Bis(2,2'-bipyridine) and Bis(1,10-phenanthroline) Complexes of Chromium(III) and Cobalt(III)

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A number of complexes of the type $[M(N-N)_2XY]^{n+}$ (M = Cr(III) or Co(III); N — N = 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen); X,Y = F, Cl, H_2O, OH or $\frac{1}{2}C_2O_4$; n = 1, 2 or 3) have been subjected to a critical preparative study. The new complex ions cis-$[M(phen)_2(H_2O)Cl]^{2+}$ have been isolated as their perchlorate salts and their stability relative to the corresponding cis-diaqua complexes determined as $K_1 \simeq 9$ l mol^{-1} (M = Cr) and $K_1 \simeq 40$ l mol^{-1} (M = Co) at an ionic strength of $ca.$ 0.11 M.

In the absence of trace impurities of the corresponding metal(II) species the dichloro complexes cis-$[M(N-N)_2Cl_2]^+$ are unusually robust with respect to acid hydrolysis. The otherwise rather slow anation of cis-$[M(N-N)_2(H_2O)_2]^{3+}$ by chloride ion is also greatly accelerated by traces of appropriate M(II) species.

Base hydrolysis of the cobalt(III) dichloro complexes is fast even in the absence of added catalyst, but this is not the case with the chromium(III) analogues.

Although some of the complex salts studied exist in a variety of polymorphic forms, only one geometric isomer has been found in each case. The interconversion of many of the chromium(III) complexes has been examined and the cleavage reactions of the racemic and optically active di-μ-hydroxobis {bis(N — N)-chromium(III)} complexes have been included in these interconversion studies to substantiate the assertion that all the complexes have the cis-configuration. The latter cleavage reactions have led to the preparation of a number of optically active chromium(III) species, including the previously unreported ions $(-)_{589}$-cis-$[Cr(phen)_2X_2]^+$ (X = F or Br), and $(-)_{589}$-cis-$[Cr(bipy)_2Br_2]^+$.

Their molar rotations at the Na D-line and circular dichroism spectra in the visible region have been measured.

The accumulated evidence indicates the generality of the cis-configuration for bis(N — N)

complexes of the trivalent metal ions Cr(III), Co(III), Rh(III), and Ir(III).

No evidence for the existence of $trans$ complexes of the title types has presented itself during the present study.

I. INTRODUCTION

The chemistry of a great variety of complexes with the heterocyclic ligands 2,2'-bipyridine * and 1,10-phenanthroline * has been the subject of many studies with different aims.[1,2] Many years ago Jaeger and Van Dijk [3] reported the preparation of several cobalt(III) bipy complexes, including chloride salts of the supposed cis-(violet) and $trans$-(green) isomers of $[Co(bipy)_2Cl_2]^+$. Pfeiffer and Werdelmann [4] prepared, among other complexes, cations of the type $[M(phen)_2Cl_2]^+$ (M = Cr(III) or Co(III)), including the supposed $trans$-chromium(III) complex.

Our studies providing evidence for the cis-configuration of bis(N — N) complexes of Cr(III), Co(III), Rh(III), and Ir(III) were first presented [5] in 1968 and published as a communication [6] in 1969. It was decided to divide the detailed documentation for our claims [6] into two parts. The first part, giving details of the X-ray powder photograph studies, has been published previously.[7] The second part is included in the present paper.

We originally studied complexes of these heterocyclic ligands from a spectroscopic view-

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* 2,2'-Bipyridine and 1,10-phenanthroline will be abbreviated in the following as bipy and phen, respectively, or by the common designation N — N.

point [8] and it was hoped that octahedral *trans*-bis(N−N) complexes of chromium(III) and cobalt(III) could give information about the ligand-field parameters of these ligands. However, as implied above, such *trans*-complexes do not appear to exist, the cause of this apparently being a large steric repulsion between opposing pairs of protons in bis(N−N) complexes, when two such ligands are coplanar.[9]

There have been a few cases of bis(N−N) complexes of divalent metal ions reported in the literature, for which a coplanar arrangement of the two heterocyclic ligands would have been expected on the basis of the general coordination properties of the metal ions. The most noteworthy of these are $[Pt(bipy)_2]^{2+}$,[10] $[Pd(bipy)_2]^{2+}$ and $[Pd(phen)_2]^{2+}$.[11] The low kinetic stability of $[Pd(phen)_2]^{2+}$,[11] the fact that the formation constant for $[Pd(phen)(en)]^{2+}$ is *ca.* 10^8 times greater than that for $[Pd(phen)_2]^{2+}$,[12] and the rather special acid-base behaviour of $[Pt(bipy)_2]^{2+}$,[13] are properties which are explicable in terms of a large steric repulsion in these complexes and which are consistent with X-ray structure analyses on salts of $[Pd(N−N)_2]^{2+}$,[14−16] which show appreciable deviations from coplanar arrangements of the ligands.

From a study of the ligand-field spectra of aqueous bis(bipy) and bis(phen) copper(II) complexes, Jørgensen [17] has shown that, in contrast to the bis(ethylenediamine)copper(II) species, they do not have the *trans*-configuration. The X-ray structures of several bis(bipy)-copper(II) species have shown that they all contain distorted trigonal bipyramidal cations of the type $[Cu(bipy)_2X]^{n+}$.[18−22]

In the present paper our chemical interconversions and correlations in the bis(N−N)-chromium(III) and cobalt(III) systems are described and the ambiguous literature on this area of chemistry is reviewed experimentally, including such properties as polymorphism and the kinetic and thermodynamic stability of some of the complexes.

II. EXPERIMENTAL

A. General

Materials. The following chemicals of analytical grade were used: 1,10-phenanthroline hydrate (BDH), 1,10-phenanthroline hydrochloride hydrate and 2,2′-bipyridine (Riedel de Haën). The 2,2′-bipyridine used for the large scale preparation of $[Cr(bipy)_2OH]_2$ $(ClO_4)_4$. $2H_2O$ (employed in prep. 42 below) was obtained by recrystallisation of a product of technical quality kindly donated by I.C.I. Ltd. All other chemicals were of reagent grade and were used without further purification.

Magnetic measurements. The magnetic susceptibility of sample 11*a* was measured at 25 °C, using the Faraday method with $Hg[Co(SCN)_4]$ as reference.[23]

Analyses. Metal analyses were performed by Dr. Hans Buchwald of this laboratory, using extremely accurate procedures developed by him and later to be published. C, H, N, and Cl analyses were carried out by the microanalytical laboratory of this institute, using standard procedures. For an unknown reason H analyses gave difficulties with some of the present complexes.

Circular dichroism measurements. The CD data in the region 400−650 nm were obtained using a Roussell-Jouan Model I Dichrographe. Data for maximum deflections are given in Table 3 as (λ_{CD}, $\Delta\varepsilon_{CD}$), with λ_{CD} in nm and $\Delta\varepsilon_{CD} = \varepsilon_l - \varepsilon_r$, in $l\ mol^{-1}\ cm^{-1}$.

Optical rotation measurements. Optical rotation was measured at 25 °C and 589 nm using a Perkin-Elmer Model 141 Spectropolarimeter. Data are given in Table 3 as molar rotation, $[M]_{589}^{25}$, in degree $l\ mol^{-1}\ m^{-1}$.

^1H NMR spectra. Spectra were measured at 30 °C on a Varian Model HA-100 instrument.

Absorption spectra. Absorption spectra in the region 400−650 nm, recorded using a Cary Model 14 spectrophotometer, were used for characterisation and identification of the complexes. Data for maxima (max), minima (min) and shoulders (sh) are given in Tables 2 and 3, with the wavelength, λ, in nm and the molar absorptivity, ε, in $l\ mol^{-1}\ cm^{-1}$. Identifying spectral data given in section IIB below are, unless otherwise indicated, given in the same order as in the columns of Table 2.

B. Preparations

The preparations of the following complexes have been described previously by us, together with their visible absorption spectra: *cis*-$[Cr(bipy)_2F_2]ClO_4$ and *cis*-$[Cr(phen)_2F_2]$-$ClO_4.H_2O$,[24] $[(bipy)_2Cr(OH)_2Cr(bipy)_2]$-$(ClO_4)_4.2H_2O$, $[(phen)_2Cr(OH)_2Cr(phen)_2]$-$Cl_4.9H_2O$, and $[(phen)_2Cr(OH)_2Cr(phen)_2]$-$(NO_3)_4.4H_2O$.[25] With the exception of the new complex ions *cis*-$[M(phen)_2(H_2O)Cl]^{2+}$ (M = Cr or Co) and the optically active species $(-)_{589}$-*cis*$[Cr(phen)_2F_2]^+$ and $(-)_{589}$-*cis*-$[Cr(N−N)_2Br_2]^+$, complexes of the same formulation as those described in this section have, apart from some differences in solid-state counter-ion, been reported in the literature. However, the preparative methods for the vari-

ous complexes have been examined more critically in the present work than before and in most cases are described in greater detail. The methods of preparation of the *cis*-dichloro-bis(N−N)cobalt(III) complexes have been improved to give chloride salts which exhibit a much greater kinetic stability in aqueous solution than previously reported.

1. *cis*-[Cr(bipy)$_2$Cl$_2$]Cl.2H$_2$O. *a*. This compound was prepared according to the literature method [26] (*cf.* prep. 4). The crude product is often brownish but the pure dihydrate is olivegreen when obtained by recrystallisation from 0.1 M hydrochloric acid and washing with 96 % ethanol until the filtrate is green. (Yield 70 %). Anal. [Cr(C$_{10}$H$_8$N$_2$)$_2$Cl$_2$]Cl.2H$_2$O: C, H, N, Cl. The characterising spectral data are given in Table 2. This compound and the corresponding nitrate and perchlorate salts are soluble in dimethylformamide (DMF).

b. The same compound was prepared by the reaction of chromium(III) chloride hexahydrate with bipyridine in methanol.[27] Bipyridine (3.2 g, 20.5 mmol) and chromium(III) chloride hexahydrate (2.67 g, 10 mmol) were dissolved in methanol (50 ml) and the green solution heated under reflux for 3 h. The red-brown solution was concentrated to 20 ml and cooled to −15 °C. The almost black crystals, which separated from a red solution, were washed with methanol (precooled to −15 °C) and when dried in air crumbled to an olivegreen product (yield 3.3 g, 65 %). Identifying spectral data (0.1 M HCl, *cf.* Table 2): (553, 474, 445, −, −, −, 0.46, 0.23).

2. *cis*-[Cr(bipy)$_2$Cl$_2$]Cl.HCl.3H$_2$O and HCl.2H$_2$O. *cis*-[Cr(bipy)$_2$Cl$_2$]Cl.2H$_2$O (0.5 g) was almost dissolved by gentle heating for 5 min with conc. hydrochloric acid (30 ml). The mixture was filtered hot, leaving a brown residue(I) which was washed with conc. hydrochloric acid and dried over CaCl$_2$.2H$_2$O. (Yield 0.1 g). The filtrate was cooled slowly to 0 °C and the brown crystals that separated were filtered off and washed and dried as above. (Yield 0.3 g, 55 %). Anal. [Cr(C$_{10}$H$_8$N$_2$)$_2$Cl$_2$]Cl.HCl.3H$_2$O: C, H, N, Cl. Identifying spectral data (H$_2$O, *cf.* Table 2): (553, 474, 445, 43.7, 19.0, 91.0, 0.435, 0.209).

The brown residue(I) was analysed. Anal. [Cr(C$_{10}$H$_8$N$_2$)$_2$Cl$_2$]Cl.HCl.2H$_2$O: C, H, N, Cl. Identifying spectral data (H$_2$O, *cf.* Table 2): (553, 474, 445, 43.7, 21.0, 89, 0.48, 0.24).

3 − 7. *cis*-[Cr(phen)$_2$Cl$_2$]$^+$ salts. The characterising spectral data for a carefully purified sample of *cis*-[Cr(phen)$_2$Cl$_2$]Cl.2H$_2$O have been given previously [25] (*cf.* Table 2).

3. The chloride dihydrate, *cis*-[Cr(phen)$_2$Cl$_2$]Cl.2H$_2$O, was prepared as in Ref. 4. Anal. [Cr(C$_{12}$H$_8$N$_2$)$_2$Cl$_2$]Cl.2H$_2$O: C, H, N, Cl. Identifying spectral data (H$_2$O, *cf.* Table 2): (558, 478, −, −, 0.450). The X-ray powder photograph of this compound showed it to be the δ polymorph of Ref. 28.

4. The chloride tetrahydrate, *cis*-[Cr(phen)$_2$-Cl$_2$]Cl.4H$_2$O. The second preparative method [29] was analogous to prep. 1*a*. The red tetrahydrate was obtained after drying in air. Anal. [Cr-(C$_{12}$H$_8$N$_2$)$_2$Cl$_2$]Cl.4H$_2$O: C, H, N, Cl, Cr. Identifying spectral data (H$_2$O, *cf.* Table 2): (558, 478, 40.2, 17.6, 0.437).

