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HYDROXO-BRIDGED CHROMIUM(III) OLIGOMERS. DANISH INVESTIGATIONS DURING THE LAST TWO DECADES

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CONTENTS

LIGAND ABBREVIATIONS

acac	acetylacetonate
bipy	2,2′-bipyridine
bispicam	bis(2-pyridylmethyl)amine
bispicen	*N*,*N*′-bis(2-pyridylmethyl)-1,2-ethanediamine
bispictn	*N*,*N*′-bis(2-pyridylmethyl)-1,3-propanediamine
cyclen	1,4,7,10-tetraazacyclododecane
edta	ethylenediaminetetraacetate
en	ethylenediamine
gly	glycinate
ibn	isobutylenediamine
mal	malonate
mhp	6-methyl-2-hydroxypyridinate
metacn	1,4,7-trimethyl-1,4,7-triazacyclononane
ox	oxalate

phen	1,10-phenanthroline
tacd	1,5,9-triazacyclododecane
tacn	1,4,7-triazacyclononane
tn	trimethylenediamine
tren	2,2′,2″-triaminotriethylamine
trien	triethylenetetramine

A. INTRODUCTION

Oligonuclear chromium(III) complexes with hydroxo bridges have fascinated many Danish scientists, primarily owing to the inspiration of S.M. Jørgensen who a 100 years ago synthesized and characterized the first well-documented species of this sort along with numerous mononuclear complex compounds of mainly chromium(III) and cobalt(III), many of which are still kept at The Technical University in Copenhagen. With the work of Alfred Werner the time had come for the understanding and solution of the molecular structure of these hydroxo-bridged oligomers with what we to-day consider simple means and eminent argumentation. The structural solutions of some of the historical oligomers had to await newer methods such as X-ray diffraction, but it had become clear that the structures involved corner-, edge- or face-sharing octahedra with typically two to four metal centres.

Two of the most famous complexes of that sort with more than two metal atoms—in fact the only two known for many decades—are Jørgensen's rhodoso with chromium(III) [1,2] (**V** in Fig. 1), which has no cobalt(III) analogue, and his brown compound with the same stoichiometry except that chromium(III) is replaced by cobalt(III) [3,4]. This compound, which had no chromium analogue until recently [5–7] (**IV** in Fig. 1), is called Werner's brown salt and the structure proposed by Werner was confirmed by X-ray diffraction in 1971 [8–11]. The structure of rhodoso was unknown and no suggestions were put forward until 1968 [12–15] when it was solved by the same method.

The major innovations within the field of hydroxo-bridged chromium(III) oligomers since the time of Jørgensen, Werner, Pfeiffer and Dubsky have been achieved within the last two decades in Denmark as well as in other countries. The main emphasis in the following sections will be on hydroxo-bridged chromium(III) oligomers with two to four chromium(III) centres as studied in Denmark in this period and on their appropriate relationship to the field in general. Thus, this article will not cover the area in full, neither in time nor internationally. A most thorough review entitled "Hydroxo-bridged complexes of chromium(III), cobalt(III), rhodium(III) and iridium(III)" has been published quite recently by Springborg [16].

B. TYPES OF OLIGOMERS

The different types of hydroxo-bridged dimers of chromium(III) can be illustrated by listing the existing dimers with NH_3 and H_2O as non-bridging ligands as in Table 1. The situation is of course far more complicated than that of the mononuclear ammineaqua complexes where all the possible compounds including *cis* and *trans* isomers and *fac* and *mer* isomers have been isolated. Table 1 shows that very few of the many possible ammineaqua dimers are known. The table gives some of the prefixes which have been used in connection with the isomerism of these species: *fac* is used to describe the configuration of $(NH_3)_3$ in the mononuclear moieties, and *cis* or *trans* is used either to give the positions of the water ligands relative to the oxygen atom of the bridge in the mono-ols or to give the positions of the water ligands relative to the $Cr(OH)_2Cr$ bridge plane in one of the listed diols. To the diversity may be added the many basic forms of these complexes resulting from deprotonation of the terminal water ligands or, at higher pH, of the μ-OH groups.

There are examples of other non-bridging ligands for all the three main types of hydroxo-bridged dimers. Mainly for the diols, besides simple monodentate anionic ligands, a great variety of typically polydentate ligands are encountered, many of which are listed above (see ligand abbreviations).

