Oxygenbridged Binuclear Chromium(III) Complexes with 2,2'-Bipyridine and 1,10-Phenanthroline

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Ions analysing as hydroxobis(2,2'-bipyridine)chromium(III) and hydroxobis(1,10-phenanthroline)chromium(III) have been shown on the basis of pH-measurements to be binuclear complexes and thus to belong to the class of bridged structures called the *diols*. For both complexes the two μ-hydroxo groups show acidity in aqueous solution, the pH-region for splitting off the first proton being about 7.5, that for the second proton about 12. The acidity constants have been estimated in 1 M potassium chloride. For both heterocyclic aromatic ligands (N-N) the μ-hydroxo-μ-oxobis{bis(N-N)chromium-(III)} and di-μ-oxobis{bis(N-N)chromium(III)} ions have been isolated as their perchlorates.

The first ligand field band has been observed for both diols, that of the bipyridine complex occurring at a higher frequency than that of the phenanthroline complex. Further, both bands are situated on the low energy side of that of the ethylenediamine-diol, thus suggesting that the Δ-values for the heterocyclic ligands, when bound to chromium(III), are lower than that for ethylenediamine. It is shown that the spectra of the tris(N-N)chromium(III) complexes do not provide positive information regarding ligand field parameters, but on the other hand do not either disagree with the above suggestion regarding Δ-values. These tris(N-N)chromium(III) complexes have been found to be formed together with the diols during their preparation.

Toward acid hydrolysis of the bridges the bipyridine-diol complex has been found to be much more robust than its phenanthroline analog. Further for both diols spectrophotometric evidence for the existence of an intermediate product between the diol and the mono-nuclear diaquabis(N-N)chromium(III) ion has been provided. The hydrolysis has been found to be faster at pH=3, than at pH=1, even though the rate of hydrolysis for the phenanthroline-diol was previously found to be first order in hydrogen ions around pH=1.

Toward base hydrolysis of the bridges the bipyridine-diol has been found to be somewhat less robust than its phenanthroline analog. Further the bipyridine ligand itself splits off in basic solution from the chromium(III) complexes faster than does the phenanthroline.

1. INTRODUCTION

In a recent paper from this laboratory [1] the structure of S. M. Jørgensen's so-called Rhodoso chloride was reported from an X-ray analysis. This complex is analogous in composition and nuclearity to S.M. Jørgensen's brown cobalt(III) salt, tris{di-μ-hydroxotetramminecobalt(III)}cobalt(III) chloride. The cation of the Rhodoso salt is a tetranuclear chromium(III) complex containing an eight-membered as well as a four-membered ring, both rings consisting of alternating chromium(III) ions and μ-hydroxo groups. To our knowledge this analysis was the first certain example of a planar four-membered ring containing chromium(III) and two oxygen ligators. Recently the corresponding ethylenediamine complex was shown to have the analogous structure.[2]

The so-called oxalato-diol complex of chromium(III) was reported by Schwarzenbach [3] on the basis of salt melt cryoscopy not to be a diol, but a trinuclear complex * and thus an anion of the type tri-μ-hydroxotris{bis-(oxalato)chromate(III)}. The corresponding complex with nitrilotriacetate was on the same basis also reported to be trinuclear.[6] Such complexes therefore contain a six-membered ring of alternating chromium(III) and μ-hydroxo groups. The nuclearity of other bridged chromium(III) complexes is not well known except for the single-bridged binuclear μ-hydroxo and μ-oxo complexes of the Rhodo and Erythro types.[7,8] However, evidence has been presented for the existence of the binuclear tri-μ-hydroxobis{(triammine)chromium(III)} complex, the *triol*.[9] Thus the so-called *diols* have only been considered to be diols on analogy with the corresponding cobalt(III) systems of which the di-μ-hydroxobis{tetramminecobalt(III)} chloride has had its structure elucidated by an X-ray analysis.[10] The same is true of tri-μ-hydroxobis{triamminecobalt-(III)} iodide.[11]

It is worth noting in this connection, that although the chromium(III) ion has a conspicuous affinity toward oxygen ligators, no carbonato complex has been reported for chromium(III) although they are well known for cobalt(III) and even the structure of carbonatotetramminecobalt(III) bromide has been reported.[12] There is X-ray structural,[1,11] as well as spectroscopic evidence [13] that the cobalt(III) ion is smaller than the chromium(III) ion, and this may be one reason for the apparent non-existence of complexes between chromium(III) and bidentate carbonate. Therefore analogies between the two metal ions with respect to systems containing four-membered rings are not obviously legitimate.

In the present paper the so-called diols of chromium(III) with the ligands 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) have been shown to be true diols, *i.e.* to be binuclear di-μ-hydroxo complexes, and thus to be actual examples of mononuclear units held together by the formation of a single four-membered ring system. Further their acidity has been studied and their corresponding bases of μ-hydroxo-μ-oxo and di-μ-oxo types have been isolated. During the investigation the stability of the diols toward hydrolysis has been qualitatively studied and new results have been obtained, some in contradistinction to results of earlier work.
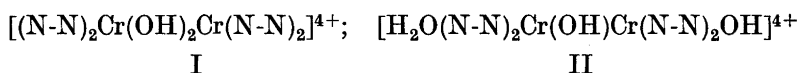
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* The question of the nuclearity of the oxalato-diol may not, however, be quite settled since the kinetic studies of Hamm [4,5] could be interpreted on the basis of binuclearity.

In addition to the chemistry of these systems, their optical spectra have been studied and evidence has been provided that the two heterocyclic ligands, when bound to chromium(III) lie below ethylenediamine in the spectrochemical series.

2. THE μ-HYDROXO COMPLEXES, CONSTITUTION AND ACIDITY

a. Distinction between terminal and bridged hydroxo groups. In equilibrium studies in solution it is in principle possible to determine the nuclearity of complexes,[9] but their stoicheiometric composition can usually only be determined up to a number of solvent molecules. For certain metals whose complexes are robust (*i.e.* kinetically stable, often called inert) the situation is a little different. Here reactions involving the breaking of metal to ligand bonds often occurs so slowly that their rates can be studied by classical methods at room temperature or even at higher temperatures. In such cases partial equilibria, for example involving simple acid-base reactions, often lend themselves to separate study.