5. The chloride hydrogen chloride,[4] *cis*-[Cr(phen)$_2$Cl$_2$]Cl.HCl.3H$_2$O. *cis*-[Cr(phen)$_2$Cl$_2$]-Cl.2H$_2$O (0.5 g) was dissolved in conc. hydrochloric acid (50 ml) at room temperature, whereupon the red-violet hydrogen chloride adduct began to precipitate almost immediately. The mixture was boiled gently for 1 min. After cooling, the red-violet crystals were isolated by filtration and washed with conc. hydrochloric acid, the last few drops of which were left on the filter. The moist product was dried in a desiccator over CaCl$_2$.2H$_2$O for three days. Anal. [Cr(C$_{12}$H$_8$N$_2$)$_2$Cl$_2$]Cl.HCl.3H$_2$O: C, H, N, Cl$^-$, Cr. Identifying spectral data (H$_2$O, *cf.* Table 2): (558, 478, 40.1, 17.4, 0.435).

6. The nitrates, *cis*-[Cr(phen)$_2$Cl$_2$]NO$_3$.3½H$_2$O and ½H$_2$O. *cis*-[Cr(phen)$_2$Cl$_2$]Cl.2H$_2$O (0.25 g, 0.45 mmol) was dissolved in water (17 ml, 90 °C). 0.1 M nitric acid (5 ml) was added to the hot, green solution which was then allowed to cool slowly. Red needles precipitated gradually. These were filtered off, washed with 0.1 M nitric acid and air-dried. (Yield 0.21 g, 77 %). They were recrystallised from water, giving the pure nitrate 3½ hydrate. Anal. [Cr-(C$_{12}$H$_8$N$_2$)$_2$Cl$_2$]NO$_3$.3½H$_2$O: C, H, N, Cl, Cr. Identifying spectral data (DMF, *cf.* Table 2): (578, 492, 42.5, 22.5, 0.530). When recrystallised from 0.1 M nitric acid a mixture of red and green crystals was obtained, the green crystals being the nitrate with lower water content. Anal. [Cr(C$_{12}$H$_8$N$_2$)$_2$Cl$_2$]NO$_3$.½H$_2$O: C, H, N, Cl.

7. The nitrate hydrogen nitrate, *cis*-[Cr-(phen)$_2$Cl$_2$]NO$_3$.HNO$_3$. *cis*-[Cr(phen)$_2$Cl$_2$]-Cl.2H$_2$O (0.3 g) was dissolved in boiling conc. nitric acid (10 ml) and the solution cooled to room temperature. The almost quantitative precipitate of red needles was filtered off and washed with 4 M nitric acid. The product was recrystallised by dissolving it in boiling conc. nitric acid (10 ml) and cooling the filtered solution to 20 °C. The crystals were filtered off, washed with 0.1 M nitric acid and dried over CaCl$_2$.2H$_2$O. (Yield 0.3 g). Anal. [Cr(C$_{12}$H$_8$N$_2$)$_2$-Cl$_2$]NO$_3$.HNO$_3$: C, H, N, Cl. Identifying spectral data (DMF, *cf.* Table 2): (578, 491, 42.5, 22.4, 0.527).

8. *cis*-[Co(bipy)$_2$Cl$_2$]Cl.2H$_2$O.[3] We employed a procedure which is essentially that used for the preparation of *trans*-dichlorotetrakis(pyridine)cobalt(III) chloride.[30] The use of liquid chlorine as an oxidising agent prevents the formation of green by-products containing cobalt(II) (*cf.* prep. 11).

Bipyridine (4.68 g, 30 mmol) was dissolved in methanol (110 ml) under reflux. To the solution was then added blue anhydrous

cobalt(II) chloride (1.95 g, 15 mmol) in portions, over a period of 5 min. The initially yellow solution gradually became red-brown. The solution was cooled to − 60 °C and liquid chlorine (6 ml, 150 mmol) added with stirring. A grey precipitate immediately began to form. Under continued stirring the temperature was allowed to rise to − 20 °C. The grey product was then quickly filtered from the green solution and washed with ice-cold 1 M hydrochloric acid. (Yield 5.7 g, 75 %). The product was recrystallised twice from 0.1 M hydrochloric acid saturated with chlorine, but it can also be recrystallised as in prep. 9. Anal. [Co(C$_{10}$H$_8$N$_2$)$_2$Cl$_2$]Cl.2H$_2$O: C, H, N, Cl, Co. The characterising spectral data are given in Table 2. The spectrum remained unchanged during a fortnight when the solution was kept in the dark at 25 °C.

9. *cis*-[Co(phen)$_2$Cl$_2$]Cl.3½H$_2$O. Ablov's method[31] gives a product slightly contaminated with [Co(phen)$_3$Cl$_2$]. An alternative method [4] (heating [Co(phen)$_3$]Cl$_3$ in chloroform) seemed not to work without the cobalt(II) compound present as a redox catalyst.[32] The procedure used here is essentially that for the bipyridine analogue (prep. 8).

Phenanthroline hydrate (4.2 g, 20.1 mmol) was dissolved in methanol (200 ml) under reflux and to the solution was then added anhydrous blue cobalt(II) chloride (1.3 g, 10 mmol). The initially yellow solution gradually became red, and the resulting solution of [Co(phen)$_2$Cl$_2$] was then cooled to about − 60 °C. To the cold red solution was added liquid chlorine (5 ml, 120 mmol) in aliquots of 1 ml, resulting in almost immediate oxidation, as indicated by the precipitation of a grey powder.

The mixture was allowed to warm up to 20 ° C. It was then heated with 10^{-3} M hydrochloric acid (100 ml) to 65 °C, resulting in complete dissolution, and cold 4 M hydrochloric acid (100 ml) was added. The resulting mixture was cooled to − 5 °C and filtered. The precipitate was washed with a little ice-cold water and then acetone, and dried in air. (Yield 4.1 g, 70 %). Recrystallisation was effected by dissolving the product on the filter in 10^{-3} M hydrochloric acid (250 ml) saturated with chlorine gas and preheated to 60 °C, and then adding an equal volume of cold 2 M hydrochloric acid. The solution was then cooled at 0 °C and filtered. The violet precipitate was washed and dried as above. Anal. [Co(C$_{12}$H$_8$N$_2$)$_2$Cl$_2$]Cl.3½H$_2$O: C, H, N, Cl, Co. Characterising spectral data are given in Table 2. The spectrum remained unchanged during a fortnight when the solution was kept in the dark at 25 °C.

The green dihydrate was prepared by heating the violet compound for 3 h at 110 °C and then leaving it to stand in air (rel. humidity ∼ 40 %). Anal. [Co(C$_{12}$H$_8$N$_2$)$_2$Cl$_2$]Cl.2H$_2$O: C, H, N, Cl. The X-ray powder pattern of this salt was very similar to that of the violet parent complex; its kinetic stability towards hydrolysis was considerably lower than that of the latter.

10. *cis*-[Co(phen)$_2$Cl$_2$]NO$_3$.3H$_2$O. This salt was originally reported to be a tetrahydrate.[31] The chloride (0.2 g, 0.35 mmol) was dissolved in water (25 ml) at room temperature and 0.1 M nitric acid (6 ml) was added dropwise to the stirred solution. The fine grey-violet crystals which rapidly separated were filtered off, washed with ethanol and air-dried. (Yield 0.18 g, 85 %). Anal. [Co(C$_{12}$H$_8$N$_2$)$_2$Cl$_2$]NO$_3$.3H$_2$O: C, N, Cl, Co.

11. *cis*-[Co(phen)$_2$Cl$_2$]$_2$ [CoCl$_4$].2H$_2$O. *a*. This green complex was prepared exactly as reported previously.[33] Its constitution has been discussed earlier.[34] Anal. [Co(C$_{12}$H$_8$N$_2$)$_2$Cl$_2$]$_2$ [CoCl$_4$].2H$_2$O: C, H, N, Cl, Co. Identifying spectral data (1.2 M HCl, *cf*. Table 2): (542, 472, −, −, 0.48). Since cobalt(II) ions in 1.2 M hydrochloric acid solution have a very small molar absorptivity at 542 nm, the molecular weight of the present sample could be calculated, from $\varepsilon_{max} = 56.6$ for *cis*-[Co(phen)$_2$Cl$_2$]$^+$ (Table 2), to be 605 (Theor. 608.5). The characterising spectral data for a nitromethane solution are given in Table 2. The magnetic susceptibility was determined as $\chi^{298} = 7850 \times 10^{-6}$ cgs per mol Co(II) which, with a diamagnetic correction of 525×10^{-6} cgs,[35] corresponds [23] to $\mu_{eff} = 4.47$ ($\pm$ 0.03) B.M.

b. The same complex, with identical X-ray powder photograph to sample *a*, was prepared directly by the addition of a hot blue solution of CoCl$_2$.6H$_2$O (4 g) in conc. hydrochloric acid (10 ml) to a solution of *cis*-[Co(phen)$_2$Cl$_2$]-Cl.3½H$_2$O (0.55 g) in boiling water (10 ml). The solution was then left until the temperature was about 20 °C. The green crystals were filtered off, washed with 6 M hydrochloric acid until the filtrate was no longer blue but green, and air-dried. (Yield 0.50 g). Anal. [Co(C$_{12}$H$_8$N$_2$)$_2$-Cl$_2$]$_2$[CoCl$_4$].2H$_2$O: C, H, N, Cl, Co. Identifying spectral data (nitromethane, *cf*. Table 2): (693, 667, 633, 588; 678, 647, 598, 477; 650, 611, 485, 215; 585, 405, 249, 59).

12. Mixed dichloro chloride, *cis*-[(Cr, Co)(phen)$_2$Cl$_2$]Cl.2H$_2$O. The initial compounds (prep. 3 and 9, 0.1 g of each) were dissolved in 0.02 M hydrochloric acid (25 ml) and the solution left to stand at room temperature. Almost black crystals separated, and were filtered off and washed with 0.1 M hydrochloric acid. (Yield 0.11 g). Anal: Cr 5.61; C 51.9; H 3.6; N 10.2; Cl 18.4, corresponding to about 60 % chromium(III) complex. The addition of a sodium sulfide solution to an aqueous solution of the product resulted in the formation of a black precipitate, demonstrating the presence of cobalt in quantity. The X-ray powder photograph of the mixed complex was very similar to that of the pure chromium complex with the same water content.

13. *cis*-[Cr(bipy)$_2$(H$_2$O)OH](ClO$_4$)$_2$. The *cis*-diaqua complex was prepared by known meth-

ods,[36] but since this compound is very soluble it was most conveniently isolated as its corresponding base. The easiest preparative method was the cleavage of the di-μ-hydroxobis-{bis(2,2'-bipyridine) chromium(III)} perchlorate [25] (the bipy-diol perchlorate). Diol perchlorate (1.9 g, 3.2 mmol Cr) was dissolved in 70 % perchloric acid (10 ml) and the solution heated at 60 °C for 24 h. The orange solution was cooled and partially neutralised with a solution of sodium carbonate decahydrate (14 g) in hot water (10 ml). It was further neutralised to pH ∼ 4 with 2 M sodium hydroxide (7 ml). At this point the aquahydroxo complex precipitated almost quantitatively. It was filtered off, washed with cold water and ethanol, and dried at 60 °C for 2 h. (Yield 1.6 g, 85 %). To purify the product it was dissolved on the filter in cold 1 M perchloric acid (10 ml), a saturated solution of sodium perchlorate (10 ml) was added to the filtrate, and finally 2 M sodium hydroxide (5 ml) added dropwise with cooling and stirring. Filtration, washing and drying were performed as above. By this procedure the unreacted diol, if any, remained on the filter. (Recrystallisation yield 85 %). Anal. [Cr(C$_{10}$H$_8$N$_2$)$_2$(H$_2$O)OH](ClO$_4$)$_2$: C, H, N, Cl. The characterising spectral data are given in Table 2.

