79	61 ↷ 64	50 51	44 39	26 27
5-Nitro-1,10-phenanthroline	225	195	152 174	167	140	125 126	113 114	99 ↷ 102	87 ↷ 89	74 77	62 63	50 51	39	30	28	27
6-Nitroquinoline	174	144	128	115	101	89	74 ↷ 77	62 63	50 51	39	30	27				
6,6′-Hydrazoquinoline HCl salt	286	269	254 255	156	143 144	128	101 102	89 90	75 ↷ 77	62 63	50 ↷ 52	38 36	27			
Hydrazobenzene HCl salt	184	165 ↷ 167	156	93 92	77	65 66	36 38									
5,5′-Hydrazophenanthroline HCl salt — 2H	386	258	229 232	209	195	179	167 168	152	140	126 125	111 ↷ 115	97 103	83, 69 85, 71	62, 78 ↷ 63, 74	50 51	36 38
5-Aminophenanthroline	195	182 → 178	168	154	140	127	113 120	101	85	83	63	48	47	17		
5-[^{15}N]Nitrophenanthroline	226	195	179	167	152	140	125 126	99 102	74 77	62 63	50 51	39	31	27		
5,5′-Azophenanthroline	386	371	356 ↷ 358	229	211 212	196	182	166	151 154	139	123 127	109 111	95 97	69, 63 71, 67	36	27

Table 4 lists all the compounds which have been examined and gives the main peaks which appear.

EXPERIMENTAL

Electronic spectra were measured on a Unicam SP 800 spectrophotometer, c.d. spectra with a Roussel–Jouan Dichrographe B, and i.r. spectra with a Perkin-Elmer 257 spectrometer. Mass spectrometric measurements were made with an A.E.I. MS 902 instrument.

Materials:—Sources of reagents were: potassium hexachlororuthenate(IV) and potassium aquopentachlororuthenate(III) (Johnson Matthey); 1,10-phenanthroline and sodium borohydride (Fisons); Sephadex G.10 (Pharmacia); 6-nitroquinoline (B.D.H.).

Reaction of 5-*Nitro*-1,10-*phenanthroline with Aqueous Sodium Borohydride*.—In general, for any set of conditions, the reduction had three distinct phases: (1) as the borohydride and insoluble nitrophenanthroline were mixed, gas was at once evolved; (2) the nitro-compound quickly dissolved giving, usually, a red solution; (3) gradually, a yellow precipitate appeared and gas evolution ceased. The reactions at three temperatures, 0, 20, and 80° are described. Properties of the uncharacterized, but useful materials denoted by A, B, *etc*., are collected under (d).

(*a*) 0° C. 5-Nitrophenanthroline (I) (1·0 g), finely ground, was suspended in water (100 ml), previously adjusted to pH 8 with ammonia. The stirred suspension was cooled to 0° and sodium borohydride (0·5 g) added, causing immediate reaction with gas evolution. After 2—3 h, a pinkish red solution had formed. This was kept overnight, when gas evolution had ceased, and a pale yellow precipitate (A) [yield *ca*. 85% by weight of the original (I)] had formed. This was collected, washed with water, and dried. (The residual borohydride in the filtrate reacted vigorously with hydrochloric acid: evaporation of the resulting solution to 20 ml gave no more products.)

Further reaction of (A) (0·5 g) with sodium borohydride (0·5 g) in water (20 ml) for 48 h at 20° gave a yellow solid (B) whose i.r. spectrum was identical with the product isolated from procedure (b) below.

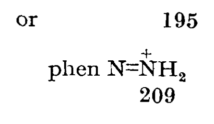
Treatment of (A) with an excess of hydroxide ion gave a red-brown solution (D), whose electronic spectrum showed absorptions at 450 and 500 nm (due to azo-chromophore?).

Chloroform extraction of (D) gave, after removal of the solvent, a red glass; i.r. and electronic spectra suggested the presence of 5-amino- and 5,5′-azo-phenanthroline. Mass spectrometry showed a high mass component at 386 in addition to a fragmentation pattern which fitted 5-aminophenanthroline.

(*b*) 20 °C. As in (a) above, but at 20°. Similar colour changes and gas evolution occurred, but the formation of the yellow precipitate (B) was quicker. The mixture was kept for 16 h, when no more gas was evolved. (B) was collected and washed with water: its dry weight was nearly 0·8 g. The filtrate afforded no further products. (B) was extracted with methanol and then chloroform. Each extracted brown matter. Evaporation of the solvents left behind sticky brown tars. Treatment of these with concentrated hydrochloric acid gave on some occasions red-brown crystalline products. Over a series of runs these varied from almost pure 5-amino-1,10-phenanthroline (II, as hydrated hydrochloride salts) (Found: C, 57·9; H, 3·6; N, 15·6; O, 12·6. $C_{12}H_{14}ClN_3O_2$ requires C, 57·8; H, 4·8; N, 16·8; O, 12·8%) to almost pure (V), 5,5′-azo-1,10-phenanthroline hydrochloride dihydrate (Found: C, 60·3; H, 3·2; N, 16·9. $C_{24}H_{17}ClN_6$ requires C, 61·3; H, 3·7; N, 17·4%). These analyses were also supported by mass spectrometric evidence. Generally, however, a mixture of (II) and (V) was obtained, and yields were low (10%). Remaining from the solvent extraction was a greenish yellow, highly soluble, infusible powder (E).

Treatment of this yellow-green (20°) substance (E) with an excess of sodium borohydride at 80° for 2 h gave a yellow solid (F).