TABLE 1

Monohydroxo, dihydroxo and trihydroxo-bridged ammineaqua chromium(III) dimers characterized in the crystalline state and in solution with references to primary characterization and structure determination

Type	Complex	Configuration	Ref.
$Cr(OH)Cr$ ("mono-ol")	$(NH_3)_5Cr(OH)Cr(NH_3)_5^{5+}$ (rhodo)		17–19
	$(H_2O)(NH_3)_4Cr(OH)Cr(NH_3)_5^{5+}$ (erythro)	*cis*	17, 20
		trans	21
	$(H_2O)(NH_3)_4Cr(OH)Cr(NH_3)_4(H_2O)^{5+}$	*cis-*, *cis*	22
	$(H_2O)_2(NH_3)_3Cr(OH)Cr(NH_3)_3(H_2O)_2^{5+}$	*fac*	23
	$(H_2O)_5Cr(OH)Cr(H_2O)_5^{5+}$	– [a]	24, 25
$Cr(OH)_2Cr$ ("diol")	$(NH_3)_4Cr(OH)_2Cr(NH_3)_4^{4+}$		26–28
	$(H_2O)(NH_3)_3Cr(OH)_2Cr(NH_3)_3(H_2O)^{4+}$	*trans* (*fac*)	23, 29
		cis (*fac*) [a]	23, 30
	$(H_2O)_4Cr(OH)_2Cr(H_2O)_4^{4+}$		31, 32
$Cr(OH)_3Cr$ ("triol")	$(NH_3)_3Cr(OH)_3Cr(NH_3)_3^{3+}$		30

[a] In solution only.

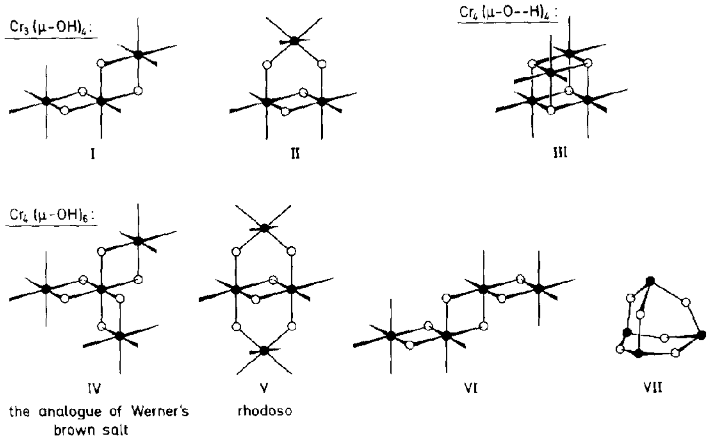


Fig. 1. Skeletons of the hydroxo-bridged trinuclear and tetranuclear chromium(III) complexes whose structures have been solved from X-ray single-crystal diffraction data or are otherwise well documented. Comments with respect to terminal ligands and references to primary characterization and structure determination are as follows: **I** with (en)$_5$ [6], **II** with (NH$_3$)$_{10}$ [7], (tacn)$_3$(H$_2$O) or (tacn)$_3$(OH) with an intramolecular hydrogen bond between an OH bridge and the terminal OH ligand [33] or with (bispicam)$_3$(SO$_4$) [34], **III** with (mhp)$_8$ [35], **IV** with (NH$_3$)$_{12}$ [7,11], (en)$_6$ with Δ{ΔΛΛ}/Λ{ΛΔΔ} configuration [6] or (bispictn)$_3$ [36], **V** with (NH$_3$)$_{12}$ [1,12–14] or (en)$_6$ [2,15], **VI** with (en)$_6$ and *meso*-ΛΛΔΔ configuration (not ΛΔΛΔ as misprinted in the reference) [6] and **VII** with [C$_5$(CH$_3$)$_5$]$_4$ [37].

Finally, many examples are known where, in addition to or instead of hydroxo bridges, other bridges such as RO$^-$ or bidentate ligands such as RCOO$^-$, SO$_4^{2-}$ or PO$_4^{3-}$ are used.

Proceeding now to the hydroxo-bridged oligomers with more than two chromium(III) centres the situation might have been too complicated to envisage. However, there are a few examples of such oligomers whose molecular structure has been well established; they are shown in Fig. 1. It is seen that most of them are extensions of the diols.

These few examples, nevertheless, in connection with those of the dimers, give a picture of the types of hydroxo-bridged oligomers we are concerned with in the case of chromium(III) without going into detail concerning the enormous number of possible isomers with polydentate ligands. An additional feature is the tendency of these oligomers to form relatively short intramolecular hydrogen bonds, primarily between neighbouring terminal H$_2$O and OH$^-$ ligands. Intramolecular hydrogen bonds involving the OH bridge or nitrogen ligands also occur. In the solid state and possibly also in concentrated solution, intermolecular hydrogen bonds between the oligomers or monomers occur as well. The consequences of these important properties are described in the following sections.

In the crystalline state the hydroxo bridge in the chromium(III) complexes is usually hydrogen bonded to a nucleophile in a neighbouring molecule when possible, whereas the establishment of four covalent/coordinate bonds to the oxygen atom is a rare, usually unstable exception. Thus aqua bridge formation has only been demonstrated in intermediates in acid-catalysed hydroxo bridge cleavage (see later). Binding of OH^- to more than two chromium(III) centres seldom needs to be taken into consideration; one exception is the cubane-like arrangement of **III** (Fig. 1). In this molecule, however, the bridging OH groups are all involved in short hydrogen bonds (2.57 Å) to nitrogen atoms in the pyridine rings of the mhp ligands, thus probably loosening the O–H bond. As to O^{2-} coordinating to three chromium(III) centres, one of the more well-known examples is the basic chromium(III) acetate [38] containing the ion $Cr_3O(CH_3COO)_6(H_2O)_3{}^+$.