Chromium(III) is one such metal and a distinction between the di-μ-hydroxo complex I and the μ-hydroxo complex II can be made by chemical as well as by spectroscopic means.

$$[(N\text{-}N)_2Cr(OH)_2Cr(N\text{-}N)_2]^{4+}; \quad [H_2O(N\text{-}N)_2Cr(OH)Cr(N\text{-}N)_2OH]^{4+}$$
$$\text{I} \qquad\qquad\qquad \text{II}$$

In these formulae N-N represents either bipy or phen.

The composition of the salts may be expressed as $[Cr(N\text{-}N)_2OH]_nX_{2n}$,aq, where X is an anion with one negative charge, and n the nuclearity of the possibly bridged species.

The following three pieces of evidence are provided as evidence for formula I. They show it to be a bridged structure, but do not tell its nuclearity. *1.* The absorption spectrum (in 0.01 M aqueous solution) of the complex with the addition of 0.25 equivalents of hydrochloric acid per chromium is the same as that in 0.1 M hydrochloric acid. This shows that no terminal hydroxo groups are present, because such groups would under the two different circumstances be partially and fully transformed into aqua groups, thereby giving rise to a pronounced spectral change (blue-shift of the absorption band). The result thus excludes both a mononuclear formula and formula II. *2.* A similar experiment has been made using a direct pH-measurement as an indicator of the aprotic character of the complex in the pH-region about 2. If the complex is added as a solid salt to a 0.01 M hydrochloric acid (pH = 2), 1 M in potassium chloride, no immediate pH change can be observed. (If on the other hand a hydroxoaquabis(bipyridine)chromium(III) salt is added up to a concentration of 1.1×10^{-2} M, a pH-change from 2 to 2.8 is observed in agreement with the pK_1-value of ~ 4 for the corresponding diaqua complex.[14]) Again the conclusion is that no terminal hydroxo groups are present. *3.* Certain hydrated salts of these complex ions can be dried so as to lose all their water of crystallization without any decomposition of the cation taking place.[15] This excludes formula II, by giving rise to a complex, *e.g.* of the

composition [Crphen$_2$OH](NO$_3$)$_2$, indicating that the stoicheiometry of these complexes is [Cr(N-N)$_2$OH]$_n^{2n+}$, thus requiring at least binuclearity in order that chromium(III) may acquire its usual coordination number of six.

    b. Titration curves, nuclearity and pK-values of the complexes. Until now the nuclearity n was only shown to be above one. The trinuclear tri-μ-hydroxo-tris{bis(N-N)chromium(III)}ion, whose type [3,6] has been proposed for certain chromium(III) complexes, has to be taken into consideration as a possible structure. Higher values of n are not probable as discussed below.

    A distinction between a binuclear and a trinuclear complex has been possible on the basis of the acidity properties of the complexes. As a by-product the pK-values of the μ-hydroxo protons have been determined. A moderate difficulty has been the fact that in addition to the splitting off of protons, the bridges also begin to break during the time required for the pH-measurement. This difficulty has also been observed previously,[15,16] but with our samples the problem has been found not to be a serious one. The rates of equilibration of the systems with respect to the metal to heterocyclic ligand bonds appear to be orders of magnitude smaller than the rates governing the bridge breaking in the acid and neutral pH-region, but as will be shown below this is possibly not true of the most basic solutions.

    In Fig. 1 are given the plots of $\bar{n}$ as a function of pH, $\bar{n}$ meaning the number of OH$^-$ consumed per chromium (*i.e.* per bridged hydroxo group). In the plots are represented the titration of the μ-hydroxo acids directly with base and the titration of the μ-oxo bases with acid, where the μ-oxo bases were prepared *in situ* by dissolving the μ-hydroxo acids in excess base. Further, the calculated
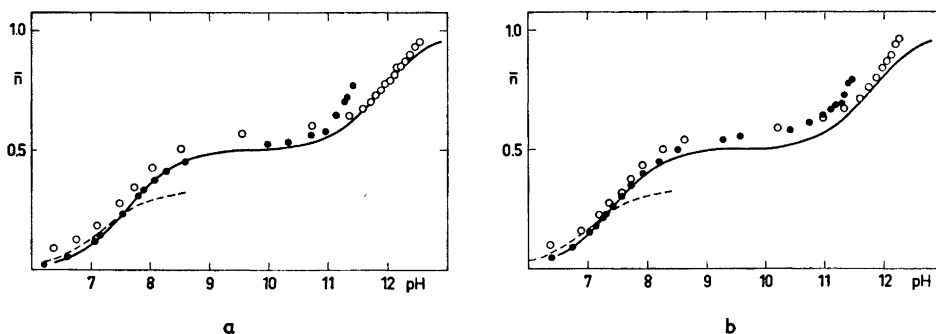

            a   b

Fig. 1. Titration curves for the [Cr(N-N)$_2$OH]$_n^{2n+}$ ions.
    The acid part of the calculated titration curves was based upon pH-measurements at $\bar{n} = 1/4$, whereas the basic part was calculated on the basis of the estimated pK$_2$-values.
    —————— Calculated curves assuming binuclearity;
    - - - - - - calculated curves assuming trinuclearity.
    ● Titration with OH$^-$ towards basic solution;
    ○ titration of freshly prepared solutions in base with H$^+$.
    a. N-N = bipy   pK$_1$ = 7.60   pK$_2$ = 11.9
    b. N-N = phen   pK$_1$ = 7.40   pK$_2$ = 11.8
    The better coincidence between the calculated and experimental curves in the acid region for the bipy-diol than for the phen-diol reflects the greater robustness of the former toward acid (see section 4b). Around pH = 12 the deviation may be attributed in part to the unreliability of the glass electrode.

curves have been given on the basis of the estimated pK-values assuming binuclearity and assuming trinuclearity. For the acid part of both theoretical curves the pK-values have been determined on the basis of a single point measurement at $\bar{n} \sim 1/4$.

Now, the shape of the curves clearly demonstrates that the nuclearity could not be three, because in that case the greatest slopes should occur at $\bar{n} = 1/6$, $1/2$, and $5/6$, corresponding to half neutralization of the first, second, and third μ-hydroxo proton, respectively. In fact the greatest slope appears at $\bar{n} = 1/4$ and $3/4$, agreeing with a nuclearity of two.