*5,5′-Hydrazo-*1,10*-phenanthroline.*—Treatment of (E) with 6M-hydrochloric acid gave a very insoluble white crystalline compound (60% by weight of the starting material) which was recrystallised from hot water at pH 5. The i.r. spectrum showed many of the characteristics of a phenanthroline derivative with, in addition, an intense sharp band at 965 cm^{-1}. The compound decomposed above 350°. Analyses for several runs coincided to within one per cent for all elements analysed, and the average gave C, 57·6; H, 4·2; Cl, 13·5; N, 16·5. The dihydrochloride dihydrate of 5,5′-hydrazo-1,10-phenanthroline, $C_{24}H_{22}Cl_2N_6O_2$ requires C, 58·2; H, 4·4; Cl, 14·2; N, 16·9%. Mass spectrometry was not satisfactory for (IV) in the light of studies of the fragmentation patterns of the models hydrazobenzene and 6,6′-hydrazoquinoline. However, ion-chamber pressures show that the compound is extremely involatile. Temperatures much higher than for the model hydrazo-compounds were used, which might account for some of the differences. A consistent but very weak peak appeared at *m/e* 386, perhaps the (*P* − 2H) peak. The highest intensity peak (and next highest *m/e* value) was at 209, and another high intensity peak occurred at 195. These two peaks might perhaps be assigned to the symmetrical and unsymmetrical cleavage products, though no metastable states could be found to verify this.



$$\text{phen}\ \underset{\text{HCl}}{\overset{+}{\text{N}}}\text{H}-\overset{\text{HCl}}{\underset{+}{\text{N}}}\text{H phen} \longrightarrow \underset{\text{(M.W. 388)}}{\text{phen·NH·NH phen}} \longrightarrow \underset{\text{or}}{\text{phen·NH·NH}} + \underset{195}{\text{phen·NH}_2}$$

$$\underset{209}{\text{phen N=}\overset{+}{\text{N}}\text{H}_2}$$

Mass spectrometry of [^{15}N](IV) was unhelpful. There was a very weak *m/e* at 388 and 387 (*cf.* 386 for unlabelled compound) and the expected *m/e* at 196 (*cf.* 195 in unlabelled species) was present, but the other major peaks were at 210 and 212 and not at the expected *m/e* of 211 for phen·^{15}NH· — ^{15}NH. However, below *m/e* 195 (or 196), the mass spectrum is entirely consistent with (IV) being a 5-substituted phenanthroline. The mass spectra of phenanthroline compounds are discussed in Appendix 2.

Reaction of 5,5′*-Hydrazo-*1,10*-phenanthroline with Hydroxide Ion.*—5,5′-Hydrazo-1,10-phenanthroline (0·2 g) added to 4M-sodium hydroxide solution (10 ml) immediately gave a red-brown solution. Extraction of this with chloroform gave a glassy red solid, which was a mixture of azo- and amino-phenanthroline (i.r. and mass spectra). The electronic spectra showed bands at 450 and 500 nm due to the azo-chromophore.

Oxidation of 5,5′*-Hydrazo-*1,10*-phenanthroline.*—5,5′-Hydrazo-1,10-phenanthroline (0·35 g) was set to reflux in concentrated nitric–sulphuric acid mixture (1 : 1, 5 ml) for 1 h. The pH of the solution was adjusted to 5 (with NaOH) and it was extracted with chloroform. Evaporation of the chloroform gave 1,10-phenanthroline-5,6-dione (0·3 g) identified by comparison with an authentic sample.

(*c*) 80 °C. As in (a) above, but at 80° for 6 h. The reaction was then complete, a yellow solid (*ca.* 0·5 g) being produced. Chloroform extracted very little material. The remaining yellow powder was treated with concentrated hydrochloric acid when yellow crystals were slowly formed, which were very similar (i.r., mass spectrum, and analysis) to the product of borohydride treatment at 80° of (E), and to the yellow solid obtained by stirring 5,5′-hydrazo-1,10-phenanthroline (0·2 g) with an excess of borohydride at 80° for 4 h.

(*d*) *Uncharacterized substances.* Oxidation of the crude yellow product (B) or (C) with nitrating mixture gave, in varying yields, depending somewhat on the pH at which the precipitate had formed, 1,10-phenanthroline-5,6-quinone (VI), suggesting that in the reduced species the 5-substituents are electron donating, and that (B) and (C) retain the phenanthroline structure. The i.r. spectra of these solids show no aromatic nitro-bands at 1521 and 1340 cm^{-1}. Many of the reduced species showed a band in the 950 cm^{-1} region; *e.g.* 5-aminophenanthroline exhibits a sharp strong band at 940 cm^{-1} [not present in the parent (I)] which disappears on salt formation with hydrochloric acid.

(A) Analysis: C, 43·8; H, 54·0; N, 12·9; O, 22·3% with 16·8% residue. Prominent in the rich i.r. spectrum was an intense sharp band at 985 cm^{-1}. The mass spectrum could not be obtained due to the extreme involatility of the compound. Decomposition set in at over 300 °C; the action of heat on a large amount caused evolution of ammonia (Nessler's reagent) from 200°, leaving a green solid which gave an analysis: C, 49·8; H, 3·4; N, 13·6; O, 15·4%. Its mass spectrum showed major peaks at 377, 225, 178—182, 167, 154, 127, 99—104, 74—78, 62—63, 50, 51, 44 (most intense), 39, 30, 17. The green powder showed no i.r. absorption at *ca.* 950 cm^{-1}.

(B) The i.r. spectrum shows no $ArNO_2$ (no absorption at 1521—1340 cm^{-1}) but is characterized by a sharp doublet of moderate intensity at 955 and 947 cm^{-1}. In the ^{15}N-labelled (B) (made from [^{15}N]phen), this doublet is centred at 942 cm^{-1}. A yellow solid with i.r. identical to that of

(B) was obtained by stirring 5,5′-hydrazo-1,10-phenanthroline (0·29 g) with an excess of sodium borohydride in water (10 ml) at pH 8 for 36 h.