14. [Co(bipy)$_2$(H$_2$O)OH](ClO$_4$)$_2$. *a. cis*-[Co(bipy)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$.2H$_2$O was prepared by a procedure analogous to that for the phen analogue [37] (yield 25 %), but it was more convenient to isolate its corresponding base. *cis*-[Co(bipy)$_2$Cl$_2$]Cl.2H$_2$O (2.05 g, 4.0 mmol) was ground with a suspension of silver oxide [precipitated from silver nitrate (2.8 g, 16 mmol) in water (20 ml) using 2 M sodium hydroxide (10 ml)] and the mixture placed in the dark. After 2 h the red suspension was filtered and the silver chloride washed with cold water (2 ml). To the filtrate was added a saturated solution of sodium perchlorate (5 ml), and it was then acidified with 6 M perchloric acid to pH∼ 5. After cooling the solution, the resulting red precipitate was filtered off, washed with a little cold water and with ethanol, and then dried for 2 h at 60 °C in air. (Yield 2.1 g, 90 %). To purify the product it was dissolved on the filter in 1 M perchloric acid (20 ml), saturated sodium perchlorate solution (20 ml) was added to the filtered solution, and finally 2 M sodium hydroxide (10 ml) added dropwise with stirring. The red crystals were isolated by filtration and washed and dried as above. The product exhibited the same spectrum as the unrecrystallised complex. Anal. [Co(C$_{10}$H$_8$N$_2$)$_2$(H$_2$O)OH](ClO$_4$)$_2$: C, H, N, Cl. The characterising spectral data are given in Table 2.

b. More elegantly, [Co(bipy)$_2$Cl$_2$]$^+$ may be hydrolysed with hydroxide ions, as described in prep. 16 for the phen analogue.

15. *cis*-[Cr(phen)$_2$(H$_2$O)$_2$](NO$_3$)$_3$.2H$_2$O. This was prepared by a method similar to that previously reported.[36] Chromium(III) nitrate

enneahydrate (4.0 g, 10 mmol) and phen hydrate (4.47 g, 22 mmol) were dissolved in 0.7 M nitric acid (40 ml), and the solution heated under reflux. After half an hour 2 M LiOH (8 ml) was added to the red solution, which was heated under reflux for a further 5 h and then cooled in ice to give orange needles which were filtered off, washed with ice-cold water and heated at 60 °C in air. (Yield 5 g, 75 %). For recrystallisation, the product was dissolved on the filter in 0.1 M nitric acid preheated to 100 °C, and the solution was filtered and cooled in ice. The crystals were washed and dried as above. (Yield 4 g). Anal. [Cr(C$_{12}$H$_8$N$_2$)$_2$(H$_2$O)$_2$](NO$_3$)$_3$.2H$_2$O: C, H, N, Cr. The characterising spectral data are given in Table 2.

16. [Co(phen)$_2$(H$_2$O)OH](ClO$_4$)$_2$. *a.* The corresponding acid to this complex ion was prepared according to Ref. 37 but the compound was isolated here in the same way as the bipy analogue (for experimental details see prep. 14). Anal. [Co(C$_{12}$H$_8$N$_2$)$_2$(H$_2$O)OH](ClO$_4$)$_2$: C, H, N, Cl, Co. The characterising spectral data are given in Table 2.

b. More elegantly, one of the qualitative kinetic observations [38] (see section III C) could be used preparatively. *cis*-[Co(phen)$_2$Cl$_2$]-Cl.3½H$_2$O (1 g, 1.7 mmol) in 1 M sodium hydroxide (10 ml) was stirred for 2 h. The solution was treated with a saturated solution of sodium perchlorate (5 ml), cooled in ice and titrated with 6 M perchloric acid until precipitation was complete. The crystals were filtered off, washed with ice-cold water and air dried. The product was recrystallised by dissolving it in 1 M perchloric acid (10 ml) and adding saturated sodium perchlorate solution (20 ml) to the filtered solution followed by addition of 2 M sodium hydroxide (*ca.* 5 ml) to give pH∼ 5. Washing and drying were performed as above. (Yield 1 g, 90 %.) Anal. [Co(C$_{12}$H$_8$N$_2$)$_2$(H$_2$O)OH](ClO$_4$)$_2$: C, H, N, Cl, Co. Identifying spectral data (0.1 M HClO$_4$ and 0.1 M NaOH, respectively, *cf.* Table 2): (496, 448, 63, 44; 512, 447, 73, 32).

17. *cis*-[Co(phen)$_2$(H$_2$O)$_2$](NO$_3$)$_3$.2H$_2$O. This was prepared according to Ref. 37. Anal. [Co(C$_{12}$H$_8$N$_2$)$_2$(H$_2$O)$_2$](NO$_3$)$_3$.2H$_2$O: C, H, N.

18. Mixed diaqua nitrate, *cis*-[(Cr, Co)(phen)$_2$(H$_2$O)$_2$](NO$_3$)$_3$.2H$_2$O. 0.2 g of each of the initial compounds (prep. 15 and 17) were dissolved in hot water (4 ml). To the hot solution was added 4 drops of 14 M nitric acid and the solution was left to stand at room temperature. The resulting orange crystals were isolated by filtration and washed with cold water and cold 96 % ethanol. (Yield 0.2 g). Anal: Cr 3.97; C 42.28; H 3.71; N 14.43, corresponding to about 50 % chromium(III) complex. The cobalt content was qualitatively demonstrated as for the mixed dichloro chloride (prep. 12). As with the latter the X-ray powder photograph was very similar to that of the pure chromium complex.

19. *cis*-[Cr(phen)$_2$(H$_2$O)Cl](ClO$_4$)$_2$.H$_2$O. *cis*-[Cr(phen)$_2$Cl$_2$]Cl.2H$_2$O (2.2 g, 4 mmol) was heated under reflux in 0.3 M hydrochloric acid (167 ml) for 3 h and the solution was then cooled in ice. Methanol (75 ml) and then 70 % perchloric acid (10 ml) were added and the solution cooled at −15 °C. The reddish precipitate was filtered off and washed with methanol. The green compound remaining on the filter is the dichloro complex as the perchlorate. The combined mother-liquor and methanol washings were treated with a saturated solution of sodium perchlorate (50 ml) and cooled at −15 °C. The light-red crystals were filtered off, washed with cold 1 M perchloric acid and water, and air-dried at 70 °C. (Yield 1.5 g). The product was recrystallised from 1 M perchloric acid to give red crystals. Anal. [Cr(C$_{12}$H$_8$N$_2$)$_2$-(H$_2$O)Cl](ClO$_4$)$_2$.H$_2$O: C, H, N, Cl. The characterising spectral data are given in Table 2.

20. *cis*-[Co(phen)$_2$(H$_2$O)Cl](ClO$_4$)$_2$.2½H$_2$O. *a.* To a solution of *cis*-[Co(phen)$_2$Cl$_2$]Cl.3½H$_2$O (1.16 g, 2 mmol) in hot water (20 ml) was added dropwise a solution of silver nitrate (0.75 g, 4.5 mmol) in water (1.5 ml). The solution was stirred and allowed to cool slowly to room temperature. The silver chloride was removed by filtration and the red filtrate diluted with methanol (30 ml). 6 M perchloric acid (10 ml) was then added, and by vigorously scratching the glass, whilst cooling the solution in ice, red-brown crystals separated. They were filtered off, washed with ice-cold water and dried at 60 °C in air for 4 h. (Yield 1.1 g, 80 %). The product was recrystallised from 0.1 M perchloric acid to give red-brown crystals. Anal. [Co(C$_{12}$H$_8$N$_2$)$_2$(H$_2$O)Cl](ClO$_4$)$_2$.2½H$_2$O: C, H, N, Cl. The characterising spectral data are given in Table 2.

b. *cis*-[Co(phen)$_2$Cl$_2$]Cl.3½H$_2$O (0.5 g, 0.85 mmol) was dissolved in 10^{-3} M hydrochloric acid (50 ml) at room temperature. 2 M aqueous trimethylamine (1 ml) was added with vigorous stirring, when the solution rapidly became red. After 5−10 s 12 M perchloric acid (2 ml) was added, resulting in the immediate formation of a dense pinkish precipitate. The mixture was allowed to stand at 0 °C for *ca.* 2 h and the now crystalline red precipitate was filtered off and washed with a little ice-cold water. The product was purified by dissolving it on the filter in hot 0.1 M perchloric acid (25 ml) and filtering the solution, leaving a grey residue of unreacted insoluble *cis*-[Co(phen)$_2$Cl$_2$]ClO$_4$. The deep-red filtrate was cooled at 0 °C for 2 h and the resulting red crystals filtered off, washed with ice-cold water and dried in air. (Yield 0.35 g, 60 %). Identifying spectral data (0.1 M HNO$_3$, *cf.* Table 2): (520, 462, −, −, 0.528).

21. [Cr(bipy)$_2$C$_2$O$_4$]Cl.4H$_2$O; *cis*-[Cr(bipy)$_2$Cl$_2$]$^+$→[Cr(bipy)$_2$ox]$^+$.[38] *cis*-[Cr(bipy)$_2$Cl$_2$]Cl.2H$_2$O (5.7 g, 11 mmol) was added with stirring to a boiling solution of potassium oxalate (2.1 g, 11 mmol) in water (22 ml). After boiling for 4 min, the red solution was cooled

in ice to give a red solid. This was filtered off, washed with ice-cold ethanol and air-dried. (Yield 3.8 g). The inhomogeneous product was extracted with a little boiling water, giving an orange solution and leaving a brownish residue. The filtered orange solution was cooled in ice and the resulting crystals washed and dried as above. (Yield 1.9 g, 30 %). Anal. [Cr(C$_{10}$H$_8$N$_2$)$_2$C$_2$O$_4$]Cl.4H$_2$O: C, N, Cl. The characterising spectral data are given in Table 2. Note that in Ref. 38 a printing error appeared for this compound. On p. 1392 the first absorption maximum is tabulated as 510 nm, whereas the curve on the same page clearly demonstrates that it is a little below 500 nm.

22. [Cr(bipy)$_2$C$_2$O$_4$]ClO$_4$; [(bipy)$_2$Cr(OH)$_2$Cr-(bipy)$_2$]$^{4+}$→[Cr(bipy)$_2$ox]$^+$. A mixture of [Cr-(bipy)$_2$OH]$_2$(ClO$_4$)$_4$.2H$_2$O [25] (2.0 g, 1.7 mmol), sodium oxalate (0.23 g, 1.7 mmol) and oxalic acid dihydrate (0.42 g, 3.3 mmol) in water (30 ml) was stirred at 70 °C until all the solids has dissolved. The flask was then stoppered tightly and heated in an oven at 80 °C for 2 h. After allowing the mixture to cool to *ca.* 50 °C, the orange crystals were filtered off, washed with cold water and methanol, and air-dried (Yield 1.2 g, 65 %). Anal. [Cr(C$_{10}$H$_8$N$_2$)$_2$C$_2$O$_4$]ClO$_4$: C, H, N, Cl. Identifying spectral data (H$_2$O, *cf.* Table 2): (497, 464, −, −, −, −, 0.722).

23. [Cr(bipy)$_2$C$_2$O$_4$][Cr(bipy)(C$_2$O$_4$)$_2$].4H$_2$O. The brownish residue from prep. 21 was dissolved in a larger quantity of boiling water, and the filtered red solution was cooled in ice to give red crystals which were filtered off, washed with ethanol and air-dried. (Yield 60 %). Anal. [Cr(C$_{10}$H$_8$N$_2$)$_2$C$_2$O$_4$][Cr(C$_{10}$H$_8$N$_2$)-(C$_2$O$_4$)$_2$].4H$_2$O: C, H, N, Cr. The spectrum of an aqueous solution showed (λ, ε)max = (518,130); (λ, ε)min = (462,70), to be compared with maxima at 497 and 535 nm [38] for [Cr(bipy)$_2$ox]$^+$ and [Cr(bipy)ox$_2$]$^-$, respectively.

24. [Cr(phen)$_2$C$_2$O$_4$]Cl.4H$_2$O; *cis*-[Cr(phen)$_2$-Cl$_2$]$^+$→[Cr(phen)$_2$ox]$^+$.[38] *cis*-[Cr(phen)$_2$Cl$_2$]Cl.2H$_2$O (3.9 g, 7 mmol) was added with stirring to a boiling solution of potassium oxalate (1.3 g, 7 mmol) in water (38 ml). The solution was boiled for 3 min. Isolation and recrystallisation were performed as in prep. 21. (Yield 2.6 g, 60 %). Anal. [Cr(C$_{12}$H$_8$N$_2$)$_2$C$_2$O$_4$]Cl.4H$_2$O: C, N, Cl. Characterising spectral data are given in Table 2.

25−27. *cis*-[Cr(bipy)$_2$F$_2$]$^+$ prepared from different initial materials. The quoted compounds were treated in each case with liquid hydrogen fluoride (50 ml) in a polythene beaker and the mixture stirred and left overnight. The red residue was dissolved (prep. 25 and 26) in water or methanol (5 ml), or extracted (prep. 27) with methanol (10 ml). The filtered solution was then treated with lithium perchlorate (*ca.* 0.2 g per mmol Cr), giving violet crystals on standing which were filtered off, washed with ethanol and air-dried. Identifying spectral data, given after each preparation, are to be

compared with the characterising data of Table 2.

25. [Cr(bipy)₂ox]⁺→cis-[Cr(bipy)₂F₂]⁺. Initial material [Cr(bipy)₂C₂O₄]Cl.4H₂O (0.56 g, 1 mmol). (Yield 0.40 g, 80 %). (519, 445, 415, 461, −, −, −, −, 0.45, 0.38).