For completeness it should be mentioned that a nuclearity of four cannot be excluded solely on the basis of the titration curve. However, in order to make a tetranuclear complex fit the curves some most improbable assumptions regarding the spacing of its pK-values are required. The first two protons should split off at pH ~ 7 with $K_1/K_2 = 4$, the statistical ratio,[17] and the third and the fourth at pH ~ 12 with $K_3/K_4 = 4$. Further, molecular models indicate that all possible conformations of a tetra-μ-hydroxotetrakis{bis(N-N)-chromium(III)} ion are too crowded to be able to exist. We therefore conclude, that our bridged complexes cannot be tetranuclear.

Because of the exclusion of the possibility of the nuclearity being four, the titration curves represent good evidence for the assumed binuclearity and the term "diol" is thus justified.

The following pK-values were found for the binuclear complexes: For the bipy-diol (Fig. 1a) p$K_1 = 7.60$; p$K_2 = 11.9$ and for the phen-diol (Fig. 1b) p$K_1 = 7.40$; p$K_2 = 11.8$. This pK_1-value has been measured previously[15] to 6.3, a value valid for 0.1 M sodium nitrate.* This value compares qualitatively well with our value of 7.4 since it seems to be a general medium effect to stabilize with increasing salt concentration a cationic acid relative to its corresponding base.**

It may be noted that the bipy-diol is slightly less acidic than the phen analog. This relationship has also been found for the diaqua complexes.[14]

A further comment should be added. *A priori* diols would be considered to exhibit the same form of optical isomerism as tartaric acid because they contain two optically active units connected together. One would therefore expect a *meso*-form as well as two optically active forms, which are mirror images of each other. However, as seen in Fig. 2 the probability of the *meso*-form to exist is very limited as noted previously.[18] When using reasonable values of distances and angles in the complexes[19] the distances between α-

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* We have taken the p$K_1 = 6.3$ to refer to 0.1 M sodium nitrate because this medium has been stated in Ref. 15, p. 758, together with the experimental data. On the other hand, on p. 756 the medium is stated to be 1 M sodium nitrate, in which case the p$K_1 = 6.3$ cannot be said to agree with our value 7.4 for 1 M potassium chloride.

** This medium dependence of acidity constants may be illustrated by the pK-value of the *cis*-aquaerythro ion, which Peter Andersen from this laboratory obtained as 3.5 in 1 M sodium nitrate, to be compared with 2.8 found in 0.14 M sodium perchlorate.[7] This salt effect was also shown in a test tube experiment: A saturated solution of the bipy-diol perchlorate in water of room temperature turned yellow with one drop of 2 M sodium acetate indicating some formation of the μ-oxo-μ-hydroxo complex. When solid sodium nitrate was added to this solution the yellow colour disappeared, showing that the acid-base equilibrium had been moved back to the acid side.
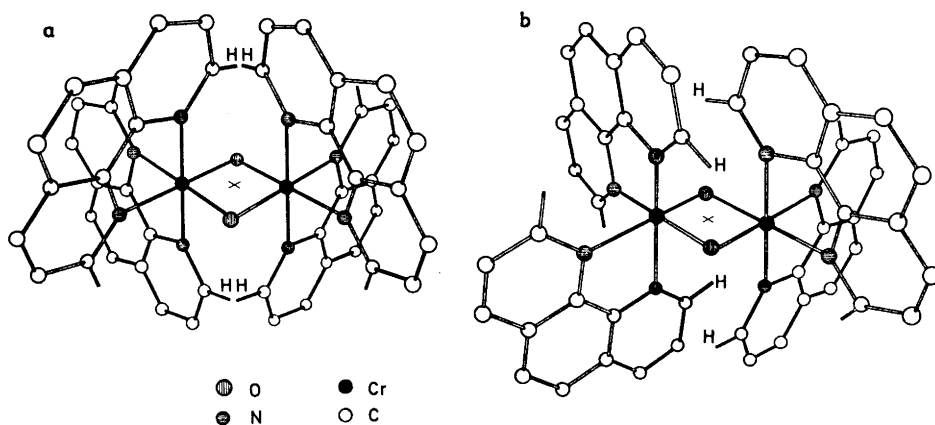
Fig. 2. The meso- and $\Lambda\Lambda$-form [25] of the phen-diol. All valence angles on the phen molecule have been taken as 120° and all distances as 1.40 Å. The C—H distances have been taken as 1.08 Å. The chromium surroundings have been assumed ideally octahedral.

a. The meso-form. Symmetry C_{2h}. The hydrogens on different ligand molecules HH near the plane of symmetry, are seen to be very close (see text).

b. $\Lambda\Lambda$-form [25] of optically active phen-diol. Symmetry D_2. Non-bonded hydrogen interactions are unimportant.

hydrogen atoms of ligand molecules attached to different metal ions within the binuclear complex is so little as 0.2 Å for the meso-form, whereas the said distance in the optically active forms is about 2.6 Å. Since the meso-form therefore must be regarded as most unlikely the titration curves represent the acidity properties of the racemic complexes.

3. STRONGLY COLOURED COMPLEXES IN BASIC SOLUTION

a. Isolation of the novel μ-hydroxo-μ-oxo and di-μ-oxo complexes. During the titration through increasing pH, the characteristic yellow colours of the bases of the type μ-hydroxo-μ-oxobis{bis(N-N)chromium(III)} ions were observed, as were the very intensely brown colours of the bases of the type di-μ-oxobis{bis(N-N)chromium(III)}ions in the more basic solutions. Both types of compounds have been isolated as yellow and brown perchlorates, whose spectra in acid solutions, by being identical to those of the diols showed that the two μ-hydroxo bridges had been maintained. To our knowledge this is the first example of isolable double-bridged binuclear chromium(III) complexes with one or two bridged oxo groups.

b. Spectroscopic check of the μ-hydroxo-μ-oxo/di-μ-oxo equilibria. The pK_2-values estimated from the titration curves are not very accurate and in order to check them and their consistency with the intense colours of basic solutions, they were estimated also spectrophotometrically. All one needs to know besides the initial concentrations are the molar extinction coefficients

of the species involved. These were taken from measurements in solvents of 1 M sodium hydroxide, giving ε for the brown di-μ-oxo complexes, and from solutions with $\bar{n} = 1/4$ the ε-values of the yellow μ-hydroxo-μ-oxo complexes were calculated. The pK_2-values calculated in this way were 12.3 and 12.2 for the bipy-diol and the phen-diol, respectively, and thus in reasonable agreement with those found from the titration curves.