(E) I.r. spectrum showed a characteristic moderately strong doublet centred at 950 cm^{-1}. The mass spectrum showed the following major peaks: 388 (very weak), 255, 195, 179, 167, 152—154, 140, 125—128, 74—78, 63, 50, 51, 44, 30, 17. The analysis gave: C, 66·5; H, 4·2; N, 18·5%.

(F) The i.r. spectrum no longer showed the 950 cm^{-1} doublet. Treatment of (F) with hydrochloric acid gave a yellow crystalline substance (G) also lacking the 950 cm^{-1} bands. Analyses for four samples of (G) from different runs were all close, the averages being: C, 56·3; H, 4·8; N, 14·5%. The mass spectrum showed major peaks at: 384, 371, 356—359, 343, 329—331, 229, 212, 211, 196, 182, 166, 154, 152, 111, 109, 97, 95, 83, 81, 71, 69, 57, 55, 44, 38, 36, 30, 17. There were many smaller peaks suggesting that the compound was not pure.

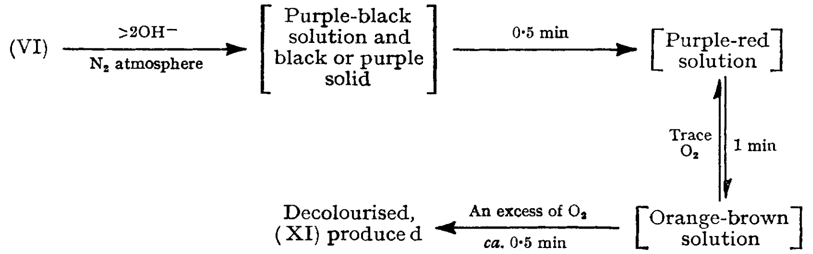
Reaction of 6-*Nitroquinoline with Borohydride.*—6-Nitroquinoline (1·0 g) was suspended in water (50 ml) made faintly alkaline (pH 8) with ammonia; sodium borohydride (0·5 g) was added to the stirred mixture which was warmed to 80°. A vigorous reaction with gas evolution occurred and the solution became black. After 4 h, when gas evolution had stopped, the solution was filtered hot and the filtrate made strongly acid with concentrated hydrochloric acid. On cooling, a mass of brown-yellow crystals separated, and were recrystallised from hot acidic water. 50% of a pale yellow crystalline salt was obtained, which analysed as follows: C, 57·5; H, 4·8; Cl, 18·2; N, 14·9. The dihydrochloride monohydrate of 6,6′-hydrazoquinoline, $C_{18}H_{18}Cl_2N_4O$ requires C, 57·3; H, 4·3; Cl, 18·18; N, 14·9%. The mass spectrum was in complete agreement with the proposed structure (see Table 4).

Preparation of Isotopically Labelled 5-$[^{15}N]$*Nitro*-1,10-*phenanthroline Hydrate.*—(*i*) Bisethylenediamine(1,10-phenanthroline)cobalt(III) perchlorate (0·5 g) was dissolved in concentrated sulphuric acid (2 ml), and ^{15}N-labelled 8M-nitric acid (0·5 ml) added to the cooled solution. The mixture was warmed on a water bath at 100 °C for 2½ min and then poured quickly into water (10 ml) containing sodium perchlorate (1·0 g). The solution was kept overnight at 0 °C, then filtered, yielding bisethylenediamine-(5-$[^{15}N]$nitrophenanthroline)cobalt(III) perchlorate trihydrate (0·45 g) (Found: C, 25·9; H, 4·3; N, 13·5. $C_{16}H_{29}Cl_3CoN_6O_{15}$ requires C, 25·6; H, 4·0; N, 13·1%).

(ii) Isolation of the $[^{15}N]$nitrophenanthroline. During (i), a small amount of the complexed 5-nitrophenanthroline is sometimes oxidised to the quinone ligand. This is removed first as follows: the full yield from (i) (*ca.* 0·45 g) dissolved in water (20 ml) containing two drops of 4M-hydrochloric acid and the disodium salt of EDTA (1·0 g) was boiled (5 min), and extracted with hot chloroform. Any quinone ligand is completely removed. The remaining aqueous solution was boiled (2 h), cooled, made alkaline and extracted with hot chloroform (3 × 10 ml). The yield should be nearly quantitative. If it is low, further boiling with EDTA and renewed extraction may be required. The average overall yield of pure 5$[^{15}N]$nitro-1,10-phenanthroline hydrate is 80%, m.p. 201° (Found: C, 59·0; H, 3·5; N, 17·3. $C_{12}H_9N_3O_3$ requires C, 59·3; H, 3·71; N, 17·3%). I.r. absorption occurs at 1480 and 1328 cm^{-1} in the 5-$[^{15}N]$nitro-derivative, replacing bands at 1518 and 1348 cm^{-1} in the unlabelled 5-nitro-compound.

(iii) *Reaction of the labelled compound with sodium borohydride.* 5-$[^{15}N]$Nitro-1,10-phenanthroline (50 mg) was slurried with water (5 ml) at $6 < \mathrm{pH} < 7{\cdot}5$. Sodium borohydride (90 mg) was added and the mixture stirred at ambient temperature for 13 h. The resultant yellow solid was separated and washed with water by centrifugation. The sample was left to dry in a desiccator. From this point, the work was carried out on a proportionally reduced scale but in the manner described for the unlabelled reaction.

Reactions of 1,10-*Phenanthroline*-5,6-*dione with Air or Oxygen in Basic Media.*—Treatment of (VI) with not less than two molar equivalents of hydroxide ion in degassed water under dinitrogen gave rise to a number of dramatic colour changes. These visual effects are summarised below.