26. [(bipy)₂Cr(OH)₂Cr(bipy)₂]⁴⁺→cis-[Cr(bipy)₂F₂]⁺. Initial material [Cr(bipy)₂OH]₂(ClO₄)₄.2H₂O ²⁵ (1.0 g, 1.7 mmol Cr). (Yield 0.56 g, 65 %). (519, 443, 416, 461, −, −, −, −, 0.47, 0.39).

27. cis-[Cr(bipy)₂Cl₂]⁺→cis-[Cr(bipy)₂F₂]⁺. Initial materials cis-[Cr(bipy)₂Cl₂]Cl.2H₂O (0.5 g, 1 mmol) and mercuric acetate (0.95 g, 3 mmol). (Yield 0.32 g, 65 %). (519, 443, 415, 461, −, −, −, −, 0.45, 0.38).

28−30. cis-[Cr(phen)₂F₂]⁺ prepared from different initial materials. The quoted compounds were treated in each case with liquid hydrogen fluoride (50 ml) in a polythene beaker and the mixture stirred and left overnight. The red residue was dissolved (prep. 28 and 29) in water or methanol (10 ml), or extracted (prep. 30) with methanol (10 ml). The product was isolated as in prep. 25−27 and recrystallised in each case from 0.01 M perchloric acid, giving violet crystals. Identifying spectral data, given after each preparation, are to be compared with the characterising data of Table 2.

28. [Cr(phen)₂ox]⁺→cis-[Cr(phen)₂F₂]⁺. Initial material [Cr(phen)₂C₂O₄]Cl.4H₂O (0.61 g, 1 mmol). (Yield 0.46 g, 80 %). (522, 455, 420, −, −, −, −, 0.37, 0.24).

29. [(phen)₂Cr(OH)₂Cr(phen)₂]⁴⁺→cis-[Cr(phen)₂F₂]⁺. Initial material [Cr(phen)₂OH]₂Cl₄.9H₂O ²⁵ (2.2 g, 3.7 mmol Cr). (Yield 1.9 g, 85 %). Anal. [Cr(C₁₂H₈N₂)₂F₂]ClO₄.H₂O: C, H, Cl. (522, 455, 420, −, −, −, −, 0.38, 0.25).

30. cis-[Cr(phen)₂Cl₂]⁺→cis-[Cr(phen)₂F₂]⁺. Initial materials cis-[Cr(phen)₂Cl₂]Cl.2H₂O (0.6 g, 1.1 mmol) and mercuric acetate (0.8 g, 2.5 mmol). (Yield 0.4 g, 65 %). Anal. [Cr(C₁₂H₈N₂)₂F₂]ClO₄.H₂O: C, H, Cl. (522, 455, 420, −, −, −, −, 0.38, 0.25).

31−34. cis-[Cr(bipy)₂Cl₂]⁺ prepared from different initial materials. Identifying spectral data, given after each preparation, are to be compared with the characterising data of Table 2.

31. [(bipy)₂Cr(OH)₂Cr(bipy)₂]⁴⁺→ cis-[Cr(bipy)₂Cl₂]⁺. The wine-red solution of [Cr(bipy)₂OH]₂(ClO₄)₄.2H₂O ²⁵ (1.0 g, 1.7 mmol Cr) in conc. hydrochloric acid (10 ml) was cooled to 0 °C and saturated with hydrogen chloride gas. Heating at 50 °C in a sealed tube overnight gave red-brown needles, separated from an orange solution. These were filtered off, washed with water and ethanol, and air-dried. (Yield 0.7 g, 75 %). (DMF: 572, 488, −, −, 0.512).

32. cis-[Cr(bipy)₂F₂]⁺→ cis-[Cr(bipy)₂Cl₂]⁺. The red solution of cis-[Cr(bipy)₂F₂]ClO₄ (0.6 g, 1.2 mmol) in conc. hydrochloric acid (10 ml) was heated in a sealed tube at 100 °C for 5 h. The red-brown salt, separated from a green

solution, was isolated as above. (Yield 0.5 g, 80 %). (DMF: 572, 488, −, −, 0.510).

33. cis-[Cr(bipy)₂(H₂O)₂]³⁺→ cis-[Cr(bipy)₂Cl₂]⁺. The orange solution of cis-[Cr(bipy)₂(H₂O) OH](ClO₄)₂ (0.65 g) in conc. hydrochloric acid (10 ml) was heated at 70 °C overnight. The red-brown crystals, separated from a green solution, were isolated as above. (Yield 0.52 g, 80 %). (DMF: 572, 488, −, −, 0.509).

34. [Cr(bipy)₂ox]⁺→ cis-[Cr(bipy)₂Cl₂]⁺. [Cr(bipy)₂C₂O₄]Cl.4H₂O (0.56 g, 1 mmol) was partially dissolved in conc. hydrochloric acid (10 ml). The mixture was cooled to 0 °C and saturated with hydrogen chloride gas, after which complete dissolution occurred. The orange solution was heated in a sealed tube at 50 °C overnight and the cooled mixture was filtered to separate the brown crystals from a red solution. While drying in air the crystals crumbled to a green powder of cis-[Cr(bipy)₂Cl₂]Cl.2H₂O. (Yield 0.40 g, 80 %). (H₂O: 553, 473, 445, −, −, −, 0.440, 0.212).

35−38. cis-[Cr(phen)₂Cl₂]⁺ prepared from different initial materials. The crude product was in all cases heated at 70 °C for 1 h, when it became green, and was then recrystallised from 0.1 M hydrochloric acid to give the pure chloride dihydrate. The identifying spectral data, given after each preparation, are to be compared with the characterising data of Table 2.

35. [(phen)₂Cr(OH)₂Cr(phen)₂]⁴⁺→ cis-[Cr(phen)₂Cl₂]⁺. The wine-red solution of [Cr(phen)₂OH]₂Cl₄.9H₂O ²⁵ (0.5 g, 0.86 mmol Cr) in conc. hydrochloric acid (5 ml) was cooled to 0 °C and saturated with hydrogen chloride gas. Heating at 50 °C in a sealed tube overnight gave red needles which were filtered off from an orange solution. (Yield 0.4 g, 80 %). (H₂O: 558, 478, −, −, 0.447).

36. cis-[Cr(phen)₂F₂]⁺→ cis-[Cr(phen)₂Cl₂]⁺. The red solution of cis-[Cr(phen)₂F₂]ClO₄.H₂O (1.0 g, 1.8 mmol) in conc. hydrochloric acid (50 ml) was cooled to 0 °C and saturated with hydrogen chloride gas. Heating for 2 days in a sealed tube at 50 °C gave red needles. (Yield 1.0 g, 90 %). (H₂O: 558, 478, −, −, 0.447).

37. cis-[Cr(phen)₂(H₂O)₂]³⁺→ cis-[Cr(phen)₂Cl₂]⁺. The orange solution of cis-[Cr(phen)₂(H₂O)₂](NO₃)₃.2H₂O (0.6 g, 0.9 mmol) in conc. hydrochloric acid (10 ml) was heated at 80 °C in a sealed tube overnight. Red needles (0.4 g, 75 %) were separated from a green solution. (H₂O: 558, 478, −, −, 0.452).

38. [Cr(phen)₂ox]⁺→ cis-[Cr(phen)₂Cl₂]⁺. [Cr(phen)₂C₂O₄]Cl.4H₂O (0.61 g, 1 mmol) was partly dissolved in conc. hydrochloric acid (10 ml). The mixture was cooled to 0 °C and saturated with hydrogen chloride gas, after which complete dissolution occurred. The orange solution was heated in a sealed tube at 50 °C overnight, and red needles (0.51 g, 80 %) were separated from a green solution. (H₂O: 558, 478, −, −, 0.447).

39. *cis*-[Cr(bipy)$_2$Cl$_2$]$^+$→ *cis*-[Cr(bipy)$_2$-(H$_2$O)$_2$]$^{3+}$. [Cr(bipy)$_2$Cl$_2$]Cl.2H$_2$O (0.6 g, 1.2 mmol) was ground with moist silver oxide and water (10 ml) and left overnight in the dark [the silver oxide was prepared, as in prep. 14, from silver nitrate (0.8 g, 4.6 mmol)]. The filtered red solution was acidified with conc. nitric acid to pH ∼1. The very slight precipitate was filtered off, and the orange solution was concentrated until precipitation began, when it was readjusted to pH ∼1 with solid lithium hydroxide hydrate and cooled at 0 °C (in more strongly acid solution crystallisation did not take place). The orange precipitate of the nitrate salt was filtered off, washed with ice-cold 96 % ethanol, and air-dried. (Yield 0.25 g, 35 %). Identifying spectral data (0.1 M HNO$_3$, *cf.* Table 2): (492, 468, −, −, 0.87). Later it was found that the aquahydroxo complex was much easier to isolate in good yield (*cf.* prep. 13).

40. *cis*-[Cr(phen)$_2$Cl$_2$]$^+$→ *cis*-[Cr(phen)$_2$-(H$_2$O)$_2$]$^{3+}$. *cis*-[Cr(phen)$_2$Cl$_2$]Cl.2H$_2$O (0.56 g, 1 mmol) was ground with moist silver oxide and water (50 ml) and left in the dark overnight. [The silver oxide was prepared, as in prep. 14, from silver nitrate (0.6 g, 3.5 mmol)]. The filtered red solution was acidified with conc. nitric acid to pH ∼1. The slight precipitate was filtered off, and the orange solution concentrated to 10 ml and readjusted to pH ∼1 with solid lithium hydroxide hydrate. Cooling at 0 °C produced orange crystals of the nitrate salt which were filtered off, washed with ice-cold 96 % ethanol and air-dried. (Yield 0.35 g, 55 %). Identifying spectral data (0.1 M HNO$_3$, *cf.* Table 2): (496, 458, −, −, 0.69).

41. [(phen)$_2$Cr(OH)$_2$Cr(phen)$_2$]$^{4+}$→ *cis*-[Cr-(phen)$_2$(H$_2$O)$_2$]$^{3+}$. This hydrolysis, using nitric acid, has been reported previously [39] and studied kinetically.[40] When the chloride salt of the diol was used we found that chloro complexes were formed together with diaqua complex. However, when the diol nitrate was used, pure diaqua complex was obtained (see also prep. 51).

42−52. Preparation of optically active complexes. Identifying absorption spectral data are given as (λ_{max}, λ_{min}, $\varepsilon_{min}/\varepsilon_{max}$) and, unless otherwise indicated, are to be compared with characterising spectral data given in Table 2. CD and optical rotation data are given in Table 3.

42. Resolution of chromium(III)(bipy)diol. A. [Cr(bipy)$_2$OH]$_2$(ClO$_4$)$_4$.2H$_2$O [25] (50 g, 41.8 mmol) and potassium trifluoroacetate (32 g, 210 mmol) were stirred in methanol (300 ml) for 1 h at 25 °C. The deep-red solution was filtered and the precipitate of potassium perchlorate washed with a little methanol. The combined filtrate and washings were then added to a stirred 25 °C solution of sodium (+)$_{589}$ antimonyl tartrate (25.8 g, 83.5 mmol: equivalent to 50 % of the diol in solution) in 10^{-3} M hydrochloric acid (300 ml), whereupon a dense

pink precipitate was rapidly formed. The mixture was stirred for 15 min and then filtered, and the diastereoisomer washed with cold 10^{-3} M hydrochloric acid, then methanol, and air-dried. (Yield 16.6 g (crop A1)).

The mother-liquor from the above mixture was then treated with a 25 °C solution of a further portion of sodium (+)$_{589}$ antimonyl tartrate (25.8 g) in 10^{-3} M hydrochloric acid (150 ml), as before, and left to stand overnight. The resulting crop of crystals was filtered off and washed and dried as above. (Yield 22.4 g (crop A2)). Treatment of the mother-liquor with a further portion of resolving agent, as above, gave (after standing for 24 h) a further, very small crop of diastereoisomer. (Yield 0.55 g (crop A3)).

Addition of a fourth portion of resolving agent (25.8 g) in 10^{-3} M hydrochloric acid (150 ml) produced no further precipitation, even after prolonged standing at 25 °C. However, on cooling the solution at 5 °C for 2 days, a good crop of large red-brown crystals was obtained and was isolated by filtration. These crystals were much more soluble in cold 10^{-3} M hydrochloric acid than the three crops isolated previously, and so were washed only with methanol and air-dried. (Yield 23.6 g (crop A4)). This difference in solubility strongly suggests that crop A4 contains predominantly the second diastereoisomer.