C. NOMENCLATURE

The naming of these hydroxo-bridged oligomers presents a problem. The IUPAC nomenclature [39] works satisfactorily for the dimers for which also the designations mono-ol, diol or triol, often used in short, are unambiguous with respect to the mono-, di- or tri-μ-hydroxochromium(III) arrangement, respectively. This practice is not satisfactory for the oligomers of higher nuclearity. Thus the designation "hexol", sometimes used, covers several different types of μ-OH-Cr skeletons (see Fig. 1).

Various suggestions for the trinuclear and tetranuclear complexes in Fig. 1 have been made. The extension of the IUPAC nomenclature by the introduction of locant designators [39] is little used. Another approach has been to consider a chromium-containing fragment of the molecule as a bridge [6,7], as suggested by Thewalt et al. [40] in connection with a description of a nomenclature symbolism for chiral and achiral isomers of bridged inorganic complexes. The relatively simple complex $(en)_2Cr(OH)_2Cr(en)(OH)_2Cr(en)_2{}^{5+}$ (**I** in Fig. 1) in this nomenclature becomes a μ-{mono(ethylenediamine)bis(dihydroxo)chromium(III)}-bis[bis(ethylenediamine)chromium(III)] ion. Such names are often too long and difficult to unravel to be of real use. No wonder that the classical colour-associated names, such as rhodoso and Werner's brown salt, once given, are still in use.

D. SYNTHESIS

As expected, most of the procedures for synthesizing the hydroxo-bridged chromium oligomers involve hydrolysis. Many of the dihydroxo-bridged dimers are prepared by condensation of monomers containing the relevant non-bridging ligands. The procedures may incorporate substitution with the H_2O or OH^- necessary for bridge formation, e.g. Hg(II)- or Ag(I)-assisted Cl^- substitution, and introduction of the final terminal ligands either in the monomer or in a later step. The condensation takes place in water, sometimes even better in organic solvents or in the solid state at elevated temperatures when the reactants are arranged in positions favourable for the condensation, as has been demonstrated with *cis*-aquahydroxo monomers held together by intermolecular hydrogen bonds [26,41–48]. A high degree of stereoselectivity in the aqueous hydrolysis is often found where different, sometimes numerous, isomers are possible. Diols with non-bridging ligands such as en [49,50], phen and bipy [51,52], pyridyl-substituted amines [34,36,53–59], trien [60], ibn [61], tacn(H_2O) [23,33], $NH_3(H_2O)$ [23,29], ox [62], mal [63] and amino acids [64] are examples where specific isomers have been isolated rather easily. Favourable crystallization behaviour supports and is sometimes the main reason for the selectivity of the syntheses, and when not present, it has in some cases been necessary to use more cumbersome methods such as column separations.

The initial product from the condensation of monomers is the monohydroxo-bridged dimer, but owing to further relatively fast bridge formation the mono-ols are usually prepared by bridge cleavage of the diols resulting in aqua (hydroxo) [22–24,43,44,46,49,50,65,66] or aniono mono-ols [67,68]. By this method a nucleophile may enter as a bridge instead of one of the hydroxo bridges [67–70]. Also isomerization reactions have been a part of the procedure to obtain dimers otherwise difficult to synthesize [23,30,50,66,71] (see later).

A difficulty in the syntheses of oligomers with coordinated ammonia is the disturbing loss of ammonia especially at intermediate and higher pH, and the difficulty increases with temperature. One of the more successful methods of preparing ammine oligomers, beside some already mentioned, has been to start with labile chromium(II) ammonium–ammonia buffer solutions. Air oxidation of such solutions is a unique method for obtaining rhodo [17] (top of Table 1) while anaerobic spontaneous oxidation by the medium, according to Jørgensen, leads to, for example, rhodoso [1] (**V** in Fig. 1). This procedure for rhodoso does not work within a reasonable time with the chemicals used nowadays. If, however, charcoal is added to such concentrated chromium(II) ammine solutions, the spontaneous oxidation with hydrogen evolution and the formation of higher oligomers is accelerated, resulting in mixtures from which Andersen et al. have isolated different species, depending on the concentration of NH_4^+ and NH_3. Rhodoso is obtained in reasonable yield by direct crystallization, as are **II** and **IV** (see Fig. 1) in lower yields after ion exchange separations [7].

Similar procedures have been used by Andersen et al. to obtain the higher oligomers with terminal ethylenediamine [6], but here and with other amine ligands an often easier way is to condense chromium(III) monomers at elevated temperatures. In favourable cases the oligomer can be crystallized directly from the reaction mixture in good yield [2,6,33] (see Fig. 1).