(a) *Production and reactions of the oxygen sensitive intermediate.* A solution of sodium hydroxide (0·2 g) in degassed water (20 ml) in a 100 ml 3-necked round bottomed flask fitted with a reflux condenser, gas bubbler, and glass stopper, was further purged of air by a vigorous stream of nitrogen for 30 min; while under reflux, under nitrogen, 1,10-phenanthroline-5,6-dione (1·0 g) was added. The described colour changes occurred, culminating in a transparent rich orange-brown. If the nitrogen atmosphere was maintained, this solution was stable (over the test times of 4 h). The introduction of a trace of oxygen produced a purple-red colour, which soon reverted to orange-brown on allowing nitrogen to flow again. This orange-brown solution was treated in three ways as follows:

(b) *Aerial conditions.* The solution made under (a) above was poured very quickly into enough degassed dilute hydrochloric acid to neutralise the hydroxide (0·2 g) present. Instantly, colour was lost and yellow crystals deposited, identified by electronic spectrum and by mass spectrometry as 1,10-phenanthroline-5,6-diol (Found: C, 68·4; H, 4·5; N, 13·2. $C_{12}H_8N_2O_2$ requires C, 68·0; H, 4·6; N, 13·3%). The slightly acid filtrate was extracted with chloroform. Removal of the chloroform left exclusively pale yellow crystalline 4,5-diazafluoren-9-one, identified by comparison with an authentic sample.

The aqueous solution remaining was evaporated to 5 ml, and cooled (refrigerator) for 6 h. White crystals formed, and were removed and dried. Treatment of a portion of this compound with base gave 4,5-diazafluoren-9-one. The m.p. was greater than 350 °C and at this temperature, in air, the compound gave the azafluorene. I.r. evidence and behaviour with sodium hydrogen carbonate solution suggested the presence of a carboxylic acid. Mass spectrometrysho wed the presence of hydrochloric acid, and analysis gave: C, 46·6; H, 4·3; Cl, 24·7; N, 9·9; O, 16·3. The dihydrochloride salt of 9-hydroxy-4,5-diazafluorene-9-carboxylic acid requires C, 48·0; H, 4·0; Cl, 23·7; N, 9·3; O, 16·0%. The mass spectrum did not reveal the molecular ion (228), but did show as the first and strongest peak the decarboxylated product (184) and carbon dioxide (44).

(c) *In the absence of air.* The solution made under (a) above was prepared in an apparatus fitted with a Schlenck tube, and poured, under an inert atmosphere of nitrogen, into degassed hydrochloric acid as described in (b) above. A much larger quantity of a yellow crystalline material was precipitated. However, this was shown (i.r.) to be a mixture of the hydroxyazafluorenecarboxylic acid and the diol. The pure diol was isolated by dissolving out the acid with sodium hydrogen carbonate. Extraction of the filtrate with chloroform gave no 4,5-diazafluoren-9-one. The remaining aqueous solution was evaporated to 5 ml: much white crystalline substance had appeared. This was filtered off and dried. Base treatment of a portion gave the azafluorenol. Its i.r. spectrum showed no acid or keto-groups, but resembled in every other way the azafluorenone. Mass spectrometry revealed the highest and most intense peak at 184. The m.p. was 350 °C and at this temperature the compound rapidly transformed into the azafluorenone. Analysis gave: C, 54·8; H, 3·1; Cl, 13·0; N, 11·7. A monohydrate of the hydrochloride salt of 4,5-diazafluoren-9-ol requires C, 55·2; H, 3·4; Cl, 14·1; N, 11·7%.

(d) *Production of* 4,5-*diazafluoren*-9-*one*. Treatment of the solution made under (a) above with a vigorous stream of oxygen caused rapid decolouration and within 60 s a mass of acicular crystals of 4,5-diazafluoren-9-one was deposited (yield >90%).

Oxidation of 1,10-*Phenanthroline*-5,6-*diol with Oxygen in Basic Media*.—(*a*) *Production of* 4,5-*diazafluoren*-9-*one*. 1,10-Phenanthroline-5,6-diol (0·5 g) was added to 4M-sodium hydroxide (20 ml) and heated to 100 °C in the presence of air in one run, and with a vigorous stream of oxygen in another run. Both reactions (the latter much faster) gave 80% yields of 4,5-diazafluoren-9-one, identified by comparison (i.r. and electronic spectra, m.p.) with an authentic sample.

(*b*) *Production of* 2,2′-*bipyridyl*-3,3′-*dicarboxylic acid*. A suspension of 1,10-phenanthroline-5,6-diol (0·5 g) in water (20 ml) was set to reflux, further agitated by a strong stream of oxygen. 4M-Sodium hydroxide solution was added dropwise, at a rate which just dispersed the brown colouration which otherwise developed. When no more brown colour developed, the resulting clear solution was evaporated to 5 ml and hydrochloric acid added equivalent to the amount of 4M-hydroxide added above. The solution was cooled for 12 h. The crop of white crystals obtained was collected, washed, and dried. The product (80% yield) was identified as 2,2′-bipyridyl-3,3′-dicarboxylic acid by comparison (i.r., electronic spectra, m.p.) with an authentic specimen.

Oxidation of 1,10-*Phenanthroline*-5,6-*diol*.—1,10-Phenanthroline-5,6-diol (0·5 g) was refluxed with concentrated nitric–sulphuric acid (1 : 1) for 30 min. The solution was cooled, adjusted to pH 5, and extracted with chloroform. Evaporation of the chloroform gave a yellow crystalline compound which was identified as 1,10-phenanthroline-5,6-dione (70%) by comparison (i.r., electronic spectra, m.p., and mass spectrometry) with an authentic sample.