B. Crops A1, A2 and A4 were converted, in each case, to the perchlorate salt by the following procedure (crop A3 was very small and was not converted). The total crop was dissolved, with stirring, in the minimum volume of cold 2 M sodium acetate solution and the red solution filtered. Addition of excess saturated aqueous sodium perchlorate solution then resulted in essentially quantitative precipitation of the perchlorate salt, which was filtered off, washed with cold 1 M perchloric acid and then methanol, and air-dried. The yields from the three crops of (+)$_{589}$ antimonyl tartrate salt were as follows: − crop B1, 9.74 g; crop B2, 13.23 g; crop B4, 13.60 g. Analysis indicated, in each case, that the dihydrate was obtained. Identifying spectral data (10^{-3} M HCl, *cf.* Ref. 25): (For B1: 537, 467, 0.443; for B2: 537, 467, 0.429; for B4: 537, 467, 0.430). The molar rotation of crop B4 (+ 9132° l mol^{-1} m^{-1}) was opposite in sign but lower in magnitude than those of crops B1 and B2 (which were virtually identical: see Table 3) and so the former was recrystallised once from hot water containing a little 2 M perchloric acid.[25] The measured molar rotation then improved to a value almost identical in magnitude to that of the first 2 crops (see Table 3). The analytical data indicate that crops B1 and B2 ((−)$_{589}$ enantiomer) comprise 46 % of the total original amount of racemic bipy diol, and this fact, together with the solubility observations on the various diastereoisomer fractions and the observed molar rotations of

the corresponding crops of perchlorate salt, suggests that essentially complete resolution has been effected.

43. Resolution of chromium(III)(phen)diol. A. The procedure employed was analogous to that for the resolution of the bipy diol. [Cr-(phen)$_2$OH]$_2$(NO$_3$)$_4$.4H$_2$O [25] (34.5 g, 29.3 mmol) was stirred with potassium trifluoroacetate (22.3 g, 147 mmol) in methanol (150 ml) for 30 min at 25 °C. The filtered red solution was then added to a 25 °C solution of sodium ($+$)$_{589}$ antimonyl tartrate (18.1 g, 58.6 mmol) in 10^{-3} M hydrochloric acid (100 ml). The resulting dense precipitate was filtered off, washed with cold 10^{-3} M hydrochloric acid and then 96 % ethanol, and air-dried (the washings were added to the mother-liquor). (Yield 19.85 g (crop A1)). The mother-liquor was then left to stand overnight, giving a further crop of red-brown needles which were isolated as above. (Yield 5.50 g (crop A2)). After further treatment of the mother-liquor with a second portion of resolving agent (18.1 g) in 10^{-3} M hydrochloric acid (100 ml), as before, the solution was left to stand for ca. 1 h and the resulting fine precipitate isolated as previously. (Yield 5.85 g (crop A3)).

On leaving the filtrate to stand overnight, a good yield of large red-brown flaky crystals was obtained. These proved to be much more soluble in 10^{-3} M hydrochloric acid than the three previous crops and were therefore washed only with 96 % ethanol and air-dried. (Yield 17.8 g (crop A4)). Addition of a third portion of the resolving agent to the residual mother-liquor, as before, followed by cooling of the solution at 5 °C for 3 days, resulted in the formation of a further crop of large crystals with solubility properties as for crop A4. (Yield 8.92 g (crop A5)).

B. Crops A1-A5 were converted to the very insoluble perchlorate salt as for the bipy analogue (prep. 42). Yields were: crop B1, 10.72 g; crop B2, 2.96 g; crop B3, 3.32 g; crop B4, 10.48 g; crop B5, 5.52 g. Analysis indicated, in each case, that the trihydrate was obtained.

For rotation, CD and absorption spectrum measurements, solutions of portions of crops B1 and B2 (($-$)$_{589}$ enantiomer), and crop B4 (($+$)$_{589}$ enantiomer) were prepared in nitromethane, a solvent in which the phen diol appears to be quite stable. The middle crop (crop B3) and the final crop (crop B5) were not examined. Measurements were not made in acidic aqueous solution because the chromium(III) phen diol is known to be somewhat unstable in this medium.[25] Characterising spectral data, measured for crop B1 (nitromethane; cf. in 0.1 M HNO$_3$, Ref. 25): (λ_{max} 540, 422 (sh); ε_{max} 113.9, 302.6; λ_{min} 462; ε_{min} 42.9; $\varepsilon_{min}/\varepsilon_{max}$ 0.386). Identifying spectral data for B2 and B4: (For B2: 540, 462, 0.421; for B4: 540, 462, 0.398). The analytical data indicate that crops B1, B2 and B3 comprise 49 % of the total original amount

of diol and this fact, together with the virtually identical magnitudes of molar rotation observed for crops B1, B2 and B4 (Table 3) and the solubility observations, again indicates essentially complete resolution.

44. ($-$)$_{589}$-[(bipy)$_2$Cr(OH)$_2$Cr(bipy)$_2$]$^{4+}$ → ($-$)$_{589}$-cis-[Cr(bipy)$_2$Cl$_2$]$^+$. This conversion was effected in the same way as for the racemic bipy diol (prep. 31), using ($-$)$_{589}$-[Cr(bipy)$_2$-OH]$_2$(ClO$_4$)$_4$.2H$_2$O (2.0 g, crop B1 from prep. 42). (Yield 1.31 g, 70 %). Anal. [Cr(C$_{10}$H$_8$N$_2$)$_2$-Cl$_2$]ClO$_4$.$\frac{1}{2}$H$_2$O: C, H, N, Cl. Identifying spectral data (DMF): (572, 488, $-$, $-$, 0.504).

45. ($-$)$_{589}$-[(phen)$_2$Cr(OH)$_2$Cr(phen)$_2$]$^{4+}$ → ($-$)$_{589}$-cis-[Cr(phen)$_2$Cl$_2$]$^+$. This reaction was performed as in prep. 35, using ($-$)$_{589}$-[Cr(phen)$_2$OH]$_2$(ClO$_4$)$_4$.3H$_2$O (1.0 g, crop B1 from prep. 43) in conc. hydrochloric acid (25 ml). After cooling the final reaction mixture at 5 °C for 24 h, the fine grey-green crystals were filtered off, washed with water and methanol, and air-dried. (Yield 0.50 g, 55 %). Identifying spectral data (DMF): (578, 493, $-$, $-$, 0.562).

46. ($-$)$_{589}$-[(bipy)$_2$Cr(OH)$_2$Cr(bipy)$_2$]$^{4+}$ → ($-$)$_{589}$-cis-[Cr(bipy)$_2$Br$_2$]$^+$. ($-$)$_{589}$ [Cr(bipy)$_2$OH]$_2$-(ClO$_4$)$_4$.2H$_2$O (2.0 g, 1.67 mmol: crop B1 from prep. 42) and potassium trifluoroacetate (1.2 g, 7.90 mmol) were stirred in methanol (20 ml) for 30 min at 25 °C. The precipitated potassium perchlorate was removed by filtration, washed with a little methanol, and the washings added to the bulk filtrate. The methanol solution was then evaporated to dryness on a rotary evaporator and the solid dissolved in conc. hydrobromic acid (20 ml, d 1.73). The deep-red solution was then cooled to 0 °C, saturated with HBr gas, and the tightly sealed flask placed in an oven at 50 °C for 24 h. The reaction mixture was then cooled at 5 °C overnight and the fine green crystals of the bromide hydrobromide salt were removed by filtration, washed twice with conc. hydrobromic acid (d 1.73) and then liberally with ether, and air-dried. (Yield 0.93 g, 35 %). Anal. [Cr(C$_{10}$H$_8$N$_2$)$_2$Br$_2$]Br.HBr. 3H$_2$O: C, H, N, Br. An aqueous solution of the complex gave a strongly acid reaction. Characterising spectral data (H$_2$O): λ_{max} 574, 518, 445 (sh); ε_{max} 52.7, 45.6, 132; λ_{min} 526, 484; ε_{min} 43.9, 29.0).

47. ($-$)$_{589}$-[(phen)$_2$Cr(OH)$_2$Cr(phen)$_2$]$^{4+}$ → ($-$)$_{589}$-cis-[Cr(phen)$_2$Br$_2$]$^+$. ($-$)$_{589}$-[Cr(phen)$_2$-OH]$_2$(ClO$_4$)$_4$.3H$_2$O (1.0 g, crop B1 from prep. 43) was dissolved in conc. hydrobromic acid (25 ml, d 1.73) and the solution saturated, at 0 °C, with HBr gas. The tightly sealed flask was then placed in an oven at 50 °C for 24 h. After cooling the reaction mixture to 0 °C an ice-cold solution of lithium perchlorate (2.0 g) in water (20 ml) was added, giving an immediate green precipitate of the perchlorate salt of the product. This was filtered off, washed with water and ethanol, and air-dried. (Yield 0.86 g, 85 %). Anal. [Cr(C$_{12}$H$_8$N$_2$)$_2$Br$_2$]ClO$_4$: C, H, N, Cl, Br. Characterising spectral data (DMF):

$(\lambda_{max}$ 598, 522, 421 (sh); ε_{max} 49.8, 42.8, 227: λ_{min} 538, 495; ε_{min} 36.5, 32.0).

48. Attempted conversion $(-)_{589}$-[(bipy)$_2$-Cr(OH)$_2$Cr(bipy)$_2$]$^{4+}$→optically active cis-[Cr(bipy)$_2$F$_2$]$^+$. Repeated attempts to perform this reaction on $(-)_{589}$·Cr(bipy)$_2$OH]$_2$(ClO$_4$)$_4$.2H$_2$O, by the procedure described in prep. 26, or by stirring the complex in liquid hydrogen fluoride in a closed polythene bottle for varying periods of time and then isolating the product as in prep. 26, gave only the racemic difluoro complex in good yield (both unrecrystallised and recrystallised products were inactive). Anal. [Cr(C$_{10}$H$_8$N$_2$)$_2$F$_2$]ClO$_4$: C, H, N. Identifying spectral data (H$_2$O): e.g. (519, 461, −, −, 0.438)).

49. $(-)_{589}$-[(phen)$_2$Cr(OH)$_2$Cr(phen)$_2$]$^{4+}$→$(-)_{589}$-cis-[Cr(phen)$_2$F$_2$]$^+$. This reaction was performed essentially as in prep. 29 for the racemic complex, using $(-)_{589}$-[Cr(phen)$_2$OH]$_2$-(ClO$_4$)$_4$.3H$_2$O (1.0 g, crop B1 from prep. 43) stirred with anhydrous hydrogen fluoride (ca. 80 ml). After leaving the crimson solution to evaporate overnight, the red residue was dissolved in 1:1 aqueous-methanol (40 ml) and the product isolated as in prep. 29. The complex was recrystallised from warm (ca. 50 °C) water by addition of lithium perchlorate (1.0 g) in water (10 ml). The crystals were filtered off, washed with 96 % ethanol, and air-dried. (Yield 0.47 g, 55 %). Identifying spectral data (H$_2$O): (522, 455, −, −, −, −, 0.352, −).

50. $(-)_{589}$-[(bipy)$_2$Cr(OH)$_2$Cr(bipy)$_2$]$^{4+}$→$(-)_{589}$-cis-[Cr(bipy)$_2$(H$_2$O)$_2$]$^{3+}$. This conversion was effected as in prep. 13 for the racemic complex, using $(-)_{589}$-[Cr(bipy)$_2$OH]$_2$(ClO$_4$)$_4$.2H$_2$O (2.0 g, crop B2 from prep. 42). The optically active complex appears to be considerably more soluble than the racemic (prep. 13) and the percentage yield of the former is thus correspondingly lower than that of the latter. (Yield 0.70 g, 35 %). Anal. [Cr(C$_{10}$H$_8$N$_2$)$_2$-(H$_2$O)OH](ClO$_4$)$_2$.2H$_2$O: C, H, N, Cl. Identifying spectral data (0.1 M HCl): (492, 468, −, −, 0.877).

51. $(-)_{589}$-[(phen)$_2$Cr(OH)$_2$Cr(phen)$_2$]$^{4+}$→$(-)_{589}$-cis-[Cr(phen)$_2$(H$_2$O)$_2$]$^{3+}$. The procedure employed here was as in prep. 13, using $(-)_{589}$-[Cr(phen)$_2$OH]$_2$(ClO$_4$)$_4$.3H$_2$O (1.0 g, crop B1 from prep. 43) and 70 % perchloric acid (10 ml). (Yield 0.55 g, 50 %). Anal. [Cr(C$_{12}$H$_8$N$_2$)$_2$-(H$_2$O)OH](ClO$_4$)$_2$.2H$_2$O: C, N, Cl. Identifying spectral data (0.1 M HCl): (496, 458, −, −, 0.695).