The successful isolation of the oligomers is, of course, very dependent on their ability to crystallize with various counter-ions. Precipitation may be difficult even when the oligomer in question is the main complex species in the solution. However, there are examples of oligomers which precipitate slowly as the only species in reasonable yields from solutions where they are undetectable, e.g. the triol $(NH_3)_3Cr(OH)_3Cr(NH_3)_3^{3+}$ [30]. It seems that the higher the nuclearity and the higher the number of terminal water ligands per chromium the more difficult is the crystallization. Thus one of the simplest well-known binuclear aqua ions, $(H_2O)_4Cr(OH)_2Cr(H_2O)_4^{4+}$, was not isolated as satisfactory crystals until quite recently [32].

E. IDENTIFICATION

Structural information obtained in the crystalline state must of course be handled carefully when used for the compound in question after dissolution. Owing to the robustness of chromium(III), most of the oligomeric complexes of this element maintain their basal structure, except for conformational changes such as the ethylenediamine chelate ring twist, for minutes up to months after dissolution in moderate solvents at room temperature. There are, however, many examples where major structural changes occur with a rate comparable to that of dissolution (see Section F).

X-ray diffraction is nowadays the most effective method for determining the detailed structure of the oligomers, and structures have thus been determined for nearly all the complexes in Table 1 and Fig. 1 and for many other dimers.

Structural information has also been achieved in various other ways in combination with elemental analysis. Hydrolysis with concentrated strong acids has been a most helpful means of identifying the mononuclear fragments of the oligomers. The complexing hydrochloric acid has been used in this way since Jørgensen [1], and Andersen and coworkers likewise used the non-complexing perchloric acid [5–7,29] to give the respective aqua amine monomers quantitatively and with retention of configuration. This method has also been used for the synthesis of monomers difficult to obtain otherwise [6,7,29].

Molecular weight determination from freezing point depression has been used in some instances [24,72–74] and also ion exchange behaviour may under certain conditions give an indication of the charge of the oligomer or of the charge per chromium atom [6,7,74,75]. Acid–base properties (see later) and pieces of evidence of less general character such as the resolution of optical isomers (cf. the legendary resolution of Werner's brown salt (the ammine complex) [76]) may be parts of the picture, and when all the evidence is combined the identity of the oligomer will in many cases be fairly well established.

The optical spectra of the oligomers have been widely studied and often give useful information on the nature of the oligomer in addition to providing identification. An example is the presence of spin-forbidden *d–d* bands with relatively high intensity and additional fine structure due to strong electronic coupling of the chromium(III) centres (see later). Another example is the easy demonstration of the presence of water ligands from the spectral pH dependence. However, spectral behaviour and dependence on, for example, pH and time are usually studied for purposes other than mere identification. This is true also for the use of several other techniques such as ESR and magnetic susceptibility measurements. Some of these studies will be considered in the next sections.

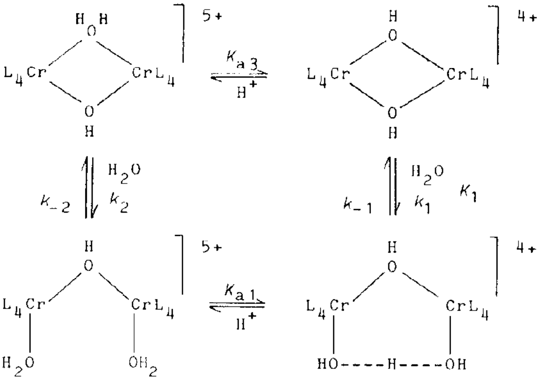
There will, however, often be configurational choices left to be settled by structure analysis from diffraction data. This is the only safe means to determine the configuration with respect to Δ or Λ around the chromium(III) centres in, for example, the higher oligomers with ethylenediamine (e.g. **IV** and **VI** in Fig. 1 [6,8,9]). Furthermore, human imagination has limitations: very few, if anyone, interested in the structure of rhodoso, had imagined the actual cyclic arrangement of this classical ion before the X-ray solution by Bang [12–15], despite the knowledge that it was composed equally of *cis*-tetraammine and *cis*-diammine monomer fragments [6,7,40,77]. The existence of specific trinuclear and tetranuclear hydroxo-bridged aqua complexes has been demonstrated by Marty and coworkers, but these $Cr_3(OH)_4^{5+}$ and $Cr_4(OH)_6^{6+}$ species have so far been isolated only in solution [75,78], and there are different opinions concerning their structure. The proposals range from structures involving OH^- coordinated to three or four metal centres [75,78] to structures similar to or derived from some of those in Fig. 1 [25].

F. EQUILIBRIA AND KINETICS

The robustness of chromium(III) has the consequence that relatively few stability or equilibrium constants have been determined for reactions involving ligand–chromium(III) bond formation. However, the kinetics of thermochemical and photochemical substitution in chromium(III) complexes has been studied rather more and is the subject of another article in this issue, with the main stress laid on mononuclear complexes [79].