Reduction of 1,10-*Phenanthroline*-5,6-*dione*.—1,10-Phenanthroline-5,6-dione (0·5 g) was treated in water (10 ml) with hydrazine hydrochloride (0·5 g). The mixture was warmed on a water bath at 100 °C for about 5 min, until the vigorous evolution of gas had ceased. The insoluble dark brown crystals resulting were removed, washed with water, and recrystallised from water–ethanol acidified with a little dilute hydrochloric acid. The hydrochloride salt was obtained in 90% yield (Found: C, 57·9; H, 3·5; N, 11·3. $C_{12}H_9ClN_2$ requires C, 58·0; H, 3·6; N, 11·3%).

The insoluble, yellow, neutral compound could be precipitated by very careful treatment of the acid salt with a stoicheiometric amount of M/100 hydroxide (Found: C, 68·8; H, 4·5; N, 13·0. $C_{12}H_8N_2O_2$ requires C, 68·0; H, 4·6; N, 13·3%).

Oxidation of 1,10-*Phenanthroline*-5,6-*dione by Hydrogen Peroxide*.—1,10-Phenanthroline-5,6-dione (0·5 g) was treated in water (20 ml) at pH 5 with 100 volume hydrogen peroxide (2 ml) for 30 min at 100 °C. Concentration to 5 ml and cooling eventually gave 80% yield of crystalline 2,2′-bipyridyl-3,3′-dicarboxylic acid, identified by comparison (i.r. and electronic spectra, m.p.) with an authentic analytical sample.

Hydrazobenzene.—This was prepared according to Vogel [37] and isolated as the hydrochloride salt.

5-*Nitro*-1,10-*phenanthroline*.— 5-Nitro-1,10-phenanthroline, prepared by the method [21] of Smith and Cagle, was recrystallised from ethanol to constant m.p. (200°).

Tris(5-*nitro*-1,10-*phenanthroline*)*iron*(II) *Perchlorate*.—Finely ground 5-nitro-1,10-phenanthroline (1·0 g) was added gradually to a stirred aqueous solution (25 ml) containing ferrous sulphate heptahydrate (0·38 g) and 4M-hydrochloric acid (one drop) heated to 60 °C. After 5 min, sodium perchlorate (0·5 g) was added causing precipitation of the metal complex. After filtration and water washing, portions of the complex were recrystallised from acetone–water (1 : 10) as required (Found: C, 41·5; H, 2·9; N, 12·0. $C_{36}H_{33}Cl_2FeN_9O_2$ requires C, 41·1; H, 3·2; N, 12·1%).

D-(+)- *and* L-(−)-*Trisphenanthrolineruthenium*(II) *Perchlorate*.—The method used was a very slight modification of the original procedure [38] of Dwyer and Gyarfas. Potassium aquopentachlororuthenate(III) (2·4 g) was dissolved in hot water (100 ml) containing 1 drop of 5M-hydrochloric acid. 1,10-Phenanthroline (3·6 g) was added, and the mixture boiled for a few minutes until it became dark greenish brown. To this was added a solution of hypophosphorous acid (2 ml, 50%) which was neutralised with 4M-sodium hydroxide solution. Refluxing was continued for another 30 min by which time the solution was orange-red. Some unchanged complex was filtered off, the filtrate cooled to 0 °C and (+)-potassium antimony tartrate (Ksbt) (2·0 g) in water (100 ml) added dropwise. The resulting orange precipitate (the filtrate was reserved) was washed well with water. Recrystallisation was effected by dissolution in M/20 sodium hydroxide solution (200 ml) acidifying with dilute acetic acid and addition of a small amount of the resolving agent. Treatment of the crystalline

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[37] A. I. Vogel, ‘Practical Organic Chemistry,’ IV, 87, p. 632.

[38] F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. New South Wales*, 1947, **80**, 212; 1949, **83**, 263.

diastereoisomer, D-(+)-[Ru(phen)$_3$] (+)-(sbt)$_2$, with sodium perchlorate afforded the D-(+)-enantiomer perchlorate.

The L-(−)-enantiomer was isolated as its perchlorate from the filtrate after this had been treated with more resolving agent to remove remaining traces of the D-(+)-enantiomer.

Attempted Resolution of Tris(5-*nitro*-1,10-*phenanthroline*)-*ruthenium*(II) *Perchlorate*.—The procedure for resolution of the phenanthroline complexes was followed exactly, substituting the following quantities: 5-nitro-1,10-phenanthroline hydrate (1·43 g), potassium aquopentachlororuthenate(III) (0·7 g), and (+)-potassium antimony tartrate (1·0 g). No resolution was obtained. Another solution prepared in the same way with ammonium (+)-bromocamphorsulphonate, and left at 0 °C overnight, also failed to achieve resolution.

(5-*Nitrophenanthroline*)*bisphenanthrolineruthenium*(II) *Perchlorate*.—This was prepared by the general method [39] of Dwyer and Broomhead for bisphenanthrolinebispyridineruthenium(II) perchlorate, substituting 5-nitro-1,10-phenanthroline for pyridine. The quantities used were [Ru(phen)$_2$Cl$_2$] (0·5 g), and 5-nitrophenanthroline (0·25 g) in water. The perchlorate was precipitated on adding sodium perchlorate (0·5 g) (Found: C, 43·2; H, 3·1; N, 9·8. $C_{36}H_{35}Cl_2N_7O_{16}Ru$ requires C, 43·5; H, 3·5; N, 9·8%).

D-(+)-*Tris*(5-*amino*-1,10-*phenanthroline*)*ruthenium*(II) *Perchlorate from* D-(+)-*Tris*(5-*nitro*-1,10-*phenanthroline*)*ruthenium*(II) *Perchlorate*.—D-(+)-Tris(5-nitro-1,10-phenanthroline)ruthenium(II) perchlorate (1·0 g) was dissolved in concentrated hydrochloric acid (10 ml) and finely granulated tin (2 g) was added. The mixture was refluxed for 30 min, cooled, and made alkaline. The aminophenanthroline complex was extracted with acetone and recrystallised from water containing some sodium perchlorate. The complex crystallised as its hexahydrate (Found: C, 43·3; H, 4·2; N, 12·7. $C_{36}H_{39}Cl_2N_9O_{14}Ru$ requires C, 43·5; H, 4·0; N, 12·9%).

