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HYDROXO-BRIDGED COMPLEXES OF CHROMIUM(III), COBALT(III), RHODIUM(III), AND IRIDIUM(III)

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I. Introduction

Polynuclear complexes are known for most metal ions and they are of current interest because of their rather special chemical and physical properties resulting from the mutual interaction of two or more metal centers. Most of the common ligands in inorganic chemistry have been shown to function as bridging groups. The bridging ligands are often monoatomic ions, such as Cl^-, O^{2-}, and S^{2-}, or simple polyatomic ions, such as OH^- or NH_2^-, in which cases a single ligating atom is bound to two (or more) metal centers. Polydentate ligands such as $RCOO^-$, SO_4^{2-}, PO_4^{3-}, etc., usually act as bidentate ligands when they form a bridge.

Polynuclear complexes with hydroxide (or oxide) as bridging ligands constitute an important class of complexes. They are formed by hydrolysis of mononuclear aqua complexes of most metal ions and they therefore constitute an important aspect of the hydrolytic chemistry of metal ions. They display a chemistry which is interesting in itself, but which is also relevant in relation to applied chemistry and to biochemistry, as mentioned in Section XIII.

The present review is concerned mainly with the chemistry of hydroxo-bridged chromium(III) and cobalt(III) complexes, but the comparatively few studies of the related rhodium(III) and iridium(III) systems which have been reported have also been included. The review deals primarily with the chemical properties of these complexes, and special emphasis has been made on reactions which involve the cleavage or formation of a hydroxo bridge. Reactions of bridging groups other than hydroxide and reactions of nonbridging ligands are also discussed, but only to the extent that they have been considered relevant to the main issue. A large number of X-ray crystal-structure determinations have been made during the last two decades and references to all the published structures are given. The hydroxo-bridged chromium(III) oligomers constitute a very interesting class of complexes from a spectroscopic and magnetochemical point of view. This interesting field, however, lies beyond the main scope of the present article and only a brief review of the latest progress is given.

The literature has, in principle, been covered completely, but since the intention has not been to describe the historical development of the subject, many of the oldest references have been left out in the following discussions. It therefore seems appropriate to round off this section by giving credit to the pioneering work done at the beginning of the century by S. M., Jørgensen (*1–4*), A. Werner (*5–13*), and N. Bjerrum (*14–15*). As early as 1882 Jørgensen (*1, 3*) made a singly bridged dichromium(III) complex, the so-called rhodo complex, $(NH_3)_5Cr(OH)Cr(NH_3)_5{}^{5+}$, and later he prepared a tetranuclear complex, the so-called rhodoso complex (*4*), $Cr_4(NH_3)_{12}(OH)_6{}^{6+}$. Jørgensen also prepared a tetranuclear cobalt(III) complex, $Co_4(NH_3)_{12}(OH)_6{}^{6+}$ (*2*). This complex was subsequently the first inorganic salt to be resolved into its optical isomers, by Werner (*9*). Werner, as well as Pfeiffer (*16, 17*) and Dubsky (*18*), synthesized a very impressive number of hydroxo-bridged chromium(III) and cobalt(III) complexes during a comparatively short period. Using classical chemical methods, they also established the structures of many of these polynuclear species correctly. The study of these complexes clearly contributed significantly to the acceptance of Werner's proposal of octahedral coordination geometry rather than the chain theory of C. W. Blomstrand and S. M. Jørgensen. At the same time that Werner studied the ammine and amine complexes, Bjerrum started investigating the hydrolytic behavior of chromium(III) aqua ions and established the formation of hydroxo-bridged oligomers (*14, 15*). Bjerrum's pioneer work was taken up during the 1950s by L. G. Sillén and co-workers (*19–21*), who have made a systematic study of the hydrolytic behavior of a large number of metal aqua ions and have introduced the use of modern computer programs for the numerical treatment of the data.

II. Structural Considerations

A. DETERMINATION OF STRUCTURES

In this section the methods which have been used to gain structural information are briefly summarized. The term structure is used in this context in its broadest sense, including more qualitative observations concerning the skeleton of the bridging atoms. As a general rule, the hydroxo-bridged polynuclear complexes of chromium(III) and cobalt(III) can be isolated as well-defined crystalline salts and it is therefore quite natural that single-crystal X-ray structure analysis has become the method of choice for obtaining unambiguous and detailed structural information.

The X-ray crystal data are often used in relation to solution chemistry, and the general question of the identity of the species in solution and those present in the crystals has to be considered, since rapid interconversion between different bridged species is frequently seen for both chromium(III) and cobalt(III). Supplementary solution measurements are therefore generally required in order to be reasonably certain that the solid-state structure corresponds to the structure in solution.

The most important methods for obtaining structural information about solutions are probably potentiometric pH measurements and visible/ultraviolet spectroscopy, but many other techniques have been applied, including bridge-cleavage experiments, magnetic measurements, and electron spin resonance (ESR) spectroscopy (*22, 23*).

A knowledge of the nuclearity, i.e., the number of metal ions per oligomer, and of the charge on the species can normally be obtained with good accuracy by classical methods. The molecular weight of the polynuclear species has been determined by measurement of the freezing point depression of a eutectic solution of a strong electrolyte in water (*24–28*). This method has been used by Ardon and Linnenberg (*25*) to determine the molecular weight of the blue dinuclear species $(H_2O)_4Cr(OH)_2Cr(H_2O)_4^{4+}$ and by Schwarzenbach and Magyar (*24*) to determine the molecular weights of the sulfate salts of the cations $(NH_3)_5Cr(OH)Cr(NH_3)_5^{5+}$ and *cis*-$(NH_3)_5Cr(OH)Cr(NH_3)_4X^{n+}$ ($X = H_2O$, OH^-, NCS^-, and F^-). The ratio charge/metal center can be determined accurately by ion-exchange chromatography, which from elution rates may also provide an estimate of the charge per species (*27, 29–31*).

It will therefore usually be possible to determine the values of x and y in the formula $M_x(OH)_y$, but the number of hydroxo bridges may remain undetermined, e.g., $M_2(OH)_2^{n+}$ may correspond to the monohydroxo-, dihydroxo-, or oxo-bridged structures: $M(OH)M(OH)^{n+}$, $M(OH)_2M^{n+}$, or $M–O–M^{n+}$. Classical methods which can often distinguish between these structures are potentiometric acid–base titration and measurements of the $d–d$ absorption spectra as a function of pH. In combination, such measurements may provide information about the number of terminally coordinated water ligands, the number of hydroxo bridges, and even about the nuclearity. The dinuclear ammine and amine chromium(III) complexes $L_4Cr(OH)_2CrL_4^{4+}$ and $(H_2O)L_4Cr(OH)L_4(OH)^{4+}$ [$L_4 = (NH_3)_4$ or $(en)_2$] can easily be distinguished from such measurements: the dihydroxo-bridged species exhibits no acid–base properties in the pH region 0–10, whereas the monohydroxobridged species does, and the spectral changes (positions of the first ligand-field bands (see Table VI) could be interpreted according to the proposed structures (*32–36*). Potentiometric and spectrophotometric acid–base studies of $\Delta,\Delta/\Lambda,\Lambda$-$(phen)_2Cr(OH)_2Cr(phen)_2^{4+}$ and its basic oxo-bridged forms showed that the nuclearity was $2n$ (n integer) and that a dinuclear ion should be dihydroxo-bridged, as later confirmed by crystal-structure analysis (*37–39*).

Hydrolysis is strong acid in which all hydroxo bridges are cleaved, followed by identification of the various mononuclear species and a determination of their molar ratios, may provide extremely valuable information. A straightforward example is the cleavage of the tetranuclear species $Cr_4(NH_3)_{12}(OH)_6^{6+}$, which yields $Cr(H_2O)_6^{3+}$ and *cis*-$Cr(NH_3)_4(H_2O)_2^{3+}$ in a ratio of 1:3 (*40*). Since it could be demonstrated at the same time that the polynuclear cation does not exhibit acid–base properties in the pH region for terminally coordinated water, it was concluded that the only possible structure was **6** in Fig. 1, as later confirmed by a crystal-structure analysis (*41*).