A pioneering work in the study of complex formation was Niels Bjerrum's determination of the stepwise stability constants of the aquathiocyanatochromium(III) monomer system [80,81]. Stability data for chromium(III) amine formation have been obtained by Andersen et al. [82–84] when use was made of the combined catalytic effect of charcoal and small amounts of chromium(II), inspired by Jannik Bjerrum's investigation of the charcoal-catalysed cobalt(III) ammine formation [85]. In that way the overall stability constants were determined for the mononuclear complexes of chromium(III) with NH_3 [82], en [83] and edta [84] together with the last stepwise constants with NH_3 and en. Reliable equilibrium data for reactions involving oligomers could not be obtained in this way, though equilibration seems to take place to some extent [6,7,82,83].

Other attempts to obtain information on the stability connected with hydroxo-bridge formation and cleavage were few—examples are systems involving the diols with phen [86] or water [87] as non-bridging ligands—until Springborg and Toftlund in 1975 announced the establishment of the reversible reaction between the *meso* diol and the mono-ol with two en at each chromium(III) centre [65]. Equilibrium was attained from both sides after the isolation of salts of the new hydroxo(aqua)amine mono-ol. At the same time they discovered the isomerization between this *meso*-(Δ,Λ-) diol and the *racemic* (Δ,Δ- and Λ,Λ-) isomer, and this isomer and its mono-ol derivative were isolated as salts [66]. The series of dimers was supplied with the heteronuclear $(en)_2Cr(OH)_2Co(en)_2^{4+}$ diol [43,44]. In the following years Springborg and coworkers determined the equilibria for most of the reactions given in Scheme 1 and made thorough kinetic studies of the reactions involved with $L_4 = (NH_3)_4$ [22], Δ,Λ-$(en)_2$ [49], $\Delta\Delta$- and $\Lambda\Lambda$-$(en)_2$ [50] and $(tn)_2$ [46].



Scheme 1

TABLE 2

Thermodynamic and kinetic data related to Scheme 1 for $L_4 = (NH_3)_4$ (25 °C, 1 M (Na,H)ClO_4) [22]

$K_{a1} = 0.0176(9)$ M	$\Delta H^\circ(K_{a1}) = 49(6)$ kJ mol^{-1}	$\Delta S^\circ(K_{a1}) = 129(20)$ J mol^{-1} K^{-1}
$k_1 = 1.21(2) \times 10^{-4}$ s^{-1}	$\Delta H^{\neq}(k_1) = 86.7(15)$ kJ mol^{-1}	$\Delta S^{\neq}(k_1) = -29(5)$ J mol^{-1} K^{-1}
$k_{-1} = 3.80(4) \times 10^{-4}$ s^{-1}	$\Delta H^{\neq}(k_{-1}) = 80.6(15)$ kJ mol^{-1}	$\Delta S^{\neq}(k_{-1}) = -40(5)$ J mol^{-1} K^{-1}
$K_1 = 0.318(11)$	$\Delta H^\circ(K_1) = 6(4)$ kJ mol^{-1}	$\Delta S^\circ(K_1) = 11(14)$ J mol^{-1} K^{-1}
$k_2/K_{a3} = 4.9(5) \times 10^{-5}$ s^{-1} M^{-1}	$\Delta H^{\neq}(k_2) - \Delta H^\circ(K_{a3}) = 82(11)$ kJ mol^{-1}	$\Delta S^{\neq}(k_2) - \Delta S^\circ(K_{a3}) = -53(35)$ J mol^{-1} K^{-1}
$k_{-2} = 2.7(3) \times 10^{-6}$ s^{-1}	$\Delta H^{\neq}(k_{-2}) = 123(11)$ kJ mol^{-1}	$\Delta S^{\neq}(k_{-2}) = 63\ (35)$ J mol^{-1} K^{-1}

Data for the system with $L_4 = (NH_3)_4$ are given in Table 2 (from ref. 22 where a comparison with other diols is given). The half-life of the reaction at 25 °C and pH 2 is 0.5 h, and the ratio between the rates of the acid-catalysed pathway and the uncatalysed pathway of the cleavage reaction is 0.4 at pH 0, which is the highest ratio among the chromium(III) systems investigated.

One of their important results was to demonstrate that the formation of an intramolecular hydrogen bond, indicated in Scheme 1, between an H_2O ligand at one chromium(III) centre and a neighbouring OH^- ligand at the other chromium(III) centre plays a major role in the kinetic behaviour as well as in the stability of the dimers involved. The increase in stability of the aquahydroxo mono-ol owing to the formation of this intramolecular hydrogen bond is 10–15 kJ mol^{-1}. The result is an increase in the acidity of *cis,cis*-$(H_2O)(NH_3)_4Cr(OH)Cr(NH_3)_4(H_2O)^{5+}$ corresponding to ca. 2 p*K* units compared with other related dimers such as erythro, the conjugate base of which has no such hydrogen bond. The O–O distance in the H–O · · · H · · · O–H hydrogen bond is expected to be relatively short and has recently been shown to be 2.43 Å in a salt of the corresponding $(H_2O)(en)_2Ir(OH)Ir(en)_2(OH)^{4+}$ ion [88].