Thus the titration and spectrometric results are consistent.

4. LIGAND FIELD SPECTRA OF THE DI-μ-HYDROXO COMPLEXES AND THE Δ-VALUE OF THE HETEROCYCLIC LIGANDS

The di-μ-hydroxo complexes show in acid solution one absorption band situated around 19.0 kK with molar extinction coefficients not far from 50 per chromium. These bands have been assigned as the first cubic-parentage ligand field transitions $[{}^4A_2(O_h) \rightarrow {}^4T_2(O_h)]$ for the two chromium(III) chromophores, which by their spectra show no apparent mutual interaction.[13] The maximum in the spectrum of the bipy-diol has been observed at a lower wavelength than that of the phen-diol case. Both maxima are, however, situated at the low energy side of the corresponding diol complex with ethylenediamine, the en-diol.[19] This hypsochromism as well as a hyperchromism of ethylenediamine relative to the heterocyclic ligands have been found to be general properties also for a series of mononuclear chromium(III) complexes.[19]

The positions of the absorption maxima therefore suggest, that the Δ-values of the heterocyclic ligands are lower than that of ethylenediamine, when bound to chromium(III). This is the opposite of the relationship for nickel(II), which is well known from Jørgensen's [20] early measurements on the nickel(II) tris-complexes.
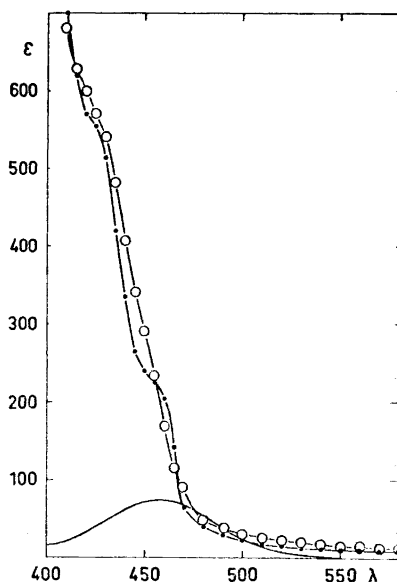
Fig. 3. Visible absorption spectra of the tris(N-N)chromium(III) perchlorates in slightly acidified water solutions, together with that of tris(ethylenediamine)chromium(III) chloride (— full line).
  •, N-N = bipy
  O, N-N = phen
These spectra do not exclude a slightly smaller Δ-value for the heterocyclic ligands than for ethylenediamine.

The absorption spectra of the chromium(III) tris-complexes of the hetero-cyclic ligands (see also section 6) have been remeasured [21,22] here and compared with that of $[Cren_3]^{3+}$ (Fig. 3).

The spectra of the tris(N-N) complexes are so intense in the region where the ligand field transition $^4A_2 \rightarrow {}^4T_2$ is expected to be found, that they present no evidence against the suggestion that the Δ-value for these ligands may be slightly smaller than that of ethylenediamine.

5. DECOMPOSITION OF THE BRIDGED COMPLEXES

a. Acid cleavage of the μ-hydroxo bridges. Aqueous solutions of the diols are not stable in time. The kinetics of the cleavage has previously been studied in acid solution for the phen-diol and a first order dependence in hydrogen ions was found,[15] when the hydrolysis took place in the region around 65°C. The reaction was followed spectrophotometrically and the product identified as the diaqua complex.[15,16] The extinction coefficient of the diaqua complex is lower than that of the diol complex at their maxima,[14,19] and a smooth decrease in intensity and a shifting of the maximum was expected and found [15] to accompany the hydrolysis at 60°C, when the diol spectra were followed in time in an acid medium.

These problems were encountered in the present investigation when the visible spectra of acid solutions of the diols were recorded at room temperature. It was observed, that the spectra varied with time, and the changes were found to be faster at pH ∼5 and 3 than at pH ∼1, though that for the bipy-diol was in all three cases very slow. The maximum for the phen-diol could in all three cases be linearly extrapolated back to the same position through increasing λ-values.*

In addition to a movement of the maxima, in both cases an increase in intensity at the maximum was found. This is indicative of an intermediate, probably one containing only one μ-hydroxo group. This means a structure of formula II (p. 0000). The same property was not detected at higher tempera-tures.[15] The intermediate is, however, analogous to that proposed for inter-preting the kinetics of the cleavage of the "oxalato-diol".[4]

The rate of spectral changes in acid medium (*i.e.* the decomposition to mononuclear diaqua complexes) was found to be very different for the two diol-complexes. While the acid cleavage of the μ-hydroxo groups for the phen-diol was reasonably fast in 0.1 M acid,[15,16] the bipy-diol was far more robust under the same conditions. Thus for preparative purposes the bipy-diol required concentrated perchloric acid at 60° for one day in order to give good yields of *cis*-diaquabis(2,2'-bipyridine)chromium(III) perchlorate.[19]

b. Decomposition in basic solution. It is clear by comparison of the experi-mental points with the theoretical curves, assuming binuclearity (Fig. 1, see also section 2*b*), that there are systematic errors. It is seen, that every-where the experimental points lie on the acid side of the calculated curves. These deviations are, for the very basic solutions, connected with the fact that the glass electrode, in this region, does not work properly. But for the

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* This extrapolated value was 541 mμ in contradistinction to the earlier findings of 530 mμ.[15,16]

rest of the experimental points the deviations must be explained by a decomposition taking place. Any possible decomposition in neutral or basic solution, *i.e.* either cleavage of the μ-hydroxo or μ-oxo bridges or loss of ligand, gives rise to only base consuming or neutral products. It is seen in Fig. 1, that the part of the curves in the pH-region of the first pK-value fits rather better with the calculated one, than does the part in the basic region around the second pK-value. This is true also when one considers single points with the same buffer capacity of the solution.