Magnetic measurements on the paramagnetic chromium(III) complexes are useful diagnostically and may distinguish a dihydroxo-bridged binuclear structure from an oxo-bridged structure (see Section III). Similarly, electron spin resonance studies on chromium(III) complexes, frozen glass mixture, or solids could be a powerful technique for distinguishing different bridged structures. Until now, however, they have been used mostly to characterize complexes of known structure (*40, 42*).

Vibrational (infrared and Raman) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and X-ray techniques are frequently used to study aqueous solutions of the hydrolysis products of metal aqua ions, but have not been applied to any great extent to the present metal complexes; few infrared studies have been reported (*43–46*). ^{59}Co NMR studies of a series of cobalt(III) oligomers suggest that NMR is a good method for establishing the structures of such complexes in solution (*47*). Similarly, ^{2}H NMR spectroscopy has recently been used to study the solution chemistry of chromium(III) oligomers (*48*).

B. CRYSTALLOGRAPHIC DATA

Figure 1 shows schematically the skeletal structures of hydroxo-bridged oligomers which have been observed in X-ray crystal structures, including a few speculative but relevant structures (**4b**, **7b**, and **7c**).

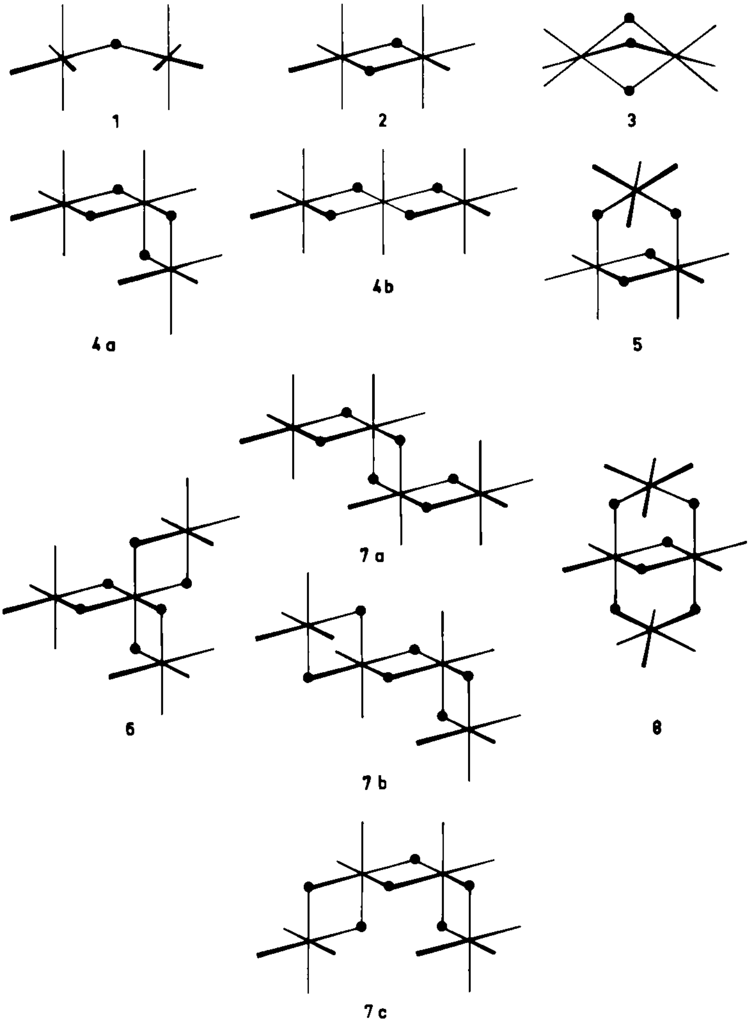


FIG. 1. The di-, tri-, and tetranuclear structures observed in X-ray crystal structures of hydroxo-bridged oligomers of cobalt(III), rhodium(III), iridium(III), or chromium(III); structures **4b**, **7b**, and **7c** have never been observed, but the last two have been mentioned as possible structures for two of the known isomers of $Cr_4(OH)_6^{6+}$

In the dinuclear complexes two octahedrally coordinated metal ions are bound together by one, two, or three hydroxide ions by sharing a corner, an edge, or a face, as shown in structures **1**–**3**. These mono-, di-, and trihydroxo-bridged binuclear structures are known for each of the metal ions chromium(III), cobalt(III), rhodium(III), and iridium(III), and many of these have been structurally characterized (cf. Tables I–III).

Further condensation of the dinuclear species may occur either by continuing the "edge-to-edge condensation," which leads to "linear" trinuclear structures such as **4a** and **4b**, or by condensation of a third chromium ion to each of the two chromium(III) centers in structure **2**, yielding the cyclic structure **5**. The $(NH_3)_4Co(OH)_2Co(CN)_2(OH)_2Co(NH_3)_4^{3+}$ cation (*49*) possesses structure **4a**, and there is good evidence that the trinuclear amine complex $Cr_3(en)_5(OH)_4^{5+}$ has the same structure (*42*). The linear trinuclear structure **4b** has not been observed in crystal structures. The cyclic, trinuclear structure **5** has been observed in crystal structures of chromium(III) complexes with ammonia, tacn, and bispicam (*40, 50, 51*).

The three different tetranuclear structures which have been observed in the crystalline state are the two compact structures **6** and **8** and the chain structure **7a**. Structure **6** is found in $[Co_4(NH_3)_{12}(OH)_6]Cl_6 \cdot 8H_2O$ and its amine analogs (*52–59*). The analogous ammonia and ethylenediamine chromium(III) complexes $Cr_4(NH_3)_{12}(OH)_6^{6+}$ and $Cr_4(en)_6(OH)_6^{6+}$ have been characterized quite recently (*40, 41, 42, 60*). Structure **7a** has so far been observed (*42*) only in a chromium(III) amine complex, $Cr_4(en)_6(OH)_6^{6+}$, but, as discussed in Section IV, both structures **7b** and **7c** are possible structures for the tetranuclear aqua chromium(III) species. Structure **8** is known from the so-called rhodoso complex, $Cr_4N_{12}(OH)_6^{6+}$ $[N_{12} = (NH_3)_{12}$ or $(en_6)]$ (*61, 62*).

In Tables I, II, and III selected bond distances and angles for mono-, di-, and trihydroxo-bridged complexes are compared. Most of the singly bridged species are chromium(III) complexes. The flexible hydroxo bridge in these complexes does not impose strain and the first coordination spheres of the two metal centers are generally close to being undistorted octahedra. The M–O–M angles vary greatly within the range 132–166°. Linear coordination is observed when oxide is the bridging ligand, as found in the so-called basic rhodo, $(NH_3)_5CrOCr(NH_3)_5^{5+}$, which has an M–O–M angle of exactly 180°.

When more than one bridge connects two metal ions, strain is imposed as reflected by the deviation from 90° for the O–M–O angles and by decreased M–O–M angles. The latter angles are typically 99–101° in dihydroxo-bridged complexes and 85–90° in trihydroxo-bridged complexes. These figures show that the triply bridged structures are, as anticipated, more strained than the doubly bridged structures. As discussed later, this correlates with the order of decreasing kinetic stability $OH > (OH)_2 > (OH)_3$.