Andersen and Døssing have recently shown that *trans*-$(H_2O)L_3Cr(OH)_2CrL_3(H_2O)^{4+}$ exhibits similar behaviour; *trans* refers to the positions of the water ligands relative to the $Cr(OH)_2Cr$ bridge plane. The reaction of the complex with L_3 = tacn, first synthesized and characterized by Wieghardt et al. [33], and of that with $L_3 =$ *fac*-$(NH_3)_3$ [29] were studied in aqueous solution in the pH interval 0–11 [23]. In acidic solution the ammonia complex behaves very similarly to the bis(tetraammine) dimer: it opens to the mono-ol with comparable rate, mono-ol : diol ratio and acidity of the +5 charged mono-ol. At pH > ca. 3 isomerization reactions dominate: the triammine as well as the tacn diol establish equilibrium with the corresponding *cis* diol, including deprotonated +3 and +2 charged cations, with reaction half-lives of 1–10 min at 25 °C. Again a stabilization of ca. 13 kJ mol^{-1} of the *cis*-$(H_2O)L_3Cr(OH)_2CrL_3(OH)^{3+}$ ion, owing to a short (2.45 Å [89]) intramolecular hydrogen bond between the non-bridging H_2O and OH^- ligands, explains the relatively high stability of this ion compared with that of the corresponding *trans* diol (their molar equilibrium ratio is ca. 8) and likewise the observed increase of ca. 2 pK units in the acidity of the conjugate *cis*-diol acids. The observed rate differences [90] between the reaction mono-ol to diol and the isomerization reaction between *trans* diol and *cis* diol for the *fac*-triammine dimer show that the latter reaction involves a mechanism without the intermediate formation of a singly bridged dimer. A transition state structure with one normal hydroxo bridge and two weaker ones has been suggested by Mønsted et al. [25].

Data concerning the two other steps, I and III, in the consecutive condensation

$$2\,Cr \underset{I}{\rightleftharpoons} Cr(OH)Cr \underset{II}{\rightleftharpoons} Cr(OH)_2Cr \underset{III}{\rightleftharpoons} Cr(OH)_3Cr \tag{2}$$

(omitting non-bridging ligands and charges; Cr = Cr(III)) are more scarce than for step II. The triol was first isolated by Wieghardt et al. with L_3 = metacn [91] or tacd [92] as non-bridging ligands and later by Andersen et al. with $L_3 =$ *fac*-$(NH_3)_3$ [30]. The triols with the cyclic tridentate ligands are remarkably inert in the entire pH range except for strong base, resulting in deprotonation of one of the bridges or cleavage of one of the bridges respectively. In contrast, the ammonia triol at room temperature opens to the *cis* diol at a rate almost equal to the rate of dissolution in water.

It is mainly the kinetics of the dissociation in step I which have been investigated for complexes such as rhodo, erythro and erythro derivatives [71,93,94]. The apparent decrease in the order of the second-order dimerization reaction in aqueous solution of *cis*-$Cr(ox)_2(H_2O)(OH)^{2-}$ observed when the chromium concentration increases [95] has been explained by Ardon and Bino by the formation of hydrogen-bonded cation pairs of the *cis*-aqua-hydroxo monomers prior to the formation of the dimer (in this case the diol) [47] in analogy to the observations in the solid state mentioned in Section D. Actually the $[H{-}O \cdots H \cdots O{-}H]^-$ arrangement with a short O–O distance (ca. 2.4–2.5 Å) is considered by some authors a useful entity in describing olation phenomena [47].

In his work on basic chromium compounds, Niels Bjerrum [31] showed that hydroxo-bridged aqua oligomers are produced by hydrolysis of monomeric aqua ions, and since then the hydrolysis of $Cr(H_2O)_6^{3+}$ has been investigated many times. Steps I and II of Scheme 2, with H_2O (and OH^-)

as the only terminal ligands, have been studied more recently by, for example, Thompson et al. [24,87] who also isolated a trimer in solution [74] and lately by Marty and coworkers [96], who succeeded in isolating crystalline salts of the aqua diol [32]. Their investigations of these early stages of the hydrolysis of aqueous chromium(III) incorporate a trimeric $Cr_3(OH)_4^{5+}$ and two isomeric tetrameric $Cr_4(OH)_6^{6+}$ species isolated in solution [75–78]. Some of their results have been commented upon by Mønsted et al. [25] in view of the formation of intramolecular hydrogen bonds between terminal water ligands and terminal or bridging hydroxo ligands to explain the interconversion rate constants and the thermodynamic stability (acidity) observed in this system.