It therefore looks, as if the decomposition is faster in the basic than in the acid region. This was confirmed spectrophotometrically. Thus the colour of the solutions of both diols in 0.1 M sodium hydroxide at room temperature gradually faded and after 3 days the original intense brown colour was appreciably reduced, pronouncedly faster for the bipy complex than for the phen complex. After a week the solution of the bipy diol was almost colourless and a white precipitate had formed in both solutions. These precipitates contained the free ligands as could be shown by extraction with ether and shaking of the extract with an iron(II) solution to form the characteristic red iron(II)-tris(N-N) complex. Therefore the loss of ligand contributes at least to some extent to the rate of decomposition in the very basic region.

This is, however, not true for the weakly basic region; in a similar experiment at pH = 9.2, which almost corresponds to pure μ-hydroxo-μ-oxo complex, the relative spectral changes in the 400 to 550 mμ region were of the same order of magnitude as those in the preceeding experiments, but no free ligand could be detected by our method after a week.

c. Kinetic and thermodynamic stabilities. It appears, as if the kinetic and thermodynamic stability largely follow one another both with respect to the bridges and the metal to heterocyclic ligand bonds.

First, regarding the bridges. It is a general consequence of thermodynamics [9] that the μ-hydroxo bridges will be stable in some intermediate pH region, because in a more acid region they will be unstable relative to mononuclear aqua complexes, and in a more basic region they will be unstable relative to mononuclear hydroxo complexes. For the partial equilibrium, *i.e.* not including equilibration with respect to the heterocyclic ligand, the following reaction is important

$$[(N\text{-}N)_2Cr(OH)_2Cr(N\text{-}N)_2]^{4+} + 2H_2O = 2[Cr(N\text{-}N)_2H_2O(OH)]^{2+} \qquad (1)$$
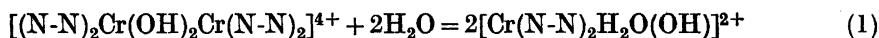
defining by its mass action constant the mononucleation ratio

$$\alpha_{(H_2O)\,(OH)} = K = \frac{[Cr(N\text{-}N)_2H_2O(OH)]}{\sqrt{[Cr_2]}} \qquad (2)$$

where $[Cr_2]$ represents the concentration of free diol complex. By two equations analogous to (1) it is, with an obvious notation, possible to define two other individual mononucleation ratios $\alpha_{(H_2O)_2}$ and $\alpha_{(OH)_2}$, and the sum of the three

$$\alpha_{(H_2O)_2} + \alpha_{(H_2O)\,(HO)} + \alpha_{(OH)_2} = \frac{[Cr_1]}{\sqrt{[Cr_2]}} = K[\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}] \qquad (3)$$

where $[Cr_1]$ is the sum of the concentrations of the three mononuclear complexes.

This gross mononucleation ratio has in (3) been expressed as a function of [H$^+$] using the mononucleation constant K of (2) and the two acidity constants K_1 and K_2 referring to [Cr(N-N)$_2$(H$_2$O)$_2$]$^{3+}$. The gross mononucleation ratio has a minimum at [H$^+$] = $\sqrt{K_1 K_2}$ which therefore within the range of validity of the concentration mass action law is the value of [H$^+$] for which the diol complex has its maximum concentration relative to the mononuclears.

Using the values of pK_1 = 3.4 and pK_2 = 6.0 given by Inskeep [14] for [Crphen$_2$(H$_2$O)$_2$]$^{3+}$ the maximum stability of the diol thermodynamically falls at pH = 4.7, while, as we have seen, its maximum stability kinetically rather falls at a pH around 1.

Second, regarding the metal to heterocyclic ligand bonds. Here a similar thermodynamic argument is valid. In the region with a high concentration of strong acids the complexes are unstable because the protons compete with chromium(III) ion on the heterocyclic ligands, and in the basic region the hydroxide ions compete with the heterocyclic ligands on the chromium(III). From the present investigation the stability regions cannot be estimated. However, it is known that the diaquabis(bipyridine) and diaquabis(phen-anthroline) chromium(III) complexes can be formed at about 100°C at pH = 1,[14] with an excess of ligands present and from the present investigation it is known that the heterocyclic ligands can be removed from the chromium by high concentrations of strong acids at high temperatures and even at room temperature in strongly alkaline solutions. On the other hand at 60°C the metal to heterocyclic ligand bonds are apparently kinetically stable even in strongly acid solutions.[19]

It may be noted, that at a temperature up to 60° and in the whole acidity region from at least pH = 9 up to that corresponding to a molar solution of a strong acid, the metal to ligand bond breaking is extremely slow as compared with the reactions involving the bridges.

6. OBSERVATIONS DURING THE PREPARATION OF THE DIOLS

For the preparation of the diols it was found sufficient to exceed the stoicheiometric amount of ligand with about 10 %. Even under these conditions small quantities of tris(N-N) complexes were invariably observed, and when a greater excess was used (*e.g.* 3 or 4 moles of ligand to 1 mole of chromium(III) salt), tris-complexes could be isolated as perchlorates in quantity and purified as such. Their visible spectra are given in Fig. 3. (For the discussion of Δ-values for the heterocyclic ligands, see section 4).

Since the perchlorate of the phen-diol was too insoluble in water for spectroscopic investigations, the nitrate and the chloride were also synthesized. The chloride is very soluble, but the nitrate is convenient in this respect. The nitrate [23] of the bipy-diol was isolated in unsatisfactory yield, following precisely the method for the phen-diol nitrate, but here the perchlorate had no solubility disadvantages and gave nice yields.

During the attempts at preparing the phen-diol chloride it was also noted, that in very concentrated solutions the *cis*-dichlorobis(1,10-phenanthroline)-chromium(III) chloride was obtained as a by-product. When such a solution

was evaporated to dryness and further heated at 130° only the dichlorochloride was isolated, and in a yield of about 50 %. By the action of concentrated hydrochloric acid on the diol chloride at elevated temperatures the *cis*-dichlorochloride was obtained in a very good yield, but full report on this subject will be given later.[19]

EXPERIMENTAL

Materials. 1,10-Phenanthroline monohydrate was purchased from B.D.H., 2,2′-bipyridine from Riedel-de-Haën. Both chemicals were of analytical grade. All other chemicals were of reagent grade and were used without further purification.