TABLE I

CRYSTALLOGRAPHIC DATA FOR MONOHYDROXO-BRIDGED COMPLEXES[a]

Complex	M–O–M (deg)	M–M (Å)	⟨M–O⟩ (Å)	Reference
$[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$	165.6(9)	3.852(9)	1.97	*63*[b]
trans-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(H_2O)]^{5+}$	155.1(3)	3.873(2)	1.98	*64*[c]
cis-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH)]^{4+}$	142.8(5)	3.744(3)	1.97	*65*[d]
Δ,Λ-$[(OH)(en)_2Cr(OH)Cr(en)_2(OH)]^{3+}$	135.4(2)	3.677(2)	1.99	*66*[e]
Δ,Λ-$[(H_2O)(en)_2Ir(OH)Ir(en)_2(OH)]^{4+}$	131.9(3)	3.797(1)	2.08	*67*[f]

[a] In this and the following tables one standard deviation is given in parentheses.

[b] Chloride monohydrate. The structure of the dihydrate has also been reported and gave a Cr–O–Cr angle of 158.4(7) deg (*68*).

[c] Chloride trihydrate.

[d] Dithionate trihydrate.

[e] Perchlorate monohydrate.

[f] Dithionate perchlorate hydrate.

TABLE II

CRYSTALLOGRAPHIC DATA FOR DIHYDROXO-BRIDGED COMPLEXES[a]

Compound	M–O–M (deg)	M–M (Å)	⟨M–O⟩ (Å)	Reference
$(NH_3)_4Cr(OH)_2Cr(NH_3)_4^{4+}$	101.54(5)	3.045(1)	1.97	*69*[b]
Δ,Λ-$(en)_2Cr(OH)_2Cr(en)_2^{4+}$	103.42(8)	3.059(2)	1.95	*70*[c]
$\Delta,\Delta/\Lambda,\Lambda$-$(phen)_2Cr(OH)_2Cr(phen)_2^{4+}$	102.1(3)	2.986(4)	1.92	*39*[d]
Δ,Λ-$(gly)_2Cr(OH)_2Cr(gly)_2$	98.2(2)	2.974(2)	1.97	*71, 72*
Δ,Λ-$(mal)_2Cr(OH)_2Cr(mal)_2^{4-}$	99.34(7)	3.031(2)	1.99	*82*[e]
$(NH_3)_4Co(OH)_2Co(NH_3)_4^{4+}$	101.1(5)	2.932(5)	1.91	*73, 74*[f]
Δ,Λ-$(en)_2Co(OH)_2Co(en)_2^{4+}$	101.1(1)	2.951(1)	1.93	*75*[g]
trans-$(H_2O)(tacn)Rh(OH)_2Rh(tacn)(H_2O)^{4+}$	100.5(3)	3.138(1)	2.04	*76*[h]

[a] The crystal structures of the uncharged complexes $[CrL_4(OH)]_2$ with L_4 = $(S\text{-pro})_2$ (*77*), $(S\text{-ala})_2$ (*78*), (dipic)(H_2O) (*79*), (hydroxodipic)(H_2O) (*80*), (chlorodipic)(H_2O) (*80*), (edda) (*81*), and (en)(mal) (*82*); of $[Rh(\eta^3\text{-}C_3H_5)_2(OH)]_2$ (*83*); and of the salt of the ions $[Cr(mepic)_2(OH)]_2^{4+}$ (*84*), $[Cr(bispicen)(OH)]_2^{4+}$ (*85*), $[Cr(bispictn)(OH)]_2^{4+}$ (*86*), $[Cr(NH_3)_3(H_2O)(OH)]_2^{4+}$ (*87*), $[Co(NH_3)_3(H_2O)(OH)]_2^{4+}$ (*88*), $[Rh(\eta^5\text{-}C_5Me_5)(dmpz)(OH)]_2^{2+}$ (*89*), and $[Cr(ox)_2(OH)]_2^{4-}$ (*90*) have also been reported.

[b] Dithionate tetrahydrate. Data for the chloride tetrahydrate have been reported both for monoclinic (*69*) and for triclinic crystals (*91*).

[c] Diperchlorate dichloride dihydrate. Data for the dithionate (*92*), chloride (*93*), and bromide (*93*) salts have also been reported.

[d] Iodide tetrahydrate. The structure of the chloride hexahydrate has also been reported (*38*).

[e] Sodium salt pentahydrate.

[f] Chloride tetrahydrate.

[g] Nitrate.

[h] Perchlorate tetrahydrate.

TABLE III

Crystal Data for Trihydroxo-Bridged Complexes

Complex	⟨M–O–M⟩ (deg)	M–M (Å)	⟨M–O⟩ (Å)	Refere
$(NH_3)_3Co(OH)_3Co(NH_3)_3{}^{3+}$	83.3(6)	2.565	1.93	*94*[a]
$(dpt)Co(OH)_3Co(dpt)^{3+}$	85	2.579(1)	1.91	*95*[b]
$(C_5Me_5)Rh(OH)_3Rh(C_5Me_5)^{+}$	89.6(1)	2.9738(8)	2.109	*96*[c]
$(C_5Me_5)Ir(OH)_3Ir(C_5Me_5)^{+}$	92.8(3)	3.0709(7)	2.120	*96*[d]
$(metacn)Cr(OH)_3Cr(metacn)^{3+}$	84.1(3)	2.642(2)	1.97	*97*[e]
$(tacd)Cr(OH)_3Cr(tacd)^{3+}$	83	2.666(3)	1.99	*98*[f]

[a] Dithionate. The bromide and iodide salts have also been described (*99*).

[b] Perchlorate, racemic isomer. The three M–O–M angles are 85.2, 84.1, and 85.0°.

[c] Hydroxide undecahydrate. C_5Me_5 = η^5-pentamethylcyclopentadienyl.

[d] Acetate tetradecahydrate.

[e] Iodide trihydrate.

[f] Bromide dihydrate. The M–O–M angles vary from 81 to 84°.

The metal–oxygen (bridge) distance is close to that for terminally coordinated water or hydroxide. There seems to be no significant change in metal–oxygen (bridge) bond distances on going from singly to triply bridged complexes.

Crystal data for the trinuclear (structure **5**) and tetranuclear (structures **6**, **7a**, and **8**) complexes reveal bond distances and angles which are comparable to those observed in the mono- and dihydroxo-bridged binuclear complexes (*40, 42, 49, 50, 53, 54, 62, 87*).

Mixed bridge systems have been reported for chromium(III), cobalt(III), and rhodium(III), and the most common types are dinuclear doubly or triply bridged species: M(OH)(X)M, $M(OH)_2(X)M$, and $M(OH)(X)_2M$. Table IV summarizes crystallographic data for M(OH)(X)M species. For $X = O_2{}^{2-}$ the M–O–M angle approximates that in dihydroxo-bridged species, whereas for larger bidentate bridging groups such as sulfate, phosphate, and carboxylates the M–O–M angle is similar to that found in singly bridged complexes. In μ-oxo–μ-hydroxo chromium(III) complexes it is the oxo bridge which has the larger Cr–O–Cr angle; cf. the linearly coordinated oxo bridge in the so-called basic rhodo, $(NH_3)_5CrOCr(NH_3)_5{}^{4+}$ (Table V). This tendency of an oxo bridge toward linear coordination is rationalized by invoking π bonding stabilization, and it is clear that linear coordination gives maximum overlap between the lone pairs of the O^{2-} ligand and the *d* orbitals (see also Section III).

Crystallographic data for $M(OH)_2(X)M$ species ($X = NO_2{}^-$, $CO_3{}^{2-}$, $SO_4{}^{2-}$, and CH_3COO^-) and for $M(OH)(X)_2M$ species [$X_2 = (CH_3COO^-)(NH_2{}^-)$ and $(SO_4{}^{2-})_2$] have also been reported (*49, 51, 100–104*).