Attempted Preparation of L-(−)-*Tris*(5-*amino*-1,10-*phenanthroline*)*ruthenium*(II) *Perchlorate from* 5-*Amino*-1,10-*phenanthroline*.—The method used was an attempted asymmetric synthesis,[37] as outlined [16] for L-(−)-[Ru(phen)$_3$]$^{2+}$, using quantities: 5-aminophenanthroline (0·42 g), potassium hexachlororuthenate(IV) (0·25 g), and potassium D-(+)-tartrate (0·65 g). The reaction was stopped after 2 h, the mixture filtered, and perchloric acid added to the filtrate. An orange crystalline precipitate was formed: this was filtered off and recrystallised with some difficulty from water–acetone. Analysis gave: C, 43·3; H, 3·5; Cl, 15·7; N, 12·6%.

5-*Amino*-1,10-*phenanthroline*.— 5-Nitro-1,10-phenanthroline (1·0 g) was dissolved in concentrated hydrochloric acid (10 ml) and finely granulated tin (2 g) was added. The mixture was allowed to reflux for 1 h, cooled, and made alkaline. The aminophenanthroline was extracted into chloroform and recrystallised from ethanol. The yield was 75% of yellow-brown crystals of the monohydrate which melted at 194—197° (Found: C, 68·7; H, 4·3; N, 20·2. $C_{12}H_9N_3,H_2O$ requires C, 68·5; H, 5·1; N, 19·9%).

Isolation of Tris(5-*amino*-1,10-*phenanthroline*)*ruthenium*-(II) *Perchlorate from Reaction with Borohydride*.—Finely ground L-(−)-tris(5-nitro-1,10-phenanthroline)ruthenium-(II) perchlorate (0·5 g) was suspended in water (30 ml) with stirring. Sodium borohydride (0·1 g) was added and the mixture warmed to about 50°. After 20 min, the vigorous reaction was quenched by adding an excess of 4M-hydrochloric acid, then the solution made just alkaline with sodium hydroxide solution. Sodium perchlorate (0·29 g) was added and the precipitated solids collected and thrice extracted with hot acetone. Evaporation of the acetone gave an orange-brown solid (0·2 g) which was recrystallised from hot water. This compound had spectroscopic properties (i.r., electronic, and c.d., including the remarkable pH effect) identical with those of L-(−)-[Ru(5-NH$_2$phen)$_3$]-(ClO$_4$)$_2$ prepared by Sn–HCl reduction of the 5-nitro-complex and also analysed satisfactorily (Found: C, 42·5; H, 3·5; N, 12·12. $C_{36}H_{39}Cl_2N_9O_{14}Ru$ requires C, 43·5; H, 4·0; N, 12·9%).

Reaction of 5,5′-*Hydrazo*-1,10-*phenanthroline with the Ruthenium* (+)-*Tartrate System*.—The ruthenium (+)-tartrate system was prepared as described [16] using potassium hexachlororuthenate(IV) (0·05 g) and potassium D-(+)-tartrate (0·13 g). To this was added 5,5′-hydrazo-1,10-phenanthroline (0·2 g). When the mixture was kept at 100° (4 h), much brown solid had precipitated. Collection of this solid followed by water washing and oven drying at 120° gave a brown powder, constituting about 70% yield, insoluble in water and all common organic solvents tried. The substance did dissolve slightly in concentrated hydrochloric acid giving an orange-brown solution. Analysis gave: C, 43·4; H, 3·5; N, 11·8%.

D-(+)- *and* L-(−)-*Trisquinoneruthenium*(II) *Diperchlorate Hexahydrate*.—(*a*) *By the Bailar–Liu method*. Preparation is as for trisphenanthrolineruthenium(II) perchlorate using potassium hexachlororuthenate(IV) (0·25 g), 1,10-phenanthroline-5,6-quinone (0·42 g), and potassium D-(+)-tartrate (0·65 g). The crude product is very impure. Methanol extraction yields up to 20% of an analytical sample (Found: C, 40·8; H, 2·8; N, 8·4. $C_{36}H_{30}Cl_2N_6O_{20}Ru$ requires C, 41·5; H, 2·9; N, 8·1%).

(b) *By oxidation of* D-(+)-*trisphenanthrolineruthenium*(II) *perchlorate*. The procedure outlined [11] for (VICo^{III})perchlorate was followed. D-(+)-Trisphenanthrolineruthenium(II) perchlorate (1·0 g) was added slowly to concentrated sulphuric acid (15 ml) kept at 0 °C, followed by sodium bromide (0·25 g). The mixture was stirred (1 min) before slowly adding concentrated nitric acid (10 ml). The resulting deep red solution was heated on a water bath at 100 °C for 35 min during which time it became green, then cooled, and poured into water (20 ml) containing sodium perchlorate (0·5 g). Some quinone complex precipitated at once, but for maximum yield * (about 50%) the solution was kept ice-cold for 12 h. The optical purity (*ca.* 95%) of the sample prepared this way, compared to the starting material, was much higher than that prepared by the method (a) (Found: C, 41·7; H, 2·7; N, 8·2. $C_{36}H_{30}Cl_2N_6O_{20}Ru$ requires C, 41·5; H, 2·9; N, 8·1%). Molar extinction at $\lambda_{295} = 4·58 \times 10^4$ mol^{-1} cm^2.