52. Attempted conversion $(-)$-$_{589}$-[(bipy)$_2$-Cr(OH)$_2$Cr(bipy)$_2$]$^{4+}$→optically active [Cr-(bipy)$_2$ox]$^+$. This attempted conversion was performed exactly as in prep. 22 for the racemic complex except that $(-)_{589}$ diol perchlorate (2.0 g, crop B1 from prep. 42) was used. The product, however, exhibited no rotation at 589 nm or CD in the region 650−400 nm, although its absorption spectrum in aqueous solution was identical with that of the complex from prep. 22.

C. Equilibrium experiments

The heterocyclic ligands are so robustly bound in the bis(N−N) complexes of both chromium(III) and cobalt(III) that the partial equilibria involving chloride and water in the last two coordination sites could be studied. The equilibrated solutions were prepared starting from both sides of the equilibrium, i.e. from the dichloro and the diaqua complexes. Solutions containing cis-[Cr(phen)$_2$Cl$_2$]$^+$ (I), cis-[Cr(phen)$_2$(H$_2$O)$_2$]$^{3+}$ (II), cis-[Co(phen)$_2$Cl$_2$]$^+$ (III) and cis-[Co(phen)$_2$(H$_2$O)$_2$]$^{3+}$ (IV) were prepared by dissolving cis-[Cr(phen)$_2$Cl$_2$]Cl.2H$_2$O, cis-[Cr(phen)$_2$(H$_2$O)$_2$](NO$_3$)$_3$.2H$_2$O, cis-[Co(phen)$_2$Cl$_2$]Cl.3½H$_2$O and cis-[Co(phen)$_2$-(H$_2$O)OH](ClO$_4$)$_2$, respectively, in 0.10 M hydrochloric acid and adding solid sodium chloride so as to give final concentrations: $C_{complex} = 3.00 \times 10^{-3}$ M and $C_{Cl^-} = 0.109$ M in each case. These concentrations were chosen so as to permit a reasonable estimate of the first complexity constant for chloride, K_1, preliminary experiments having indicated that the fraction of dichloro species in the equilibrated solutions was small for both the chromium(III) and cobalt(III) systems at the above chloride concentration. After heating the solutions for 3 days at 60 °C, they were cooled to 25 °C and their absorption spectra recorded. The two chromium(III) solutions (I and II) exhibited identical spectra: $(\lambda, \varepsilon)_{max} = (505, 40)$; $(\lambda, \varepsilon)_{min} = (458, 23)$. The spectra of the two cobalt(III) solutions (III and IV) were likewise identical: $(\lambda, \varepsilon)_{max} = (516, 56)$; $(\lambda, \varepsilon)_{min} = (462, 33)$. Further heating at 60 °C did not produce any further change in the positions of the absorption maxima but the intensities of the bands decreased very slowly, possibly due to displacement of phenanthroline.

From the recorded spectra of the equilibrium mixtures, the absorptivities were measured at every 10 nm between 600 and 460 nm and the resulting sets of data were fitted, by the least-squares method, to a linear combination of the corresponding data for the appropriate diaqua, aquachloro, and dichloro systems. The resulting complexity constants calculated for the chromium(III) system were $K_1 = 8.7 \pm 0.5$ and $K_2 = 0.3 \pm 0.2$ l mol^{-1}, whilst for the cobalt(III) system the calculated values were $K_1 = 38 \pm 2$ and $K_2 = 0.5 \pm 0.1$ l mol^{-1} (K_1 and K_2 being defined as given in section III C). These complexity constants are valid at 60 °C and an ionic strength of ca. 0.11 M, but are expected to be rather sensitive to the medium and decrease with increasing ionic strength.

III. DISCUSSION OF DICHLORO COMPLEXES

A. Polymorphism and colour variation

The dichlorobis(N−N) complexes of chromium(III) and cobalt(III) [section II B, prep. 1−10] exhibit remarkably dichroic properties. In daylight, aqueous solutions of all these ions appear in low concentrations green to olive-green but in higher concentrations violet to red. However, solutions of these ions in various organic solvents (e.g. dimethylformamide, dimethyl sulfoxide) maintain their colours, viz. green (chromium) and violet (cobalt), irrespective of concentration.

The solid salts also give varying colour impressions. In many cases the anhydrous salts and lower hydrates are green to brown whereas higher hydrates or acid hydrates are violet to red.*

It is also often observed that samples which are green in daylight show a pronounced colour change on going to normal artificial light (whose intensity distribution is shifted toward the red), when they appear red-brown (chromium) or red-violet (cobalt). However, many of the crystals are extremely pleochroic and much more so than crystals of corresponding aliphatic amine complexes.

The two hydrates of dichlorobis(phen)chromium(III) chloride that we have encountered have strange stability relations. When crystallised from methanolic solution and dried in air the red tetrahydrate [section II B, prep. 4] is obtained, but crystallisation from aqueous solution gives a green dihydrate [section II B, prep. 3] with a different X-ray powder photograph. At room temperature the latter salt is the stable one of the two hydrates, the red tetrahydrate turning green and reverting to the dihydrate even when (and particularly rapidly when) kept over water in a desiccator. The [Co(phen)$_2$Cl$_2$]$^+$ cation may be crystallised into the stable hydrate, [Cr(phen)$_2$Cl$_2$]Cl.2H$_2$O,[7]

and likewise the cation [Co(phen)$_2$(H$_2$O)$_2$]$^{3+}$ may be crystallised into [Cr(phen)$_2$(H$_2$O)$_2$](NO$_3$)$_3$.2H$_2$O [section II B, prep. 18].

B. cis-Dichlorobis(1,10-phenanthroline)cobalt(III) tetrachlorocobaltate(II)

We previously reported evidence [34] to show that one [33] of the several green phen- (or bipy-) containing cobalt(III) complexes which had been believed to contain a trans-[Co(N−N)$_2$-Cl$_2$]$^+$ cation* actually is cis-[Co(phen)$_2$Cl$_2$]$_2$-[CoCl$_4$].2H$_2$O [section II B, prep. 11]. We also stated that the apparent difference [33] between its ^{1}H NMR spectrum and that of the violet cis-[Co(phen)$_2$Cl$_2$]Cl.3½H$_2$O in DMSO solution could be explained partly by a difference in the resolution of the two reported spectra, and partly by a difference in the internal standards relative to which the chemical shifts were given. Further details of our ^{1}H NMR results are given here and are compared with those reported previously [33] (Table 1).

It was previously stated and qualitatively explained by us [34] that the ^{1}H NMR spectra of green cis-[Co(phen)$_2$Cl$_2$]$_2$[CoCl$_4$].2H$_2$O in DMSO-d_6 and aqueous (D$_2$O) solution are completely different, partly because one chloride ligand in the cation is hydrolysed rather rapidly in aqueous solution when appropriate cobalt(II) species are present [32] and partly because the paramagnetic anion, [CoCl$_4$]$^{2-}$, which persists in DMSO, reacts with water to give the hexaaquacobalt(II) cation which, although still paramagnetic, is less likely to interact with the investigated cation because of its positive charge. It would appear that the effect of the presence of the paramagnetic anion is only small, since the ^{1}H NMR spectra of low concentration DMSO solutions of cis-[Co(phen)$_2$Cl$_2$]$_2$[CoCl$_4$].2H$_2$O and cis-[Co(phen)$_2$-Cl$_2$]Cl.3½H$_2$O are virtually identical (Table 1). However, line broadening is observed in the spectrum of the former salt when the concentration exceeds ca. 10^{-2} M, presumably because ion-pairing then becomes significant. Fig. 1 shows the ^{1}H NMR spectrum of cis-

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* For the chlorides of [Co(phen)$_2$Cl$_2$]$^+$ four differently coloured salts have been reported [41] and five chlorides of [Cr(phen)$_2$Cl$_2$]$^+$ have been characterised by having different X-ray powder photographs.[28,42] However, the experimental conditions for preparing these different salts have not been specified in detail.

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* All of these green complexes have been shown by various methods not to contain such a cation.[9,43,44]

Table 1. Chemical shifts for protons in bis(phen)cobalt(III) complexes, in ppm relative to the signal for the methyl protons of *tert*-butanol (except in the fourth row).

Solvent	Proton assignments according to Ref. 33 (apart from last 2 rows)						
	2	4	7	3	5+6	8	9
cis-[Co(phen)₂Cl₂]Cl.3½H₂O							
D₂O[a,b]	−8.76, −8.71	−7.88, −7.79	−7.36, −7.27	−7.16[c]	−6.99[c]	−6.20[c]	−6.03[c]
d₆-DMSO[a]	−8.98, −8.94	−8.26, −8.18	−7.77, −7.68	−7.47	−7.36[c]	−6.54[c]	−6.42[c]
DMSO[d]	−8.92	−8.20	−7.71	−7.45	−7.36	−6.56	−6.44
Proposed *trans*-[Co(phen)₂Cl₂]⁺salt							
DMSO[d,e]	−0.29, −0.25	0.3 to 0.6	0.8 to 1.05	1.20		2.20	
DMSO[d,f]	−9.19, −9.15	−8.6 to −8.3	−8.1 to −7.85	−7.70		−6.70	
DMSO[d,g]	−9.01, −8.97	−8.4 to −8.1	−7.9 to −7.65	−7.52		−6.52	
cis-[Co(phen)₂Cl₂]₂[CoCl₄].2H₂O							
d₆-DMSO[a,h]	−8.94, −8.88	−8.20 to −8.12	−7.74 to −7.64	−7.44	−7.34	−6.53	−6.41
D₂O[a,b,i]	−8.95,	−8.26,	−7.98,	−7.25,	−6.30,	−5.99	
cis-[Co(phen)₂(H₂O)Cl](ClO₄)₂2½H₂O							
D₂O[a,b]	−8.98,	−8.29,	−8.02,	−7.27,	−6.34,	−6.01	

[a] Measured at 30 °C using a Varian HA-100. [b] Slightly acidic solution. [c] Band-group centre positions. [d] Given in Ref. 33, measured at 35 °C using either a Varian HR-100 or a Perkin-Elmer R10. [e] Apparently given in the τ scale ($\tau_{TMS}=10.0$) [f] Translated to the present scale using the fact that the methyl protons of *tert*-butanol give a signal 1.10 ppm downfield from that of TMS (*i.e.* at τ 8.90) when both compounds are dissolved in d₆-DMSO. The numbers in the fifth row are thus obtained by subtracting 8.90 from those in the fourth row. [g] Translated to the present scale using a table value[45] of τ 8.72 for the methyl proton signal of *tert*-butanol. The numbers in the sixth row are thus obtained by subtracting 8.72 from those in the fourth row. [h] 5.6×10^{-3} formula units per litre. [i] 9.3×10^{-3} formula units per litre. Only band group maxima of the highly-resolved spectrum obtained by accumulation over 22 scans are given; species present: *cis*-[Co(phen)₂(H₂O)Cl]²⁺.

[Co(phen)₂Cl₂]₂[CoCl₄].2H₂O in DMSO at two concentrations. It is remarkable that a variation in concentration by a factor of less than two can produce such a pronounced effect. More dilute solutions give, of course, less intense spectra which exhibit, however, the same number of peaks at the same positions and with essentially the same line-widths as the lower spectrum of Fig. 1.

It can be seen from Table 1 that the present and previous[33] ¹H NMR results for DMSO solutions of the violet *cis*-[Co(phen)₂Cl₂]Cl.3½H₂O and the green *cis*-[Co(phen)₂Cl₂]₂[CoCl₄].2H₂O are consistent. In a previous communication[34] we also stated that our ¹H NMR results for aqueous (D₂O) solutions of the green species were in agreement with those reported previously.[33] The latter statement is now known to be incorrect, the error arising from an incorrect calibration of the relevant spectra with respect to the reference signal. We have subsequently re-examined the spectrum of the green species in D₂O and find it to be quite different to that reported by the previous authors[33] (Table 1). Furthermore, our previous contention[34] that the cation in green *cis*-[Co(phen)₂Cl₂]₂[CoCl₄].2H₂O undergoes aquation to *cis*-[Co(phen)₂(H₂O)Cl]²⁺ in aqueous solution is clearly supported by a comparison of the ¹H NMR spectra of D₂O solutions of the green complex and of pure *cis*-[Co(phen)₂(H₂O)Cl](ClO₄)₂.2½H₂O (Table 1).