TABLE IV

Variations of the M–O–M Geometry with the Ligand X^{n-} in Hetero-Bridged Complexes

Complex	M–O–M (deg)	M–M (Å)	⟨M–O⟩ (Å)	Reference
Δ,Λ-$[(en)_2Cr(OH)(HPO_4)Cr(en)_2]^{3+}$	138.2(1)	3.662(1)	1.96	*105*[a]
Δ,Λ-$[(en)_2Cr(OH)(SO_4)Cr(en)_2]^{3+}$	137.4(2)	3.706(2)	1.99	*106*[b]
Δ,Λ-$[(en)_2Cr(OH)(CF_3COO)Cr(en)_2]^{4+}$	134.9(6)	3.616(2)	1.96	*107*[c]
Δ,Λ-$[(en)_2Co(OH)(O_2)Co(en)_2]^{3+}$	117.2(4)	3.289	1.93	*108*[d]
$\Delta,\Delta/\Lambda,\Lambda$-$[(en)_2Co(OH)(O_2)Co(en)_2]^{3+}$	114.4	3.272	1.95	*109*[e]
$[(NH_3)_4Co(OH)(NH_2)Co(CO_3)_2]$	96.4(1)	2.862(1)	1.92	*110*[f]
$\Delta,\Delta/\Lambda,\Lambda$-$[(mepic)_2Cr(OH)(O)Cr(mepic)_2]^{3+}$	95.0(2)	2.883(2)	1.96	*111*[g]

[a] Perchlorate monohydrate.

[b] Dithionate monohydrate.

[c] Bromide triperchlorate hydrate.

[d] Perchlorate.

[e] Nitrate dithionate dihydrate. The corresponding superoxo-bridged complex has similar structural data (*109*).

[f] Pentahydrate; Co–N–Co angle is 97.2(*1*)°.

[g] Bromide pentahydrate; see also Table V.

TABLE V

Crystallographic Data for Oxo-Bridged Complexes

Complex	M–O(H)–M (deg)	M–O–M (deg)	M–M (Å)	⟨M–O(H)⟩ (Å)	⟨M–O⟩ (Å)	Reference
$[(NH_3)_5Cr(O)Cr(NH_3)_5]^{5+}$	—	180	3.642(1)	—	1.82	*112, 113*[a]
$[(SCN)(tpyea)Cr(O)Cr(tpyea)(NCS)]^{2+}$	—	176.5(6)	3.628(12)	—	1.82	*114*[b]
$\Delta,\Delta/\Lambda,\Lambda$-$[(mepic)_2Cr(OH)(O)Cr(mepic)_2]^{3+}$	95.0(2)	100.6(2)	2.883(2)	1.96	1.87	*111*[c]

[a] Chloride monohydrate. [b] Tetraphenyl borate. [c] Bromide pentahydrate.

Each of the polynuclear systems (structures **1**–**8**) may exist in a number of isomers, depending on the nature of the nonbridging ligands. As seen from Tables I–V, the nonbridging ligands are in most cases polydentate amine ligands, and, particularly when these are unsymmetrical, a considerable number of geometric or optical isomers are possible. A few very common examples are discussed in the following paragraphs and other examples are given in subsequent sections.

The monohydroxo-bridged complexes of the type $L_5M(OH)ML_4X^{n+}$ are known for M = Cr(III) and may exist as cis and trans isomers; cis and trans refer to the position of X relative to the bridge. Both isomers of the "aqua erythro" cation $(NH_3)_5Cr(OH)Cr(NH_3)_4(H_2O)^{5+}$ are known and crystal structures of their salts have been reported (cf. Table I).

The dihydroxo-bridged binuclear complexes are among the most common, structurally well-characterized polynuclear complexes. For symmetrical bidentate nonbridging ligands, LL, the cation $(LL)_2M(OH)_2M(LL)_2^{n+}$ may exist in three isomeric forms: a meso isomer (Δ,Λ) with configuration Δ and Λ, respectively, at the two metal centers, and a racemic pair of isomers (Δ,Δ and Λ,Λ) with configuration Δ or Λ at each of the two metal centers (cf. Fig. 2). If the bidentate

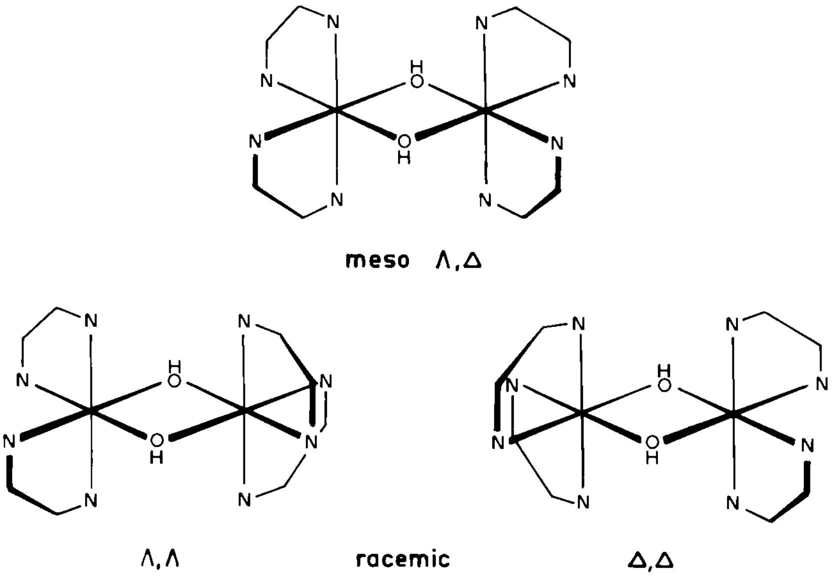


FIG. 2. Both the meso (Δ,Λ) and the racemic (Λ,Λ/Δ,Δ) isomers of the $(en)_2Cr(OH)_2Cr(en)_2^{4+}$ cation are known.

ligand is unsymmetrical or asymmetrical, the number of isomers increases considerably, and as an example it may be mentioned that unsymmetrical ligands, such as 1-(2-pyridyl)methylamine, give rise to 24 possible isomers (*115*). With chiral ligands such as 1-(2-pyridyl)-ethylamine, the number of possible isomers increases considerably (*84, 116*).

When higher polynuclears are taken into account, the number of isomers becomes enormous. Figure 1 shows five bridged skeletons for tetranuclear species containing six hydroxo bridges, but it is easily seen that there are many more possibilities. Each of these possible structures may further exist as a number of isomers, depending on the nature of the nonbridging ligand. The ethylenediamine complex $Co\{(OH)_2Co(en)_2\}_3^{6+}$—"Werner's brown salt"—can be taken as an example. This compound has structure **6**, and all eight possible configurational isomers, Δ(ΔΔΔ), Δ(ΔΔΛ), Δ(ΔΛΛ), and Δ(ΛΛΛ) and their enantiomers, have been characterized (*57*) (the first chirality symbol refers to the configuration about the CoO_6 chromophore and those in brackets to the remaining three CoN_4O_2 chromophores). If the conformations of the chelate ring systems are also considered, then these eight *configurational* isomers embrace a total of 208 *conformational* isomers (*117*).

Intramolecular hydrogen bonds play a significant structural role; the most important interactions involve hydroxide, either as a terminally coordinated ligand (α-type interactions) or as a bridging ligand (β-type interactions). In α-type interactions the hydrogen donor group may be a terminally coordinated water or ammonia ligand or another terminal hydroxide ligand (Fig. 3A). Interaction of this kind was first proposed to account for the unusual acid properties of monohydroxo-bridged

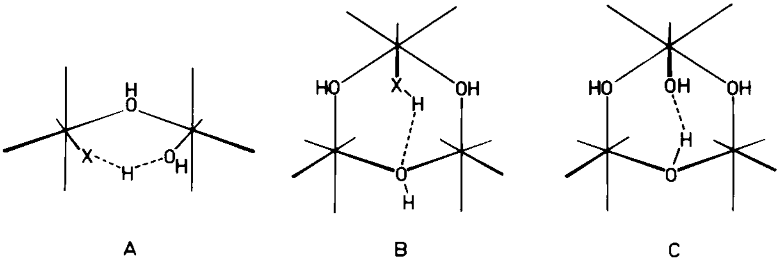


FIG. 3. Intramolecular hydrogen bonds involving two terminally coordinated ligands (α type) as shown in A ($X = OH_2$, NH_3, or OH^-) or a terminally coordinated ligand and bridging hydroxide (β type) as shown in B ($X = OH_2$ or NH_3) or in C.