Reaction of D-(+)-*Trisquinoneruthenium Perchlorate with Hydroxide Ions*.—(*i*) *Conversion to sodium* D-(+)-*tris*(3,3′-*dicarboxy*-2,2′-*bipyridyl*-N,N)*ruthenate*(II). D-(+)-Trisquinoneruthenium(II) perchlorate (0·2 g) was added all at once to 4M-potassium hydroxide solution (5 ml) at room temperature. The complex dissolved almost immediately to give a clear orange solution. On standing, or more quickly on warming, this solution darkened to a brown-black colour. Elution on a Sephadex G10 column (30 in × ½ in)

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* See footnote to page 1220.

[39] F. P. Dwyer and J. A. Broomhead, *Austral. J. Chem.*, 1963, **16**, 544.

gave one large band, which was the first to elute, and three minor bands. Evaporation of the large fraction gave potassium D-(+)-tris(3,3′-dicarboxy-2,2′-bipyridyl-*N*,*N*)-ruthenate(II) hexahydrate (0·15 g) entirely consistent in properties (i.r., electronic, and c.d. spectra) with an analytical specimen prepared *via* permanganate oxidation of the trisphenanthrolineruthenium(II) cation (Found: C, 39·2; H, 3·2; N, 7·9. $C_{36}H_{36}K_4N_6O_{18}Ru$ requires C, 39·4; H, 3·3; N, 7·6%).

(*ii*) *Reaction with hydroxide ion at high dilution.* In silica cells (2·5 ml), solutions of D-(+)-trisquinoneruthenium(II) perchlorate, 100 and 50 mg l^{-1}, were treated respectively with 10 and 5 mg potassium hydroxide. The visible and u.v. spectra altered appreciably, but if the solutions are kept near or below 25°, the quinone complex is completely regenerated on acidification, and without significant loss of optical activity. Action of heat for a few minutes, especially in the presence of air or oxygen, gives an irreversible change and the electronic spectrum of the product is suggestive of a mixture of the tris complexes of 2,2′-bipyridyl-3,3′-dicarboxylic acid and 2,2′-bipyridyl-3-carboxylic acid.

Tris(4,5-*diazafluorene*-9-*one*)*ruthenium*(II) *Perchlorate*.—This was prepared in exactly the same way as trisphenanthrolineruthenium(II) perchlorate (Bailar–Liu asymmetric synthesis [35]) with only slight changes in quantities, *e.g.* potassium hexachlororuthenate(IV) (0·25 g), 4,5-diazafluoren-9-one (0·35 g), potassium D-(+)-tartrate (0·65 g). The yield was 80% and the complex could be recrystallised from hot water at pH 6, to give the hexahydrate (XIRu)-$(ClO_4)_2,6H_2O$ (Found: C, 43·5; H, 2·6; N, 8·5. $C_{33}H_{30}Cl_2N_6O_{17}Ru$ requires C, 43·9; H, 3·2; N, 8·8%).

Sodium Tris(3-*carboxy*-2,2′-*bipyridyl*-N,N′)*ruthenate*(II).—The perchlorate of (XIRu) (0·3 g) was added all at once to 4M-sodium hydroxide (5 ml). The complex dissolved at once to give a clear red-orange solution. The reaction could not be reversed by acidification. Elution on Sephadex G10 (using a 30 in × ½ in column) showed only one large band which after evaporation gave a dark red glassy solid. This compound analysed satisfactorily for the hexahydrate of the sodium salt of tris(3-carboxy-2,2′-bipyridyl-*N*,*N*′)-ruthenate(II) (Found: C, 47·1; H, 4·2; N, 10·3. $C_{33}H_{33}N_6NaO_{12}Ru$ requires C, 47·6; H, 4·3; N, 10·1%).

D-(+)-*Tris*(5-*nitro*-1,10-*phenanthroline*)*ruthenium*(II) *Perchlorate*.—The opposite hand of this has been prepared previously *via* an asymmetric synthesis. The present method offers a route to a more optically pure sample. D-(+)-Tris(*o*-phenanthroline)ruthenium(II) perchlorate (1·0 g) was dissolved, with ice-cooling, in concentrated sulphuric acid (5 ml) (great care—slow addition: an **explosive reaction** occurs if the addition is made too quickly), and sodium nitrate (0·25 g) was added. The initially formed beautiful blue solution was heated for 30 min on a water bath at 100 °C (the solution turns green), quickly cooled, then poured into ice-cold water (20 ml) containing sodium perchlorate (0·5 g). The crude material contained some trisquinone complex, which was removed by repeating the following procedure four times. The precipitate was dissolved in 4M-sodium hydroxide (10 ml), the solution warmed to 40 °C for 1 min, then poured into an ice-cold 5% sodium perchlorate solution, and filtered. The quinone complex was removed by reaction to form the very soluble 2,2′-bipyridyl-3,3′-dicarboxylate complex. C.d. indicates that some loss of optical activity in the nitrated complex occurs with each such purification (Found: C, 40·5; H, 2·6; N, 12·0. $C_{36}H_{33}Cl_2N_9O_{20}Ru$ requires C, 40·0; H, 3·0; N, 11·6%).