Spectra. Absorption spectra in the 400—650 mμ region, recorded using a Cary Model 14 spectrophotometer, were used as characterization of the compounds. Data for maxima and minima have been given below usually as (λ,ε), the wavelength λ in mμ, the molar absorptivity ε per chromium in liter mol^{-1} cm^{-1}.

pH-measurements. A Radiometer pH meter 25 was used in connection with a glass electrode (Radiometer type G 202 B) and a saturated calomel electrode (Radiometer type K 401) as the reference. The pH was defined to be 3.000 in 1.000 × 10^{-3} hydrochloric acid, 1.0 M in potassium chloride. The temperature in each experiment did not vary more than 1°C and all measurements were done within the temperature range from 24 to 27°C. The initial concentration of diols by the titrations were in the range of 1.0—2.0 × 10^{-2} M. The medium was in all cases 1.0 M potassium chloride, in which $-$log ([H$^+$][OH$^-$]) at 25° was calculated on the basis of previous work [24] as 13.8.

Analyses. The chromium analyses were performed by Dr. Hans Buchwald in this laboratory by an extremely accurate procedure developed by him and later to be published.

C, H, N, Cl analyses were done by the microanalytical laboratory of this institute using standard procedures. For an unknown reason H analyses give occasional difficulties with the present complexes.

Preparations. 1. Di-μ-hydroxobis{bis(2,2′-bipyridine)chromium(III)}perchlorate, [bipy$_2$Cr(OH)$_2$Crbipy$_2$](ClO$_4$)$_4$,2H$_2$O. A mixture of 4.0 g of chromium(III) nitrate enneahydrate (10 mmol) and 3.45 g of 2,2′-bipyridine (22 mmol) in 24 ml of 1 M perchloric acid was refluxed while the acid was gradually neutralized by adding 5 ml of 2 M lithium hydroxide every half hour three times and approximately 2 ml after 2 h (34 mmol OH$^-$). The red solution was refluxed for further 4 h and then allowed to cool slowly, while being kept stirred during the crystallization. The red-brown crystals were separated on a glass filter and washed with ethanol (yield 4.5 g or 75 %). The product was recrystallized by dissolving it on the filter in water, slightly acidified with perchloric acid and preheated to 90°. The solution was allowed to cool slowly and the red-brown crystals were separated and washed with ethanol. (70 % was obtained in this way and a further 17 % with identically the same spectrum was obtained by adding dropwise 2 ml of a saturated solution of lithium perchlorate in water to the mother liquor.) The product recrystallized twice in this way was analyzed. (Found: Cr 8.68; C 40.27; H 2.97; N 9.38; Cl 11.97. Calc. for [Cr(C$_{10}$H$_8$N$_2$)$_2$OH]$_2$(ClO$_4$)$_4$,2H$_2$O: Cr 8.69; C 40.15; H 3.20; N 9.36; Cl 11.85). The visible spectrum in 10^{-3} M hydrochloric acid was constant during at least 20 min: (λ,ε)$_{max}$=(537, 53.1) and = (447, 79). (λ,ε)$_{min}$=(467, 21.9) and =(443, 78). The spectrum of the salt dissolved in 0.1 M sodium hydroxide did not change during at least 10 min and showed a broad maximum at 432 mμ (ε=1250) and a broad minimum around 385 mμ (ε=1180). After about 10 min the solution was acidified to pH ~1, and the spectrum was recorded in a 10 cm cuvette: (λ, ε)$_{max}$=(536, 57). (λ, ε)$_{min}$=(467, 26), showing that the di-μ-hydroxo compound had been reformed.

The crude chloride was obtained by dissolving 2 g of the perchlorate in 10 ml of dimethylformamide, adding 35 ml of pyridine, at which the solution turned yellow, and finally adding 10 ml of 4 M hydrochloric acid. The mother liquor was almost colourless (1.4 g or 90 %). It dissolves, as does the perchlorate in concentrated perchloric acid and precipitates by addition of about 30 % water.

Di-μ-hydroxobis{bis(1,10-phenanthroline)chromium(III)} salts, preparation No. 2, 3 and 4. 2. The nitrate, [Crphen$_2$OH]$_2$(NO$_3$)$_4$,4H$_2$O. The method of the literature [15,16]

was used with slight modifications: 2.0 g of chromium(III) nitrate enneahydrate (5 mmol) and 2.2 g of 1,10-phenanthroline hydrate (11 mmol) was dissolved in 10 ml of hot water and 3 ml of hot 4 M nitric acid, and the blue solution was refluxed; about 8.5 ml of 2 M sodium hydroxide was added in about 2 ml aliquots every half hour. Thereby the solution gradually turned red. The reflux was continued for 5 h in all and cooling to 10° gave fine violet needles, which were filtered off and washed with cold 0.1 M nitric acid and ethanol. (Yield 2.1 g or 90 % of almost pure diol-nitrate.) The product was recrystallized by dissolving it on the filter in 0.1 M nitric acid preheated to the boiling point (85 %). This and the product recrystallized twice showed in 0.1 M nitric acid almost identical spectra, the data of which could be linearly extrapolated back to the time of dissolution. $(\lambda, \varepsilon)_{max} = (541, 49.5)$. $(\lambda, \varepsilon)_{min} = (462, 16.5)$ $\varepsilon_{min}/\varepsilon_{max} = 0.334$. The spectrum shifted the maximum position to 537 mμ and $\varepsilon_{min}/\varepsilon_{max}$ to 0.44 during half an hour at room temperature. The twice recrystallized product was analyzed. (Found: Cr 8.82; C 48.87; H 3.11; N 14.13. Calc. for $[Cr(C_{12}H_8N_2)_2OH]_2(NO_3)_4,4H_2O$: Cr 8.82; C 48.90; H 3.59; N 14.26). When recrystallized in identically the same way using 0.01 M nitric acid, the octahydrate with exactly the same spectrum separated in bigger needles. (Found: C 45.93; H 3.88; N 13.42. Calc. for $[Cr(C_{12}H_8N_2)_2OH]_2(NO_3)_4,8H_2O$: C 46.09; H 4.03; N 13.44). The tetrahydrate was used for the spectral measurements in basic solution. When dissolved in 0.1 M sodium hydroxide the spectrum did not change during 10 min and showed a broad maximum at 438 mμ ($\varepsilon = 1470$) and a broad minimum at 406 mμ ($\varepsilon = 1380$). After about 10 min the solution was acidified to pH 1, and the spectrum was recorded in a 10 cm cuvette (λ, ε) max = (539, 50); (λ, ε) min = (463, 21), again showing that the di-μ-hydroxo compound had been reformed.