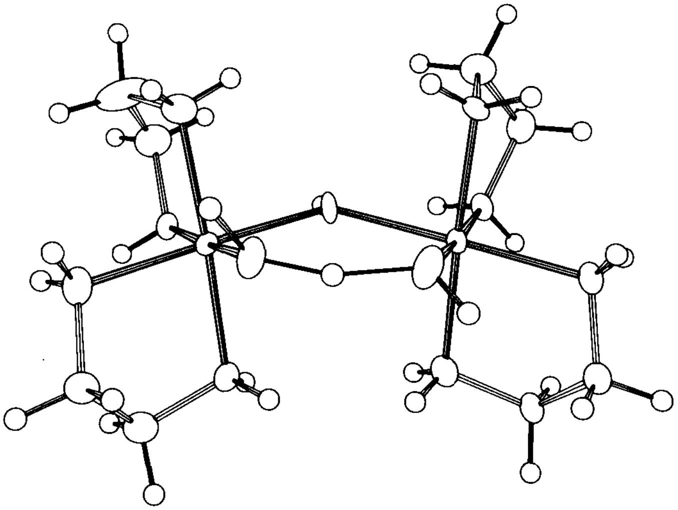


FIG. 4. The Δ,Λ-$(H_2O)(en)_2Ir(OH)Ir(en)_2(OH)^{4+}$ cation is forced into a fixed conformation by a strong and symmetrical intramolecular hydrogen bond interaction of the α type. The O_1–O_2 distance is 2.429(9) Å. Reprinted with permission from Galsbøl, F., Larsen, S., Rasmussen, B., and Springborg, J., *Inorg. Chem.* **25**, 290 (1986). Copyright (1986) American Chemical Society.

complexes of the cis type, $(H_2O)L_4M(OH)ML_4(H_2O)^{5+}$, as further discussed in Section VI. Evidence for such α-type interactions in the solid state has recently been obtained from an X-ray crystal-structure analysis (*67*) of the perchlorate dithionate salt of the Δ,Λ-$(H_2O)(en)_2Ir(OH)Ir(en)_2(OH)^{4+}$ cation (Fig. 4). The terminally coordinated hydroxo and aqua groups in this cation interact by a very short symmetrical hydrogen bond with an O–O distance of 2.429(9) Å. A similar, but weaker, α-type interaction has been observed in the structure (*66*) of Δ,Λ-$[(OH)(en)_2Cr(OH)Cr(en)_2(OH)](ClO_4)_3$, as shown in Fig. 5. The M–O–M angle in the latter complex (135.4°) is larger than that in the aqua hydroxo iridium(III) complex (131.9°), but both angles are much smaller than the Cr–O–Cr angle in, e.g., the $(NH_3)_5Cr(OH)Cr(NH_3)_5{}^{5+}$ cation (165.6°). The fact that the cis hydroxo "erythro" ion has a significantly smaller M–O–M angle than that of the trans aqua isomer is also explicable in terms of a weak α-type interaction in the former cation. These variations demonstrate how hydrogen bond interactions force the monohydroxo-bridged cation into a fixed conformation, with the result that the M–O–M angle

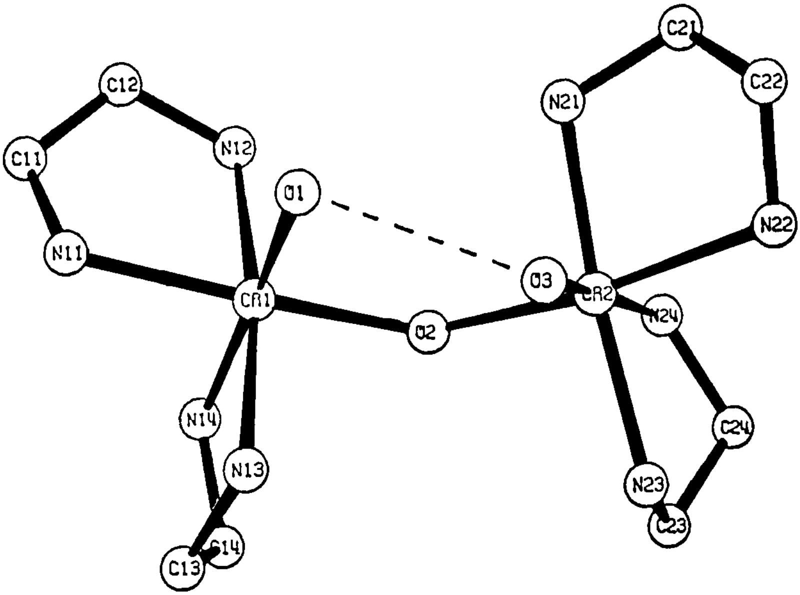


FIG. 5. The Δ,Λ-$(HO)(en)_2Cr(OH)Cr(en)_2(OH)^{3+}$ cation, like the iridium(III) analog in Fig. 4, is forced into a fixed conformation by a hydrogen bond interaction of the α type. The O O distance is 3.004(6) Å. Redrawn with permission from Kaas, K., *Acta Crystallogr.* *B* **35**, 1603 (1979).

approaches that in M(OH)(X)M complexes, where X is a bidentate-bridging ligand (cf. Tables I and IV.)

In β-type interactions the hydroxo bridge may act as hydrogen acceptor when the other group is a stronger acid, such as a terminally coordinated ammonia or water ligand (Fig. 3B); it may also act as hydrogen donor with a basic group such as a terminally coordinated hydroxide ligand (Fig. 3C). Interaction of the first kind has been observed in the crystal structures of the trinuclear complex (*40*) $Cr_3(NH_3)_{10}(OH)_4^{5+}$ (structure **5**, Fig. 1) and the tetranuclear rhodoso complexes (*61, 62*) $Cr_4L_{12}(OH)_6^{6+}$ [$L_{12} = (NH_3)_{12}$ or $(en)_6$; structure **8**, Fig. 1]. Figure 6 shows how the CrN_4O_2 units in the tetranuclear rhodoso complexes are tilted as a result of two β-type interactions. Similar interactions ($X = H_2O$ in Fig. 3B) have been proposed to play an important role in the stability differences observed for various isomers of the aqua chromium(III) oligomers (*118*). The crystal structure (*50*) of the trinuclear complex $Cr_3(tacn)_3(OH)(\mu\text{-}OH)_4^{5+}$ indicates a β-type interaction of the kind shown in Fig. 3C.

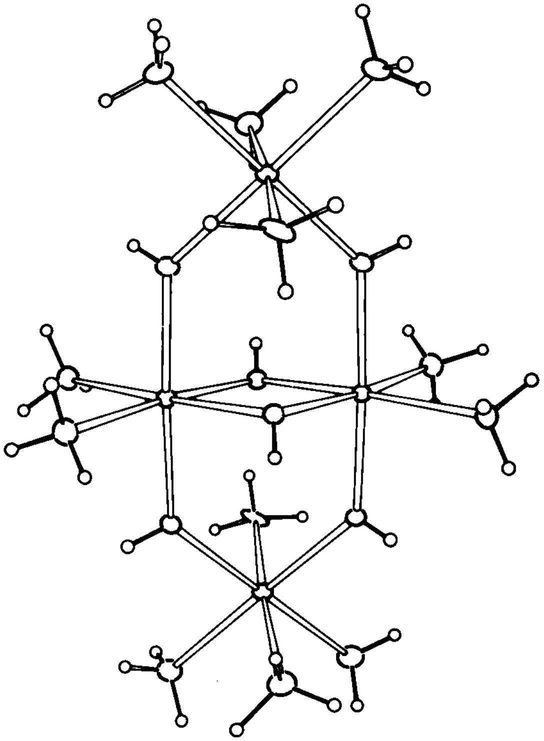


FIG. 6. The cation $Cr_4(NH_3)_{12}(OH)_6^{6+}$. The two CrN_4O_2 units are tilted, owing to hydrogen bond interaction of the β type (between μ-OH and NH_3). Reprinted with permission from Bang, E., *Acta Chem. Scand.* **A38**, 419 (1984).