Reaction of D-(+)-*Tris*(5-*nitrophenanthroline*)*ruthenium*(II) *Perchlorate with Hydroxide*.—D-(+)-Tris(5-nitrophenanthroline)ruthenium(II) perchlorate (0·5 g) was warmed in water (20 ml) with sodium hydroxide (0·25 g). The complex rapidly dissolved giving a dark orange-brown solution. Very soon, a black precipitate (VIIIRu) appeared and ammonia was evolved (smell; Nessler's reagent). A manometric measurement of yield showed that ammonia : original Ru was *ca.* 40%. Ammonia was identified as the sole volatile product by its i.r. spectrum. We checked that the 5-aminophenanthroline complex of ruthenium(II) was not an intermediate by boiling it with hydroxide ion for 30 min. There was no reaction. After 30 min, the reaction appeared to be complete and the mixture was made acid. A black substance was collected, washed with water and a little acetone, then dried at 120 °C. The yield by weight was 40% of a complex which was analysed: C, 51·8; H, 2·9; N, 15·1; O, 11·7%. The nature of the substance (VIIIRu) is not yet clear: its i.r. spectrum is devoid of aromatic nitro-bands; there are new absorptions at 3500—3100 cm^{-1} (very broad and strong), 1610 cm^{-1} (intense, broad), and 1240 cm^{-1} (strong, broad). The perchlorate gegenion is usually absent, but can be reintroduced with the sodium ion, suggesting the presence of readily ionizable protons. The i.r. and electronic spectra are consistent with (VIIIRu) containing a 5-hydroxy-derivative of phenanthroline, as are the chemical properties (see Scheme 2): protonation produces (IXRu) with some changes in the vibrational and electronic spectra.

(*ii*) *Repeat with tris*(5-*nitrophenanthroline*)*iron*(II) *perchlorate*. The above procedure was repeated for tris(5-nitrophenanthroline)iron(II) perchlorate but there was no corresponding reduction and the complex rapidly broke up. Extraction into chloroform gave only an essentially quantitative yield of the unchanged free ligand.

Reduction of Trisquinonecobalt(III) *Perchlorate With Hydrazine*.—D-(+)-Trisquinonecobalt(III) perchlorate (1·0 g) was suspended in water (20 ml) and hydrazine hydrochloride (1·0 g) added. The mixture was warmed on a water bath at 100° and a vigorous reaction with gas evolution started. The complex dissolved and soon a brown crystalline solid deposited. When gas evolution ceased, the mixture was cooled to 0° and filtered. The product lacked perchlorate bands in its i.r. spectrum and so is the chloride salt. The crystals were boiled with 10% sodium perchlorate solution (10 ml) whence the perchlorate salt was obtained. This product ($XIVCo^{II}$), which was racemic, is tris(1,10-phenanthroline-5,6-diol)cobalt(II) perchlorate hexahydrate (Found: C, 42·9; H, 3·3; N, 8·2. $C_{36}H_{36}Cl_2CoN_6O_{20}$ requires C, 43·1; H, 3·6; N, 8·4%). The oxidation state (II) for cobalt was supported by a magnetic moment measurement (Gouy method) of 4·4 B.M.

Reaction of Trisquinonecobalt(III) *Perchlorate With Hydroxide*.—Trisquinonecobalt(III) perchlorate ($VICo^{III}$) (0·2 g) in water (5 ml) was treated with sodium hydroxide (0·05 g). The solution rapidly darkened and a heavy black precipitate was formed. This mixture was quickly acidified (HCl) when the precipitate dissolved giving, initially, a clear brown solution, which deposited brown crystals. After cooling for 2 h at 0 °C, these were collected, preserving the filtrate (B), dissolved in water, and boiled with sodium perchlorate (0·2 g). The product was identified (i.r., electronic spectra, analysis) as (XIVCo) perchlorate hexahydrate

(Found: C, 43·0; H, 3·5; N, 8·3. $C_{36}H_{36}Cl_2CoN_6O_{20}$ requires C, 43·1; H, 3·6; N, 8·4%).

The filtrate (B, above) was evaporated to give a green hygroscopic glass (0·08 g), whose electronic spectrum was very similar to that of the product of the reaction of trisquinonecobalt(II) perchlorate with hydrogen peroxide, also a green glass.

Tris(1,10-*phenanthroline*-5,6-*diol*)*ruthenium*(II) *Perchlorate.*— Tris(1,10-phenanthroline-5,6-dione)ruthenium(II) perchlorate (0·5 g) was dissolved in water (20 ml) and hydrazine hydrochloride (0·5 g) added. The solution was warmed on a water bath (100 °C) for 1 h; by this time the electronic spectrum had usually ceased changing. Addition of sodium perchlorate (1·0 g) precipitated a dark brown complex. This was recrystallised from slightly acidified water. The yield was almost 60% (Found: C, 40·5; H, 3·6; N, 8·0. $C_{36}H_{36}Cl_2N_6O_{20}Ru$ requires C, 41·2; H, 3·4; N, 7·9%).

Reaction of Tris(1,10-*phenanthroline*-5,6-*diol*)*ruthenium*(II) *Perchlorate with Hydroxide Ion.*—Treatment of (XIVRu) perchlorate with either concentrated or very dilute hydroxide ion solutions, usually *in situ* in a u.v. cell, showed a rapid reaction with production of a species absorbing strongly near 295 nm.

Tris(1,10-*phenanthroline*-5,6-*diol*)*cobalt*(II) *with Hydroxide Ion.*—Tris(1,10-phenanthroline-5,6-diol)cobalt(II) perchlorate (0·5 g) was treated with 4M-potassium hydroxide solution (10 ml). A black precipitate appeared within 30 s. This was quickly filtered off and washed several times with water. Attempts to recrystallise the product from water were unsuccessful: the crude material was analysed (Found: C, 39·5; H, 2·6; N, 8·4. The hexahydrate of $C_{36}H_{20}CoK_4N_6O_{12}$ requires C, 40·9; H, 3·0; N, 8·1%).

Reacidification of the complex with hydrochloric acid gave a brown crystalline complex. This was boiled with sodium perchlorate giving a darker brown crystalline material which analysed precisely for the parent (phendiol) hexahydrated complex (Found: C, 43·0; H, 3·5; N, 8·3. $C_{36}H_{36}Cl_2CoN_6O_{20}$ requires C, 43·1; H, 3·6; N, 8·4%).

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