3. The perchlorate, $[Crphen_2OH]_2(ClO_4)_4,3H_2O$. A mixture of 4.0 g (10 mmol) chromium(III) nitrate enneahydrate and 4.37 g of 1,10-phenanthroline hydrate (22 mmol) in 50 ml of 0.5 M perchloric acid was refluxed and 17.5 ml of 2 M lithium hydroxide was added in aliquots (about 5 ml every half hour). The red solution from which fine red crystals separated was refluxed for further 4 h and then allowed to cool while it was stirred and the crystallization completed. The red crystals were separated on a glass filter and washed with ethanol (5.8 g or 90 %). The product was recrystallized from water, slightly acidified with perchloric acid and preheated to the boiling point. After cooling violet red fine crystals separated, which were filtered off and washed with ethanol. (4.2 g ~70 %). (Found: Cr 7.94; C 43.66; H 2.78; N 8.57; Cl 11.03. Calc. for $[Cr(C_{12}H_8N_2)_2OH]_2(ClO_4)_4,3H_2O$: Cr 7.93; C 43.99; H 3.08; N 8.55; Cl 10.82). The compound was too insoluble in water for good spectroscopic measurements, but dilute solutions in 0.1 M hydrochloric acid gave $\lambda_{max} = 540$; $\lambda_{min} = 463$; $\varepsilon_{min}/\varepsilon_{max} = 0.37$.

The product could be dissolved in concentrated perchloric acid and reprecipitated by the addition of water. It dissolves in dimethylformamide, turns yellow with pyridine and precipitates by adding 4 M hydrochloric acid a salt which is neither the perchlorate, nor the chloride, but probably a mixed chloride perchlorate.

4. The chloride, $[Crphen_2OH]_2Cl_4,9H_2O$. A mixture of 4.8 g of phenanthroline hydrate (24 mmol) and 3.2 g of green chromium(III) chloride (12 mmol) was dissolved in 10 ml of hot water and the green solution was refluxed for 5 h while adding 5.5 ml of 2 M lithium hydroxide in aliquots (1 ml every half hour). The deep wine-red solution was then cooled and precipitated with 50 ml absolute ethanol.

The red product was filtered on a sintered filter (G4) and washed with 96 % ethanol giving 4 g (60 %) of a red finely crystalline product. It was dissolved in 30 ml of equal amounts of 0.1 M hydrochloric acid and ethanol at room temperature, filtered and precipitated by adding 100 ml of absolute ethanol dropwise while stirring, and the resulting mixture was cooled to −15°. The fine crystals which separated were filtered off and washed with ethanol (60 % by recrystallization). (Found: Cr 8.93; C 49.45; H 4.48; N 9.41; Cl 12.24. Calc. for $[Cr(C_{12}H_8N_2)_2OH]_2Cl_4, 9H_2O$: Cr 8.94; C 49.58; H 4.51; N 9.64; Cl 12.20). The data of the visible spectrum in 0.1 M hydrochloric acid extrapolated linearly back to the time of dissolution were: $(\lambda, \varepsilon)_{max} = (541, 49.7)$, $(\lambda, \varepsilon)_{min} = (462, 17.6)$, $\varepsilon_{min}/\varepsilon_{max} = 0.354$. After 3 h at room temperature the same solution showed shifts to $\lambda_{max} = 533$, $\lambda_{min} = 463$, $\varepsilon_{min}/\varepsilon_{max} = 0.53$. The product is very soluble in water with a violet colour which turns reversibly yellow by addition of 2 M sodium acetate or pyridine.

5. cis-Dichlorobis(1,10-phenanthroline)chromium(III) chloride, cis-$[Crphen_2Cl_2]Cl,$-2H_2O$. When phenanthroline hydrochloride hydrate was used in preparation 4 (5.27 g (22 mmol) to 2.7 g green chromium(III) chloride (10 mmol) in 20 ml of water) a greater

volume of 2 M lithium hydroxide was added (16 ml) and to obtain a good yield the reaction mixture was concentrated. When evaporated to dryness and further heated for 2 h at 130° a partial conversion into the *cis*-dichlorochloride occurred. The product was recrystallized from 0.1 M hydrochloric acid (3.5 g or 50 %) until further recrystallizations did not change the visible absorption spectrum of its solutions in 0.1 M hydrochloric acid: $(\lambda, \varepsilon)_{max} = (558, 40.1)$, $(\lambda, \varepsilon)_{min} = (478, 17.5)$. The visible spectra of the substance in organic solvents showed a strong bathochromic shift. For example in dimethylformamide $(\lambda, \varepsilon)_{max} = (578, 42.5)$, $(\lambda, \varepsilon)_{min} = (492, 22.8)$. (Found: Cr 9.33; C 51.75; H 3.40; N 9.94; Cl 19.11. Calc. for $[Cr(C_{12}H_8N_2)_2Cl_2]Cl,2H_2O$: Cr 9.37; C 51.96; H 3.63; N 10.10; Cl 19.17).

6 and 7. Tris(2,2′-bipyridine)chromium(III) perchlorate, $[Crbipy_3](ClO_4)_3$, and tris-(1,10-phenanthroline)chromium(III) perchlorate, $[Crphen_3](ClO_4)_3,2H_2O$. Both compounds were isolated from the mother liquor of recrystallization of the diol-perchlorates (prep. 1 and 3, resp.), which had been prepared using 3 or more moles of ligand per chromium(III) ion. The recrystallized compounds were analyzed. (Found: C 43.70; H 3.06; N 10.15; Cl 13.09. Calc. for $[Cr(C_{10}H_8N_2)_3](ClO_4)_3$: C 44.00; H 2.95; N 10.26; Cl 13.00. Found: C 46.08; H 2.79; N 9.05; Cl 11.63. Calc. for $[Cr(C_{12}H_8N_2)_3](ClO_4)_3,2H_2O$: C 46.65; 3.05; N 9.07; Cl 11.47).