III. Spectroscopic and Magnetic Properties

Cobalt(III), rhodium(III), and iridium(III) complexes are d^6 systems with diamagnetic ground states. The absorption spectra of the hydroxo-bridged cobalt(III) complexes usually show two broad bands in the visible region assigned as spin-allowed transitions from $^1A_{1g}$ to $^1T_{1g}$ and $^1T_{2g}$ (O_h symmetry), respectively. In, e.g., the dihydroxo-bridged complexes $(NH_3)_4Co(OH)_2Co(NH_3)_4^{4+}$ and Δ,Λ-$(en)_2Co(OH)_2$-$Co(en)_2^{4+}$, the second ligand-field bands are partially obscured by overlap with an intense charge transfer band. The visible absorption spectra of the rhodium(III) and iridium(III) complexes are interpreted in the same way, but for these complexes the second ligand field is normally completely obscured by an intense charge transfer band.

TABLE VI

ABSORPTION SPECTRA OF SOME HYDROXO-BRIDGED AMMINE AND AMINE COMPLEXES IN AQUEOUS SOLUTION

Complex	$(\varepsilon, \lambda)_{max}$[a]			Reference
$(NH_3)_5Cr(OH)Cr(NH_3)_5^{5+}$	(95, 498)	(76, 372)		*129*
trans-$(NH_3)_5Cr(OH)Cr(NH_3)_4(H_2O)^{5+}$	(76, 502)	(78, 373)		*129*
cis-$(NH_3)_5Cr(OH)Cr(NH_3)_4(H_2O)^{5+}$	(96, 505)	(69, 376)		*129*
cis,cis-$(H_2O)(NH_3)_4Cr(OH)Cr(NH_3)_4(H_2O)^{5+}$	(98, 514)	(63, 380)		*36*
cis,cis-$(H_2O)(NH_3)_4Cr(OH)Cr(NH_3)_4(OH)^{4+}$	(98, 520)	(77, 386)		*36*
cis,cis-$(HO)(NH_3)_4Cr(OH)Cr(NH_3)_4(OH)^{3+}$	(100, 534)	(91, 402)		*36*
$(NH_3)_4Cr(OH)_2Cr(NH_3)_4^{4+}$	(125, 536)	(67, 387)		*36*
Δ,Λ-$(en)_2Cr(OH)_2Cr(en)_2^{4+}$	(199, 540)	(107, 386)		*33*
$\Delta,\Delta/\Lambda,\Lambda$-$(en)_2Cr(OH)_2Cr(en)_2^{4+}$	(190, 539)	(102, 384)		*35*
$(metacn)Cr(OH)_3Cr(metacn)^{3+}$	(103, 505)	$(56, 378)_{sh}$	(90, 342)	*97*
$(NH_3)_5Co(OH)Co(NH_3)_5^{5+}$	(174, 529)[b]	$(282, 370)_{sh}$[b]		*130*
$(NH_3)_4Co(OH)_2Co(NH_3)_4^{4+}$	(195, 528)	$(187, 370)_{sh}$	(2650, 287)	*131*
$(NH_3)_3Co(OH)_3Co(NH_3)_3^{3+}$	(135, 526)	(263, 364)	(1780, 296)	*132*
cis,cis-$(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(H_2O)^{5+}$	(464, 338)	(426, 274)		*133*
$(NH_3)_4Rh(OH)_2Rh(NH_3)_4^{4+}$	(305, 336)			*133*
$(tacn)Rh(OH)_3Rh(tacn)^{3+}$	(437, 340)			*76*
Δ,Λ-$(H_2O)(en)_2Ir(OH)Ir(en)_2(H_2O)^{5+}$	(520, 271)			*67*
Δ,Λ-$(en)_2Ir(OH)_2Ir(en)_2^{4+}$	(393, 271)			*67*

[a] ε in liters cm^{-1} (mol dinuclear)$^{-1}$ and λ in nanometers.

[b] Medium is dimethyl sulfoxide.

Some representative spectral data are given in Table VI. The spectroscopic properties of μ-hydroxo–μ-peroxo and μ-hydroxo–μ-superoxo dicobalt(III) complexes have recently been reviewed by Fallab and Mitchell (*119*) and seem reasonably well rationalized in terms of the molecular orbital (MO) models formulated by Lever and Gray (120). The spectra of μ-hydroxo–μ-peroxo and μ-hydroxo–μ-superoxo complexes of rhodium(III) show features similar to those of the cobalt(III) species (*121–124*).

The spectral and magnetic properties of hydroxo-bridged polynuclear chromium(III) complexes have been studied intensely during the last two decades and two slightly different theoretical models have been presented by Güdel and co-workers and by Glerup, Hodgson, and Pedersen (*125–128*). The contributions from each of these two groups of authors suffer from a complete lack of discussion of the work done by the other group. For a nonspecialist within this field, such as the present author, it has therefore been difficult to decide to what extent the two groups employ different physical models rather than merely different formalisms. The following presentation is based essentially on the work presented by Glerup, Hodgson, and Pedersen.

The visible absorption spectra typically show (Table VI) two broad and intense bands which correspond to the spin-allowed transitions from $^4A_{2g}$ to $^4T_{2g}$ and $^4T_{1g}$ (O_h symmetry), respectively, observed in mononuclear species. In addition, weak but sharp absorption bands are often observed (*131*), and this is particularly pronounced in the spectrum of the classical compound "basic rhodo," $(NH_3)_5CrOCr(NH_3)_5^{4+}$, which also shows three very intense and sharp bands in the near UV region, as shown in Fig. 7. The oxo-bridged basic rhodo has a magnetic moment of about 1 BM per chromium at room temperature,which is very much lower than the theoretical "spin-only" value of 3.87 BM and the values found experimentally for monomeric chromium(III) complexes (in the range 3.5–4.0 BM) (*134*). This is explained in terms of coupling between the two paramagnetic ($S = 3/2$) chromium(III) centers. This mixing of the two quartet ground states ($^4B_1$ in C_{4v} or $^4A_{2g}$ in O_h symmetry) gives rise to $^1A_{1g}$, $^3A_{2u}$, $^5A_{1g}$, and $^7A_{2u}$ ground levels (D_{4h} symmetry). The Heisenberg Hamiltonian $H = JS_1 \cdot S_2$ describes the splitting of these levels. As shown by Pedersen, the magnetic properties of basic rhodo are in accordance with such a model, a separation of $J = 450$ cm^{-1} between the singlet ground state and the triplet state being found (*134*). Within the framework of the Angular Overlap Model, Glerup has presented a model to calculate the antiferromagnetic coupling and absorption spectra of basic rhodo (*125*). The model assumes that two *p* orbitals of the bridging