G. SUPEREXCHANGE COUPLING

In 1972 Glerup published a model for the calculation of antiferromagnetic coupling and absorption spectra of $(NH_3)_5CrOCr(NH_3)_5^{4+}$, the so-called basic rhodo [97]. The calculations were based on the angular overlap model [98,99] and contained three parameters, two related to interelectronic repulsion and one to the π overlap between oxygen *p*-orbitals and chromium *d*-orbitals. The model gives the Landé interval rule for antiferromagnetic coupling with the singlet as ground state, calculates seven transitions (double excitations/charge transfer) in good agreement with the observed band positions and calculates the triplet–singlet separation (450 cm^{-1}) in accordance with magnetic susceptibility measurements.

This work was an inspiration in our country for further studies of such coupling phenomena, and not only the dihydroxo-bridged dimers but also other dimers and higher oligomers of chromium(III) have been the main objects of investigation. In a series of papers, structural parameters have been correlated with the magnetic interaction, i.e. with the sign and magnitude of the exchange coupling parameter J, as obtained from magnetic susceptibility measurements.

The so-called Glerup, Hodgson and Pedersen (GHP) model [100], has been successful in this respect for salts of dihydroxo- (or dialkoxo-)bridged dimers of chromium(III) with non-bridging ligands such as NH_3, en, cyclen, phen, acac, mal and pyridyl-substituted amines [28,34,36,58,59,100–102], whereas a ferromagnetic salt of the aqua diol apparently fits less well to this model [103]. According to the GHP model, as well as to the above-mentioned model for $(NH_3)_5CrOCr(NH_3)_5^{4+}$, the splitting of the ground level is the result of configurational interaction with charge transfer levels. Simple hybridization of the 2*s* and 2*p* orbitals on the bridging oxygen atoms accounts for the different bridge geometries. This explanation is based on the observations by Josephsen and Pedersen [104] that J has a relatively large dependence on the angle θ between the Cr–O–Cr plane and the OH vector of the bridging group in addition to the previously proposed dependence on the Cr–O–Cr angle ϕ and on the Cr–O distance r [104,105]. According to the GHP model, J is calculated as

$$J = J(\text{antiferromagnetic}) - J(\text{ferromagnetic})$$
$$= e^{-a(r-1.8)}\left\{ b \cos^4\theta/[1 - \sin^2\theta/\tan^2(\phi/2)]^2 - c \sin^2\phi/[1 - \cos\phi]^2 \right\}$$

where a, b and c are parameters; b and c depend on charge transfer energy separation, d-electron energy splitting and interelectronic repulsion parameters. If the OH(OR) vector lies in the bridging plane of the diol, the oxygen atom is left with a lone pair which is a pure p-orbital not participating in the three σ-bonds. This lone pair then gives maximum π-overlap integrals with chromium d-orbitals, resulting in maximum antiferromagnetic contribution to J.

Some of the monohydroxo-bridged dimers in Table 1, e.g. *trans*-erythro [21] and some of the higher oligomers in Fig. 1 have also been investigated with regard to a similar correlation of structure and magnetic properties [7], and particularly in the case of the zigzag-shaped tetranuclear complex (**VI** in Fig. 1) the GHP model is in good agreement with the susceptibility data [106]. Wigner–Racah algebra developed by Damhus and coworkers [107–109] was used as a powerful tool for the evaluation of the matrix elements in these examples of trinuclear and tetranuclear complexes.

The triols, $L_3Cr(OH)_3CrL_3^{3+}$, with L_3 = metacn [91], tacd [92] or $(NH_3)_3$ [30] isolated recently all have a triplet–singlet separation of the order of magnitude of 100 cm^{-1} [110–112]. The ESR spectra of the triol complex with L_3 = metacn and $(NH_3)_3$ have been interpreted. The antiferromagnetic coupling results in a ground level singlet, triplet, quintet and septet, and for the ammine triol (in a cobalt triol host) Andersen et al. observed ESR transitions only within the quintet [30]. These quintet transitions were split in accordance with a mononuclear zero-field splitting parameter, $D_1 = D_2 =$ 1.2 cm^{-1}, not far from the value found by Kremer [112] in the metacn complex. The ESR spectra of the chromium oligomers have otherwise generally been difficult to interpret, primarily because of the complexity of the spectra involving several anisotropic spin multiplets but also because of the lack of a suitable diamagnetic host for magnetic dilution.

Methods other than those mentioned above have been used in the study of superexchange coupling in chromium oligomers. Luminescence and absorption spectroscopies are important approaches and inelastic neutron scattering is another to which Güdel et al., for example, have made major contributions. These subjects have recently been covered in two reviews by Güdel [113] and will not be considered here. In the same series, Hodgson gives more details on the magneto–structural correlations in binuclear chromium(III) complexes [114].

H. HETERONUCLEAR HYDROXO-BRIDGED OLIGOMERS WITH CHROMIUM(III)

Λ,Δ-(en)$_2$Cr(OH)$_2$Co(en)$_2{}^{4+}$ is the first example of a classical chromium(III) oligomer in which one of the chromium(III) centres has been exchanged by another centre, in this case by cobalt(III). The compound was synthesized by Springborg and Schäffer by heating crystals of the active racemate [Λ-Cr(en)$_2$(OH)(H$_2$O)][Δ-Co(en)$_2$(OH)(H$_2$O)](S$_2$O$_6$)$_2$ [43,44] with a packing of cations favourable for the condensation (see previous sections). This heteronuclear diol has been a useful member of a series of diols for the determination [22] of the characteristic thermodynamic and kinetic properties of the dimers described above.