8. μ-Hydroxo-μ-oxobis{bis(2,2′-bipyridine)chromium(III)} perchlorate, $[bipy_2Cr(OH)-OCrbipy_2](ClO_4)_3$, $4H_2O$. 1 g of bipy-diol perchlorate (0.84 mmol diol) was dissolved in 25 ml of 90° hot water, and to the hot solution was added 25 ml of 2 M sodium hydroxide followed by 25 ml of a saturated-solution of sodium perchlorate in water, both of room temperature. The resulting solution was cooled in ice and the golden iridescent crystals were filtered off. They were washed with a little cold concentrated ammonia and ethanol. Yield 0.79 g. (Found: Cr 9.19; C 42.55; H 3.18; N 10.02; Cl 9.61. Calc. for $[Cr_2(C_{10}H_8N_2)_4-O(OH)](ClO_4)_3,4H_2O$: Cr 9.19; C 42.44; H 3.65; N 9.90; Cl 9.39). The spectrum of 0.1 M hydrochloric acid solutions confirmed that the compound was a deprotonated diol: $(\lambda, \varepsilon)_{max} = (537, 54), (447, 80)$; $(\lambda, \varepsilon)_{min} = (467, 23)$.

9. Di-μ-oxobix{bis(2,2′-bipyridine)chromium(III)} perchlorate, $[Crbipy_2O]_2(ClO_4)_2,-6H_2O$. Prep. 8 was followed but for the use of 25 ml of 10 M sodium hydroxide. The dark-brown crystals were washed with cold concentrated ammonia and air dried (0.65 g). (Found: C 45.37; H 3.63; N 10.49; Cl 6.68. Calc. for $(Cr(C_{10}H_8N_2)_2O)_2(ClO_4)_2,6H_2O$: C 45.00; H 4.15; N 10.49; Cl 6.64). The spectrum of 0.1 M hydrochloric acid solutions showed: $(\lambda, \varepsilon)_{max} = (537, 54), (447, 79)$ $(\lambda, \varepsilon)_{min} = (467, 23)$.

10. μ-Hydroxo-μ-oxobis{bis(1,10-phenanthroline)chromium(III)} perchlorate, $[phen_2-Cr(OH)OCrphen_2](ClO_4)_3,5H_2O$. 1.0 g of phen-diol perchlorate (0.76 mmol diol) was dissolved in 50 ml of a hot solution of 0.05 M lithium hydroxide and allowed to cool without stirring in an icebath. 0.55 g of brown crystals separated, which were filtered off and washed with 5 ml of cold concentrated ammonia. In bigger crystals the compound is brown but as a powder it is yellow. (Found: Cr 8.35; C 45.59; H 3.19; N 8.95; Cl 8.48. Calc. for $[Cr_2(C_{12}H_8N_2)_4O(OH)](ClO_4)_3,5H_2O$: Cr 8.34; C 46.26; H 3.48; N 8.99; Cl 8.53). Although very insoluble in 0.1 M hydrochloric acid as its parent diol-compound, the spectrum could be obtained from dilute solution as $\lambda_{max} = 540$, $\lambda_{min} = 462$, $\varepsilon_{min}/\varepsilon_{max} = 0.37$.

11. Di-μ-oxobis{bis(1,10-phenanthroline)chromium(III)} perchlorate, $[Crphen_2O]_2-(ClO_4)_2,5H_2O$. 0.25 g of the phen-diol chloride (0.22 mmol diol) was dissolved in 10 ml of water and 8 ml of 2 M sodium hydroxide was added, the solution becoming very intensely coloured. Dropwise addition of 5 ml of a saturated solution of sodium perchlorate in water precipitated dark brown crystals, which were filtered off and washed with 2×20 ml of concentrated ammonia, and dried at 60° overnight. (0.2 g). (Found: C 49.93; H 3.28; N 9.75; Cl 6.40. Calc. for $[Cr(C_{12}H_8N_2)_2O]_2(ClO_4)_2, 5H_2O$: C 50.32; H 3.70; N 9.78; Cl 6.19). The visible spectrum with the same comments as in prep. 10: $\lambda_{max} = 540$, $\lambda_{min} = 462$, $\varepsilon_{min}/\varepsilon_{max} = 0.38$.

Spectroscopic check of pK_2-values. From spectra of solutions containing equal amounts of di-μ-hydroxo and μ-hydroxo-μ-oxo complex the extinction coefficient for the latter, $\varepsilon_{DH^{2+}}$, was calculated. At 600 mμ this was 26 for the bipy case and 25 for the phen case. The wavelength at 600 mμ was chosen because of the very strong absorption of the brown di-μ-oxo complexes at lower wavelengths; this could not be compensated for by taking very dilute solutions because of the poor buffer capacity in that case, but had to be compensated partly by the choice of wavelength and partly by using a 1 mm cell. At 600

mμ the extinction coefficients for the brown di-μ-oxo complexes, $\varepsilon_{D^{4+}}$, are 250 for the bipy complex and 265 for the phen complex.

0.15 mmol of diol was dissolved in 4 ml of 1 M potassium chloride containing 0.30 mmol of potassium hydroxide, and at 600 mμ the extinction coefficients, ε, of these solutions were 120 in the bipy case and 130 in the phen case.

The procedure for the calculation of the pK_2 was to combine the following equations:

I $\{[D^{2+}]+[DH^{3+}]\}\varepsilon=[D^{2+}]\varepsilon_{D^{2+}}+[DH^{3+}]\varepsilon_{DH^{3+}}$

II $[OH^-]_{free}=[OH^-]_{total}-[DH^{3+}]-2[D^{2+}]$

III $pK_2=pK_w-pOH-\log([D^{2+}]/[DH^{3+}])$

or for the particular choice of concentrations used here II can be written as

II′ $[OH^-]_{free}=[DH^{3+}]$.

Using these equations and a value for pK_w of 13.8, the pK_2 values for the bipyridine and phenanthroline di-μ-hydroxo complexes can be calculated as 12.3 and 12.2, resp., in reasonable agreement with the values determined from the titration curves.

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