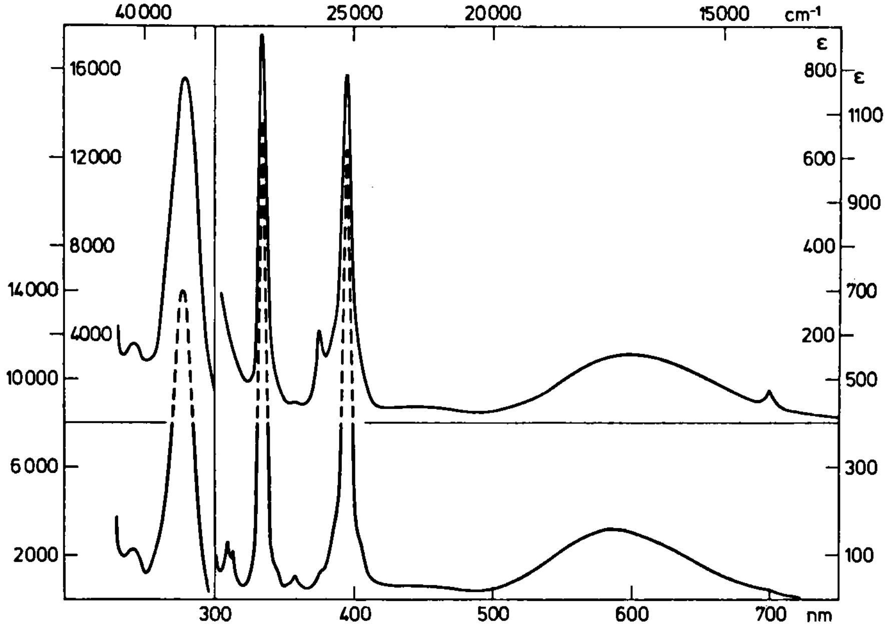


FIG. 7. Antiferromagnetic coupling. Absorption spectra of $(NH_3)_5CrOCr(NH_3)_5{}^{4+}$ in 4 : 1 ethanol : methanol mixture. The upper curve is measured at 230 K and the lower curve at 121 K. Reprinted with permission from Glerup, J., *Acta Chem. Scand.* **26**, 3775 (1972).

oxygen participate in π bonds with d orbitals at each of the chromium centers. The antiferromagnetic coupling in the dinuclear system is then explained by a one-electron interaction between atomic orbitals situated on each of the chromium atoms. Through configuration interaction between the lowest levels and the charge transfer levels this one-electron interaction gives rise to the Landé interval rule for an antiferromagnetic coupling with the singlet as the ground state. Furthermore, one-electron interaction mixes doubly excited levels with allowed one-electron charge transfer levels, whereby transitions to doubly excited levels become allowed. The sharp bands mentioned above (Fig. 7) are thus assigned as spin-allowed transitions (double excitations) between the singlet and triplet ground states of the coupled chromophores ($^1A_{1g}$ and $^3A_{2u}$) to the excited singlet and triplet states.

Glerup's model can be extended to many other systems (*135, 136*). For example, an extension of the model has been used to interpret the magnetic properties of di-μ-hydroxo dichromium(III) complexes. It was shown (*126*) that the model semiquantitatively relates the magnitude of the antiferromagnetic coupling to the Cr–O–Cr bridging angle, the Cr–O bond length, and the angle Θ between the bridging plane and the OH vector of the bridging group. The model uses these parameters in the Angular Overlap Model to account for the influence of geometry on competing ferro- and antiferromagnetic contributions. These have previously been expressed either by the van Vleck Hamiltonian $H = JS_1 \cdot S_2$, the expanded Hamiltonian including a biquadratic exchange term $j\ (S_1 \cdot S_2)^2$ or an entirely generalized Hamiltonian. A very satisfactory contribution made by the Angular Overlap Model is a dominating relationship between the angle Θ and the magnitude of the exchange coupling. This correlation demonstrates clearly the π interaction between d orbitals at the two chromium(III) centers (d_{zx} and d_{yz}) through the p_z orbitals on the bridging oxygens. If the hydrogen atom of the bridging OH lies in the Cr_2O_2 ring plane ($\Theta = 0°$), then the lone pair is a pure p_z orbital perpendicular to the plane, corresponding to a maximum value of the π-overlap integral. This value decreases as the hydrogen atom moves out of the plane. The model therefore predicts, in agreement with experiment, that an increasing Θ angle is associated with a decreasing π interaction and therefore also with a decreasing J value (*69, 85, 86, 91, 126*). The model has been applied equally successfully to di-μ-oxo and di-μ-alkoxo complexes (*111, 126*). Table VII illustrates how J varies with Θ for some dibridged binuclear complexes.

Only a few trihydroxo-bridged chromium(III) complexes have been studied. The cation $(\text{metacn})Cr(OH)_3Cr(\text{metacn})^{3+}$ has $J = 128\ \text{cm}^{-1}$ (137, 138), and the corresponding tacd complex has $J = 96\ \text{cm}^{-1}$ (*98*).

Inelastic neutron scattering experiments have been used to study the ground state splitting of singly bridged dichromium(III) complexes of

TABLE VII

VARIATION OF THE COUPLING CONSTANT J WITH THE ANGLE Θ BETWEEN THE OH VECTOR AND THE BRIDGING PLANE[a]

Compound	Θ (deg)	J (cm^{-1})
Δ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2](S_2O_6)_2$	57(3)	3.4(1)
$[(NH_3)_4Cr(OH)_2Cr(NH_3)_4]Cl_4 \cdot 4H_2O$	41(3)	5.23(1)
$[(NH_3)_4Cr(OH)_2Cr(NH_3)_4](S_2O_6)_2 4H_2O$	24(3)	9.12(1)
Δ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2]Cl_4 \cdot 2H_2O$	5(3)	29.4(5)
Δ,Δ/Λ,Λ-$[(\text{mepic})_2Cr(OH)_2Cr(\text{mepic})_2](S_2O_6)_2 \cdot 2H_2O$	0(5)	32.9(1)
Δ,Δ/Λ,Λ-$[(\text{phen})_2Cr(OH)_2Cr(\text{phen})_2]Cl_4 \cdot 6H_2O$	0(10)	43.0(5)

[a] From Ref. *126*.

the type mentioned above, and the calculated exchange parameters were found to agree with those obtained from the optical and magnetochemical studies (*139–141*).

Only a very few polynuclear complexes containing more than two chromium(III) centers have been studied so far. However, magnetochemical and inelastic neutron scattering studies, heat capacity measurements, and emission spectroscopy have been reported for various tetranuclear species (*40, 142–151*). Two review articles dealing with the spectroscopic and magnetic properties of chromium(III) oligomers have recently appeared (*127, 128*).

The circular dichroism (CD) spectra of optically active di-, tri-, and tetranuclear complexes of chromium(III) and cobalt(III) have been reported and used to establish the complexes' absolute configurations (*55–59, 111, 115, 116, 152–157*). The changes in circular dichroism resulting from ion pairing have been studied for the tetranuclear "hexol" $\mathrm{Co\{(OH)_2Co(NH_3)_4\}_3^{6+}}$ and have been shown to be attributable to the vicinal effect of the chiral oxygen centers produced stereospecifically by the ion-pair formation (*56*). For a series of trinuclear cobalt(III) amine complexes, *cis*-$\mathrm{Co(CN)_2\{(OH)_2Co(N_4)_2\}^{3+}}$, it was shown that the main CD contributions due to the two chiral $\mathrm{Co(OH)_4(CN)_2}$ and $\mathrm{Co(N_4)(OH)_2}$ centers are additive (*155*). In the case of the related tetranuclear complex $\mathrm{Co\{(OH)_2Co(en)_2\}_3^{6+}}$ this postulate of additivity of CD spectra proved unsatisfactory (*57*).