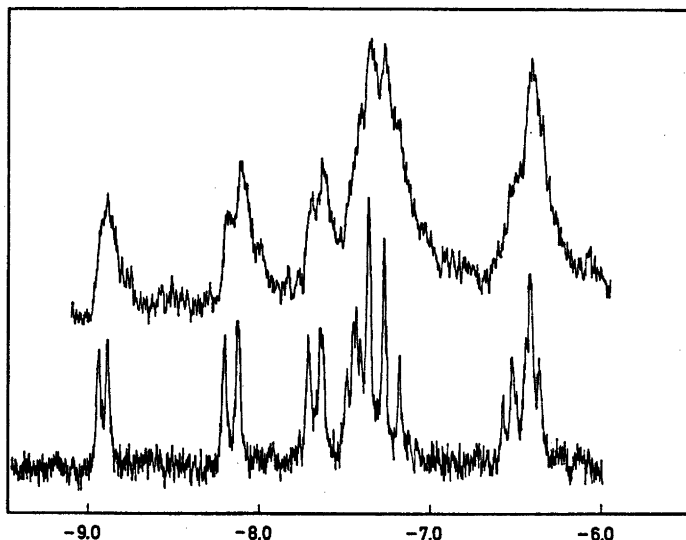The present samples of the green complex have been prepared both by the previous pro-

Fig. 1. ¹H NMR spectra of *cis*-[Co(phen)₂Cl₂]₂[CoCl₄].2H₂O at two different concentrations in DMSO-d_6. The scale is given in ppm relative to the signal for the methyl protons of *tert*-butanol. Lower spectrum: 7.4×10^{-3} formula units per litre; upper spectrum 12.3×10^{-3} formula units per litre. A pronounced line-broadening effect is observed on going from the more dilute to the more concentrated solution. The concentration difference is very small but the effect is still considerable, probably because of increased interaction of the cation with the paramagnetic anion.

cedure [33] and by a method involving direct addition of a solution containing [CoCl₄]²⁻ ion to an aqueous solution of pure *cis*-[Co(phen)₂Cl₂]-Cl.3½H₂O [section II B, prep. 11]. Both methods gave products exhibiting identical X-ray powder photographs and absorption spectra.

C. Kinetic and thermodynamic stability

In the absence of catalysts, the *cis*-dichloro-bis(N−N) complexes of cobalt(III) are remarkably robust [33] relative to the ethylenediamine analogue *cis*-[Co(en)₂Cl₂]⁺,[46] at least with respect to acid hydrolysis of the cobalt-to-chloride bonds. There has been considerable disagreement in the literature concerning the robustness of the metal-chloride bonds in the dichlorobis(N−N)cobalt(III) complexes.[3,4,28,31,32,47−55] It has been shown that these conflicting results are caused by the action of catalytic impurities.[32]

A method of preparation has been devised here which yields samples of the *cis*-dichloro-

bis(N−N)cobalt(III) salts for which the hydrolysis of the first chloride, in 10⁻³ M hydrochloric acid, could not be detected spectrophotometrically within two weeks. However, this was only the case when the solutions were kept in the dark. When exposed to diffuse daylight the solutions underwent a colour change within one day. This light sensitivity of the acid hydrolysis reaction was not appreciated by us at the time of publication of our previous communication.[32]

Moreover, the robustness with respect to loss of the heterocyclic ligands in acidic solution exceeds that towards loss of chloride ion by several orders of magnitude, so that the latter reactions can effectively be studied independently of the former.

The robustness of the pure *cis*-[Co(N−N)₂-Cl₂]⁺ species towards acid hydrolysis does not hold for base hydrolysis.[32] For example, treatment of aqueous solutions of *cis*-[Co(N−N)₂-Cl₂]Cl.aq with ammonia results in a rapid change in colour at room temperature from the violet to violet-green colour of the dichloro

complexes to pinkish red, and in the phen case the absorption spectrum of the resulting solution, made strongly acidic after a few minutes with hydrochloric acid, is very similar to that of the cis-[Co(phen)$_2$(H$_2$O)Cl]$^{2+}$ cation (cf. Table 2). When similar experiments are performed using sodium hydroxide a rapid colour change also takes place. The resulting solutions, on acidifying after ca. 5 min with hydrochloric acid, are orange-red in colour and exhibit absorption spectra agreeing closely with those of the species cis-[Co(N−N)$_2$-(H$_2$O)$_2$]$^{3+}$ (cf. Table 2).

The influence of pH on the hydrolysis behaviour of the cis-[Co(N−N)$_2$Cl$_2$]$^+$ cations is further exemplified by the fact that solutions of cis-[Co(bipy)$_2$Cl$_2$]$^+$ in a pyridine buffer (pH 4.4) were found to undergo no change in absorption spectrum within 24 h at room temperature, whereas solutions of the complex in a buffer of 2,4,6-trimethylpyridine (pH 7.5) showed spectral evidence of hydrolysis within a few minutes under the same conditions.

Hydrolysis reactions of the type described above were adapted for use in the preparation of the complexes cis-[Co(phen)$_2$(H$_2$O)Cl]·(ClO$_4$)$_2$.2½H$_2$O [section II B, prep. 20 b] and cis-[Co(N−N)$_2$(H$_2$O)OH](ClO$_4$)$_2$ [section II B, prep. 14 b and 16 b] in good yield. Since the use of ammonia for the synthesis of cis-[Co-(phen)$_2$(H$_2$O)Cl]$^{2+}$ was found to give an impure perchlorate salt, the poorly-coordinating base trimethylamine (which has a pK value very close to that of ammonia) was employed instead in prep. 20 b.

It would be expected that a conjugate-base (CB) mechanism for the base induced hydrolysis of cis-[Co(N−N)$_2$Cl$_2$]$^+$ would not be operative, since it would involve a deprotonation of the aromatic ring system of the N−N ligand. This expectation was borne out by means of ^{1}H NMR experiments. Almost saturated solutions of the cis-[Co(N−N)$_2$Cl$_2$]Cl.aq complexes in D$_2$O were basified by addition of sodium hydroxide and, after 5 min, acidified with hydrochloric acid. The ^{1}H NMR spectra of the resulting solutions were found to be identical with those of the appropriate pure cis-[Co(N−N)$_2$(H$_2$O)$_2$]$^{3+}$ species in acidic D$_2$O. If some kind of CB mechanism for base hydrolysis were operating, involving the exchange of a proton of the heteroaromatic ring system

of the N−N ligands with a deuterium ion, the ^{1}H NMR spectra of the resulting deuterated diaqua species should be different from those of the non-deuterated.

For the cis-dichlorobis(N−N)chromium(III) complexes, as with the Co(II)-free cobalt(III) complexes, the robustness of the metal-to-chloride bonds towards acid hydrolysis is also orders of magnitude greater than for the corresponding cis-dichlorobis(ethylenediamine)-chromium(III)[52] complex. The chromium(III) species, however, exhibit no special behaviour in basic solution. For example, the visible spectrum of cis-[Cr(phen)$_2$Cl$_2$]$^+$ in 0.1 M sodium hydroxide solution, at room temperature, is identical to that in 0.1 M hydrochloric acid.

It seems possible that the catalytic effect of hydroxide ion on the hydrolysis of the cis-[Co(N−N)$_2$Cl$_2$]$^+$ ions arises because of reduction by the former, a phenomenon which is known to be operative in the reaction of [Fe-(N−N)$_3$]$^{3+}$ with hydroxide ion.[53] The failure of the cis-[Cr(N−N)$_2$Cl$_2$]$^+$ ions to exhibit base hydrolysis behaviour comparable to that displayed by the cobalt(III) analogues is in keeping with this hypothesis, since the chromium(III) complex ions are expected to be much less easily reduced than the cobalt(III) species.

Because of the particular electronic characteristics of the heterocyclic ligands we have made some attempt to assess whether or not the greater robustness of the cis-[M(N−N)$_2$Cl$_2$]$^+$ ions than their cis-[M(en)$_2$Cl$_2$]$^+$ analogues (M = Cr or Co) towards acid hydrolysis is accompanied by a greater thermodynamic stability. This was done spectrophotometrically by heating acidic aqueous solutions of the cis-diaqua- and dichlorobis(phen) chromium(III) or cobalt-(III) complexes, containing the same complex concentration and chloride ion concentration, at 60 °C for 3 days and monitoring their absorption spectra. Since the spectra of the solutions prepared from both types of complex of a given metal became identical, equilibrium was believed to have been attained. Assuming the resulting spectra to be linear combinations of those for the cis-diaqua, aquachloro and dichloro complexes, the value of K_1, = {[M(phen)$_2$-(H$_2$O)Cl]$^{2+}$}/{[M(phen)$_2$(H$_2$O)$_2$]$^{3+}$}{Cl$^-$}, could be estimated to be about 9 l mol^{-1} for the chromium(III) system and about 40 l mol^{-1} for the cobalt(III) system (for the estimated

values of $K_2 = \{[M(phen)_2Cl_2]^+\}/\{[M(phen)_2-(H_2O)Cl]^{2+}\}\{Cl^-\}$, see section II C). Whilst no corresponding data appear to have been reported for the strictly analogous cis-bis(ethylenediamine) systems, the above values for K_1 do not appear to be more than ca. one order of magnitude greater than those reported for the comparable chromium(III) [54] and cobalt-(III) [55] pentaammine systems. The indication is, therefore, that the metal-to-chloride bonds in these bis(N−N) complexes are not especially thermodynamically stable.

As communicated previously,[32] the cis-[Cr-(N−N)_2Cl_2]^+ cations undergo catalysed acid hydrolysis reactions under appropriate conditions. For example, addition of fresh zinc amalgam (prepared by addition of zinc powder to a dilute mercury(II) chloride solution) to a small aliquot of a ca. 10^{-2} M stock solution of cis-[Cr(phen)_2Cl_2]Cl.2H_2O in 10^{-3} M hydrochloric acid, without agitation, results in a fairly rapid colour change from red-violet to yellow-green (owing to reduction to Cr(II) species). Careful withdrawal of this solution and its addition to a 20-fold volume of the same stock chromium(III) solution which has been briefly bubbled with nitrogen gas causes a very rapid colour change from red-violet to orange-red. After allowing this solution to oxidise in air and acidifying it with nitric acid the visible absorption spectrum exhibits a maximum at λ_{max} 507 nm, indicating a mixture of cis-[Cr(phen)_2(H_2O)Cl]^{2+} and cis-[Cr(phen)_2(H_2O)_2]^{3+} species (cf. Table 2). This result is thus in agreement with the results of the equilibrium experiments described above, in that the thermodynamically less stable chromium-to-chloride bonds become hydrolysed to a greater extent than in the cobalt(III)[32] system.

As well as examining the effect of catalysis on the rate of aquation of cis-[M(N−N)_2Cl_2]^+,[32] we have made a qualitative comparative study of the anation of the complexes cis-[M(N−N)_2-(H_2O)_2]^{3+} by chloride ion under catalytic and non-catalytic conditions. Approximately 10^{-2} M solutions of cis-[Co(N−N)_2(H_2O)_2]^{3+} in 0.05 M perchloric acid containing a very large excess of lithium chloride ([Cl^-]≃7 M) undergo no apparent change within several hours at room temperature. However, addition to such solutions of a minute quantity of the cobalt(II)

complex [Co(phen)_2Cl_2] results in gradual but essentially quantitative precipitation of the cis-dichlorobis(N−N)cobalt(III) complexes within ca. 1 h under the same conditions. Similar behaviour is observed for the chromium(III) analogues: Approximately 10^{-2} M solutions of cis-[Cr(N−N)_2(H_2O)_2]^{3+} in 10^{-3} M hydrochloric acid containing lithium chloride ([Cl^-]≃7 M) undergo no apparent change on prolonged standing at room temperature. Addition to such solutions, however, of a little freshly prepared zinc amalgam results in the rapid precipitation of the cis-dichlorobis(N−N) chromium(III) complexes under the same conditions.

The catalytic influence of the lower oxidation state species on the acid hydrolysis and anation reactions is, however, not very useful for the study of the chloride-water coordination equilibria, since these species also catalyse equilibration with respect to the heterocyclic N−N ligands themselves, and thereby complicate the issue.[32] Although the aquation-anation equilibria are established much faster in the absence of a catalyst than the equilibria involving the N−N ligands, the two types of reactions take place simultaneously when the lower oxidation state catalysts are present.

IV. CHEMICAL CORRELATIONS AND DISCUSSION OF CONFIGURATION IN BIS(N−N)CHROMIUM(III) COMPLEXES

The classical demonstration of cis-configuration, which in the chemistry of chromium(III) has always been confirmed by subsequent work, is the chemical correlation with the corresponding oxalato or di-μ-hydroxo ("diol") complexes. For example, Pfeiffer et al.[56] treated
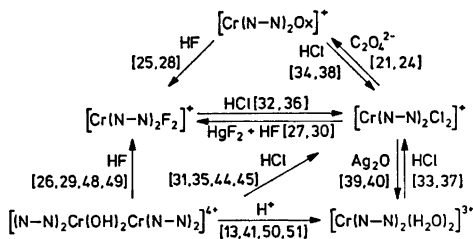

Fig. 2. Chemical interconversions of bis(N−N) chromium(III) complexes. The numbers in square brackets refer to the preparations in section II B.

Table 2. Spectral data characterising the compounds.