Wieghardt and coworkers have used the ligand tacn and related ligands such as metacn for a large number of interesting coordination compounds with a variety of metal ions [115], among them heteronuclear compounds. Thus a series of [(metacn)Cr^{III}(μ-OH)(μ-CH$_3$COO)$_2$M^{II}(metacn)](ClO$_4$)$_2$ with M = Mn, Fe, Co, Ni, Cu and Zn have been synthesized and characterized with respect to magnetic and redox properties, electronic spectra and molecular structure (M = Fe and Co) [116].

Recently Fujii et al. [117] and Cannon and Benjarvongkulchai [118] have studied the complex formation between *cis*-CoL$_4$(OH)$_2{}^+$ (L$_4$ = tren or (en)$_2$) and divalent metal ions and determined the stability constants. Michelsen has extended this field substantially by showing that *cis*-CrL$_4$(OH)$_2^+$ (or the cobalt analogue), where L$_4$ is, for example, (NH$_3$)$_4$, (en)$_2$ or bispictn, reacts

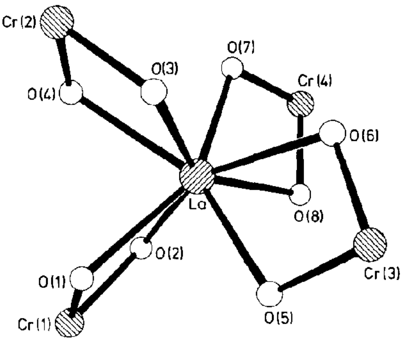


Fig. 2. The structure of the central part of the cation in [La{(OH)$_2$Cr(NH$_3$)$_4$}$_4$]I$_7$·aq (by kind permission of K. Michelsen [120]).

as a bidentate ligand to form stable heteronuclear hydroxo-bridged oligomers with two, three or four chromium atoms surrounding the central metal ion which may be a main group element or a transition metal in oxidation state II, III or IV, or a rare earth metal. These chromium(III) heteronuclear oligomers are of particular interest from a magnetic point of view. Typical series are salts of $[M^{II}\{(OH)_2CrL_4\}_2 \cdot aq]^{4+}$ or $[M^{II}\{(OH)_2CrL_4\}_3]^{5+}$ with M = Mg, Mn, Co, Ni, Zn [119] and $[M^{III}\{(OH)_2CrL_4\}_3]^{6+}$ with M = Al, In, V, Cr, Fe, Co (cf. Werner's brown salt). With M = Sc, Y, La, Ce, Pr, Eu, Gd, Yb, Michelsen has isolated salts of $[M^{III}\{(OH)_2Cr(NH_3)_4\}_4]^{7+}$ with a nearly tetrahedral arrangement of the chromium atoms (see Fig. 2) [120]. The compounds are being characterized structurally, magnetically and by ESR and absorption spectra [121].

I. CONCLUSION

Hydroxo-bridged oligomers are of course not confined to those of chromium(III). Apart from the fact that they have been studied significantly in this country the present choice of chromium(III) is not accidental. The convenient robustness of this metal ion is one of the main reasons for the large number of well-documented oligomers in solution as well as in the solid state when compared with those of other metal ions. Another consequence of this convenient robustness is that chromium oligomers have revealed many new aspects of interconversion and oligomerization reactions, as described in the section on their thermodynamic and kinetic properties, important for the understanding of the behaviour of corresponding oligomers with other metals. Another fascinating aspect is their role as a link to solid state physics. These oligomers with hydroxo bridges or other bridges provide possibilities for the study of metal–metal interactions within molecules of limited size, such as those described in the section on superexchange coupling, and thereby provide a better understanding of metal–metal interactions in infinite systems. The heteronuclear oligomers mentioned in the previous section are very promising in this respect.

The hydroxo-bridged oligomers of metal ions other than chromium(III), which have also been thoroughly studied, are mainly those of cobalt(III), rhodium(III) and iridium(III), and there are many similarities in chemical properties. Reactivity studies of hydroxo-bridged cobalt(III) dimers show that the hydrolytic cleavage of the first bridge in cobalt triols is considerably faster than the cleavage of the next two bridges which open with comparable rates [122–126]. It has, however, not been possible to isolate the monohydroxo-bridged hydrolysis product of the cobalt diol. These problems are not present with rhodium(III) and iridium(III) where the first bridge-cleavage step of the diol (en or NH_3 as non-bridging ligands), as for chromium(III), is much faster than the second, and where well-characterized mono-ols have been isolated in analogy with the chromium case. Important thermodynamic and kinetic data for rhodium(III) and iridium(III) dimers have appeared in recent years [88,127–129] and have been compared with the corresponding chromium(III) data [16].

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