Complex ion	Ref.	λ_{max}	λ_{min}	λ_{sh}	ε_{max}	ε_{min}	ε_{sh}	$\varepsilon_{min}/\varepsilon_{max}$ [a]	$\varepsilon_{min}/\lambda_{sh}$	Medium
cis-[Cr(bipy)₂Cl₂]+	prep. 1a	553	474	445	43.7	18.9	90.0	0.433	0.210	H₂O or 0.1 M HCl
cis-[Cr(bipy)₂Cl₂]+	prep. 1a	572	488		47.3	24.0		0.507		DMF
cis-[Cr(phen)₂Cl₂]+	25	558	478		40.1	17.5		0.437		H₂O or 0.1 M HCl
cis-[Cr(phen)₂Cl₂]+	25	578	492		42.5	22.8		0.537		DMF
cis-[Co(bipy)₂Cl₂]+	prep. 8	538	458		57.8	18.1				10⁻³ M HCl
cis-[Co(phen)₂Cl₂]+	prep. 9	542	472		56.6	23.6		0.416		10⁻³ M HCl
cis-[Cr(bipy)₂(H₂O)₂]³+ b	prep. 13	492	468		44.8	39.2		0.875		0.1 M HClO₄
		448	442		94.2	89.2		0.947		
cis-[Cr(phen)₂(H₂O)₂]³+	prep. 15	496	458		43.7	29.4		0.673		0.1 M HNO₃
cis-[Cr(bipy)₂(OH)₂]+	prep. 13	517	465	440	42.0	35.1	69.7			0.1 M NaOH
				424			160			
cis-[Cr(phen)₂(OH)₂]+	prep. 15	519	468		41.5	34.8				0.1 M NaOH
cis-[Co(bipy)₂(H₂O)₂]³+	prep. 14	489	428		60.7	25.2				0.1 M HClO₄
cis-[Co(phen)₂(H₂O)₂]³+	prep. 16a	496	448		62.2	41.9				0.1 M HCl
cis-[Co(bipy)₂(OH)₂]+	prep. 14	505	441		73.8	33.4				0.1 M NaOH
cis-[Co(phen)₂(OH)₂]+	prep. 16a	512	447		74.5	32.0				0.1 M NaOH
cis-[Cr(phen)₂(H₂O)Cl]²+	prep. 19	522	461		41.2	17.0				0.1 M HNO₃
cis-[Co(phen)₂(H₂O)Cl]²+	prep. 20	520	462		59	31		0.525		0.1 M HNO₃
cis-[Cr(bipy)₂F₂]+	24	519	461		48.6	22.0		0.452		H₂O
		443			57.3			0.384		
		415			144					
cis-[Cr(phen)₂F₂]+	24	522	455	420	46.5	16.6	69.2	0.357	0.240	H₂O
cis-[Co(phen)₂Cl₂]₂·[CoCl₄].2H₂O	prep. 11a	693	678		655	585				nitromethane
		667	648		613	407				
		633	598		489	258				
		589	477		209	64				
[Cr(bipy)₂ox]+	prep. 21	497	464	448	66.5	48.7	90.4	0.732		H₂O
				417			220			
[Cr(phen)₂ox]+	prep. 24	501	454		62.6	33.0				H₂O

[a] When ratios between molar absorptivities are given, ε for the first minimum is always measured relative to ε for the first maximum and eventually, where applicable, relative to ε for the second maximum (or shoulder). [b] Data in the second line here are not included in any identifying spectral data for this complex (see prep. 39 and 50).

[Cr(en)₂ox]+ salts with concentrated hydrochloric acid at 40 °C and isolated a violet cis-dichloro salt. By treatment of the latter with oxalate ions they were then able to regenerate the initial cation, but this was not possible with the green trans-dichloro complex. Correlations of this type have been established[6] for bis(bipy) and bis(phen) chromium(III) complexes of the types [Cr(N − N)₂F₂]+, [Cr(N − N)₂Cl₂]+ and [Cr(N − N)₂(H₂O)₂]³+ and the interconvertibility of these mononuclear complexes has, in general, been demonstrated. The interconversion reaction scheme is shown in Fig. 2, with numbers referring to the preparations in the Experimental (section II B). All the conversions have been performed in satisfactory

yield, thereby demonstrating that the isolated species at least comprise the major reaction products.

A number of different preparative routes to the dichloro complexes exist in the literature (see references in section II B). These have all been put to the test and it has been shown that they all give a single, identical, dichlorobis-(N − N)chromium(III) complex ion. The same is true for the diaqua and difluoro complexes. The method of identification of reaction products has, in addition to chemical analysis, been the measurement of the visible absorption spectrum under specified conditions.

The ligand-field spectra of complexes of the type [M(N − N)₂X₂]ⁿ+ (M = Cr or Co) (Table 2)

Table 3. Chiroptical data for optically active bis(N—N) chromium(III) complexes.

Complex	Prep. No.	Solvent	[Complex]^a for [M] and CD	[M]$_{589}$^{25}	Absorption λ_{max}	ε_{max}	Circular dichroism λ_{CD}	$\varDelta\varepsilon_{CD}$
(−)$_{589}$-[Cr(bipy)$_2$OH]$_2$-(ClO$_4$)$_4$.2H$_2$O	42							
crop B1			1.539 × 10^{-3}	−9 510			not measured	
crop B2			1.992 × 10^{-3b}	−9 528			615	+0.18
		10^{-3} M HCl			537^f	106.2	518	−6.62
					447	158.0	402	+0.79^c
(+)$_{589}$-[Cr(bipy)$_2$OH]$_2$-(ClO$_4$)$_4$.2H$_2$O	42							
crop B4			1.568 × 10^{-3}	+9 464			615	−0.19
							518	+6.65
							402	−1.29^c
(−)$_{589}$-[Cr(phen)$_2$OH]$_2$-(ClO$_4$)$_4$.3H$_2$O	43							
crop B1			2.193 × 10^{-3d}	−14 080			529	−6.89
							409	+1.18
crop B2		nitro-methane	1.669 × 10^{-3}	−14 120	540^g	114	529	−7.13
					422(sh)	303	409	+1.17
(+)$_{589}$-[Cr(phen)$_2$OH]$_2$-(ClO$_4$)$_4$.3H$_2$O	43							
crop B4			1.554 × 10^{-3}	+14 080			528	+7.10
							409	−1.16
(−)$_{589}$-cis-[Cr(bipy)$_2$Cl$_2$]-ClO$_4$.½H$_2$O	44	DMF	3.848 × 10^{-3}	−3 412	572^h	47.3	607	+0.79
							530	−0.45
							452	+0.43
(−)$_{589}$-cis-[Cr(phen)$_2$Cl$_2$]ClO$_4$	45	DMF	4.618 × 10^{-3}	−6 676	578^h	43.2	612	+1.12
					420(sh)	178	533	−0.78
							453	+0.42
(−)$_{589}$-cis-[Cr(bipy)$_2$Br$_2$]-Br.HBr.3H$_2$O	46	H$_2$O	5.055 × 10^{-3}	−2 820	574^h	52.7	600	+0.76
					518	45.6	522	−0.36
					445(sh)	132	427	−0.27
(−)$_{589}$-cis-[Cr(phen)$_2$Br$_2$]ClO$_4$	47	DMF	5.221 × 10^{-3}	−6 863	598^h	49.8	622	+1.17
					522	42.8	541	−0.65
					421(sh)	227	521(sh)	−0.56
							470	+0.13
(−)$_{589}$-cis-[Cr(phen)$_2$F$_2$]ClO	49	H$_2$O	6.280 × 10^{-3}	−3 207	522	46.5^i	565	+1.15
					420(sh)	69.2	494	−1.33
							415	+0.22
(−)$_{589}$-cis-[Cr(bipy)$_2$(H$_2$O)$_2$]$^{3+}$^{e}	50	0.1 M HCl	8.240 × 10^{-3}	−1 510	492	44.8	523	+0.42
					448	94.2	464	−0.68
							420(sh)	−0.27
(−)$_{589}$-cis-[Cr(phen)$_2$(H$_2$O)$_2$]$^{3+}$^{e}	51	0.1 M HCl	5.910 × 10^{-3}	−3 460	496	43.7	574	−0.04
					422(sh)	141	531	+0.07
							475	−0.80
							428(sh)	−0.30

^{a} In mol litre^{-1}, determined from molar absorptivity of longest wavelength absorption band, unless otherwise stated. ^{b} Concentration for CD = 2.095 × 10^{-3} M. ^{c} $\varDelta\varepsilon_{CD}$ value not very accurate because of large slit-width. ^{d} Concentration for CD = 0.975 × 10^{-3} M. ^{e} Solution of aquahydroxo complex, as perchlorate salt, in 0.1 M HCl. ^{f} Spectrum taken from Ref. 25. ^{g} Spectrum measured for sample of crop B1. ^{h} Spectrum measured for this sample. ^{i} ε_{max} values from Ref. 24.

with a particular ligand X are so similar that one may safely conclude that each set of four complexes have the same configuration. Furthermore, there is a conspicuous system in the relationship between these spectra and those of the corresponding *cis*- and *trans*-bis(ethylenediamine) complexes as far as the first spin-allowed cubic parentage ligand-field transition is concerned,[8] although the second transition of this type is masked in the bis(N—N) com-

plexes. This observation can, on the basis of Yamada's and Tsuchida's empirical concept of hyperchromism/hypochromism,[57] be used to assign the configuration of the bis(N−N) complexes.

We have found [8] that the first spin-allowed ligand-field bands of the bis(N−N) complexes of chromium(III) and cobalt(III) which unquestionably have the *cis*-configuration, *i.e.* the chromium(III) diols, the carbonato complexes of cobalt(III), and the oxalato complexes of both metals, all exhibit lower molar absorptivities than those of the corresponding *cis*-bis(ethylenediamine) complexes, and we conclude that both N−N ligands are hypochromic relative to ethylenediamine. When the molar absorptivities of the first spin-allowed ligand-field bands of our other bis(N−N) chromium(III) and cobalt(III) complexes are compared [8] with those of the corresponding *cis*- and *trans*-bis(ethylenediamine) complexes it is found that this hypochromism of the N−N ligands relative to ethylenediamine is borne out for the *cis*-configuration but not for the *trans*.

A more sophisticated classical "proof" of the *cis*-configuration of such octahedral complexes would be their resolution into optical enantiomers. However, in the systems under discussion, such a resolution does not, in itself, constitute irrefutable evidence for the *cis*-configuration, since a slight out-of-plane twist, relative to one another, of the two N−N ligands in a distorted (hypothetical) *trans*-bis(N−N) complex would produce the symmetry properties necessary for the existence of enantiomeric forms. Amongst bis(N−N) complexes of chromium(III) and cobalt(III), a direct resolution into enantiomers has been reported for the chromium(III) diols [58,59] and for the complexes [M(N−N)₂ox]⁺ (M=Cr or Co).[38,59,60] Another publication [61] also reports the resolution of [M(bipy)₂Cl₂]⁺ (M=Cr or Co) and [Cr(phen)₂Cl₂]⁺, but gives no quantitative data. The optically active diols were further cleaved with dilute nitric acid to give the optically active diaqua complexes, but no detailed procedures or data were given.[58]

In the present work, as well as studying the cleavage of the racemic bipy and phen diols, we have re-examined their resolution and studied the cleavage, by concentrated hydrochloric, hydrobromic and perchloric acids and

by liquid hydrogen fluoride, of their (−)₅₈₉ enantiomers, giving the (−)₅₈₉ enantiomers of the *cis*-dichloro-, dibromo- and diaquabis-(N−N)chromium(III) and the *cis*-difluorobis-(phen)chromium(III) mononuclear complexes (we were unable to prepare optically active difluorobis(bipy)chromium(III) by this method). The circular dichroism and optical rotation data in the visible region for the optically active complexes obtained in this work are reported in Table 3. The CD and rotation data for the bipy diol indicate a comparable degree of resolution to that reported earlier [58,59,62] and from other observations we believe that essentially complete resolution of both the bipy and phen diols has been effected (see Experimental, section II B). Since the configuration of the heterocyclic ligands in the diols is *cis*,[25,63] the chemical identity of the cleavage products with complexes of the same formulation obtained by other preparative routes provides very strong evidence for the *cis*-configuration of the ligands in bis(N−N)chromium(III) complexes.

Thus, when the above conclusions concerning the configuration of bis(N−N) chromium(III) and cobalt(III) complexes are taken together with the results of our X-ray powder photograph studies [7] on bis(N−N) M(III) complexes (M=Cr, Co, Rh, or Ir) and with the results of previous X-ray structure analyses of [Co(bipy)₂·Cl₂]₂[CoCl₄] [44] and [Co(phen)₂Cl₂]Cl.3H₂O,[44] the combined conclusions are readily seen to be complementary and to provide extremely strong evidence for the generality of the *cis*-configuration of bis(N−N) complexes of these four trivalent metals, both in the solid state and in solution.

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