IV. Formation of Polynuclear Complexes

A. HYDROLYSIS REACTIONS

Formation of hydroxo-bridged complexes by hydrolysis in aqueous solution is, not surprisingly, the most common preparative method. As a rule, such reactions give quite complex product mixtures containing species with different nuclearities, each of which may be present in many isomeric forms. The fact that most of the preparative procedures employed lead to the isolation of one single and pure isomer probably more often reflects favorable solubility properties rather than stereospecificity. In some cases ion-exchange chromatography has been used to isolate the polynuclear species, but systematic analysis of hydrolysis mixtures by this technique has been reported for only a few systems.

1. Dinuclear Complexes

The majority of the oligomers which have been prepared are dinuclear species containing one, two, or three hydroxo bridges. Although the hydrolysis process must always lead to initial formation of monohydroxo-bridged species, these are practically never synthesized by this route, essentially because of their unfavorable thermodynamic properties. For example, single bridged chromium(III) and cobalt(III) species of the type $L_5M(OH)ML_5^{(2n-1)+}$ (L is an inert ligand such as ammonia) are well known but have never been prepared by hydrolysis of $ML_5(H_2O)^{n+}$, probably as a consequence of small formation constants (Q_{21}; see Section V). The brown monohydroxo-bridged cobalt(III) complex $[(PBu_3)(salen)Co(OH)Co(salen)(PBu_3)]^+$ has been isolated as a perchlorate by adding aqueous NaOH to an ethanolic solution of the green monomer $[Co(PBu_3)(salen)]ClO_4$. The binuclear complex is stable only as a solid or in a nonpolar solvent (*158*). A report to the effect that the trans isomers of $Co(en)_2(Cl)(H_2O)^{2+}$ and $Co(en)_2(Cl)(OH)^+$ react together in cold aqueous solution to give a monohydroxo-bridged species would seem to require further corroboration (*159*). Singly bridged species of the type $(H_2O)L_4M(OH)ML_4(OH)^{4+}$ are in general easily formed from the corresponding mononuclear species, but they are often (although not always; see Table XXVIII) unstable with respect to further condensation to, e.g., dihydroxo-bridged species, and they are therefore more conveniently prepared via the dihydroxo-bridged species, as described in Section IV,D.

A very large number of dihydroxo-bridged chromium(III) and cobalt(III) complexes have been synthesized from the parent mononuclear species by aqueous hydrolysis, as shown in Eq. (1) for a cationic species, but also neutral and

$$2\,cis\text{-}ML_4(H_2O)(OH)^{n+} \rightleftharpoons L_4M(OH)_2ML_4^{2n+} + 2H_2O \qquad (1)$$

anionic species have been made by this reaction. Cationic chromium(III) complexes which have been prepared by reaction Eq. (1) have been reported for $L_4 = (H_2O)_4$ (*26, 28, 29*), $(NH_3)_4$ (*131*), $(NH_3)_3(H_2O)$ (*87*), ibn (*160*), $(en)_2$ (*131*), (tacn)(H_2O) (*50*), (tame)(H_2O) (*50*), $(phen)_2$ (*37, 161*), $(bipy)_2$ (*37, 161*), and (phen)(bipy) (*153*), and for a series of pyridyl-substituted bi-, tri-, and tetradentate N ligands (*51, 55, 85, 86, 111, 115, 116, 152, 154, 157, 162*). Neutral complexes have been reported for L_4 = edda (*81, 163*), (en)(mal) (*82*), (H_2O)(dipic) (*79*), (H_2O)(chlorodipic) (*80*), (H_2O)(hydroxodipic) (*80*), and a very large number of amino acids, $L_4 = [RCH(NH_2)COO^-]_2$ (*77, 78, 164–169*). Anionic complexes are known for $L_4 = (ox)_2$ (*8*), $(mal)_2$ (*170*), and nta (*48, 171*). The ligand squarate leads to formation of a quadruply bridged complex, $(H_2O)_2Cr(C_4O_4)_2(OH)_2Cr(H_2O)_2$, which has been characterized by a crystal-structure analysis (*172, 173*). One of the few cationic cobalt(III) complexes which can be prepared by reaction Eq. (1) is the tren complex (*174*). Neutral cobalt(III) complexes made by reaction Eq. (1) have been reported for $L_4 = (NO_2)_2(NH_3)_2$ (*174*), $(RCH(NH_2)COO^-)_2$ (*169*), and for $(H_2O)(bh)$ (*175*) (bh is a series of benzoyl hydrazones). Anionic cobalt(III) complexes made by reaction Eq. (1) have been reported for $L_4 = (ox)_2$ (*176*), nta (*177–179*), and for a series of analogs of nta (*180*).

The yields of the dihydroxo-bridged complexes vary and are often relatively low, probably owing to the formation of different isomers and higher polynuclear complexes and to hydrolysis of the ligand L. For many of the complexes listed above, the preparative procedures involved the preparation of the mononuclear species *in situ*.

The chromium(III) complexes with the ligands 1,10-phen and 2,2′-bipy have been obtained by boiling aqueous chromium(III) solutions in the presence of the ligand and slowly adding the appropriate amount of strong base (*37, 161, 181*). Similarly, the chromium(III) complexes with pyridyl-substituted bidentate and tetradentate amines (*86, 111, 115, 116, 152, 157*) have been prepared by the reaction of $Cr(H_2O)_6^{3+}$ with the amine in the presence of zinc dust [or chromium(II)]. The use of organic solvents such as 2-methoxyethanol seems to facilitate the formation of dinuclear hydroxo-bridged complexes to a greater extent than the formation of mononuclear complexes. Chromium(III) complexes with amino acid anions as nonbridging bidentate ligands have been prepared by allowing an aqueous solution of $Cr(NH_3)_6^{3+}$ to react with amino acid at the appropriate pH (*77, 164–166*). Strictly speaking, therefore, it is by no means certain that these reactions proceed via Eq. (1), although such a route seems very feasible.

It should be stressed that some of the complexes mentioned above are more easily made by other routes. The complex $(H_2O)_4Cr(OH)_2(H_2O)_4^{4+}$ is produced quantatively by the Tl^{3+} oxidation of aqueous chromium(II), but only in low yield by reaction Eq. (1) (*30, 31*). The complex Δ,Λ-$(en)_2Cr(OH)_2Cr(en)_2^{4+}$ is obtained (*16*) in good yield by reaction Eq. (1), and the yield may be increased by working in methanolic solution (*182*). However, the solid-state reaction (*131*) described below (Section IV,B) gives this complex in essentially quantitative yield.

With a few exceptions, all of the dihydroxo-bridged complexes listed above may exist in several, and often many, isomeric forms. The topic is discussed briefly in Section II, and a few additional comments seem relevant in the present context.

Hydrolysis of *cis*-$Cr(en)_2(H_2O)(OH)^{2+}$ probably gives a mixture of racemic (Δ,Δ and Λ,Λ) and meso (Δ,Λ) isomers (Fig. 2). Both forms are known but only the meso isomer has been isolated from the reaction mixture as the sparingly soluble bromide salt (*33*, *35*). The bromide salt of the racemic form is very soluble, and it has been prepared as described in Section IV,D.

Hydrolysis of the analogous mononuclear 1,10-phen and 2,2′-bipy chromium(III) complexes yields the racemic (Δ,Δ and Λ,Λ) dinuclear isomers in high yield, the formation of the meso (Δ,Λ) isomer not being observed. The apparent stereospecificity in these reactions has been explained in terms of steric hindrance in the meso isomer arising from repulsion between the α-hydrogen atoms of ligand molecules attached to each metal ion, as illustrated in Fig. 8 (*37*). Direct resolution of both the 1,10-phen and the 2,2′-bipy complex into the enantiomers has been reported (*161*, *183*), thereby providing evidence for the racemic configuration; this has later been confirmed by a single-crystal X-ray structure analysis of the 1,10-phen complex (*38*, *39*). The $(-)_{589}$ isomers of these 1,10-phen and 2,2′-bipy complexes have been tentatively assigned (*153*) the absolute configuration Δ,Δ on the basis of the

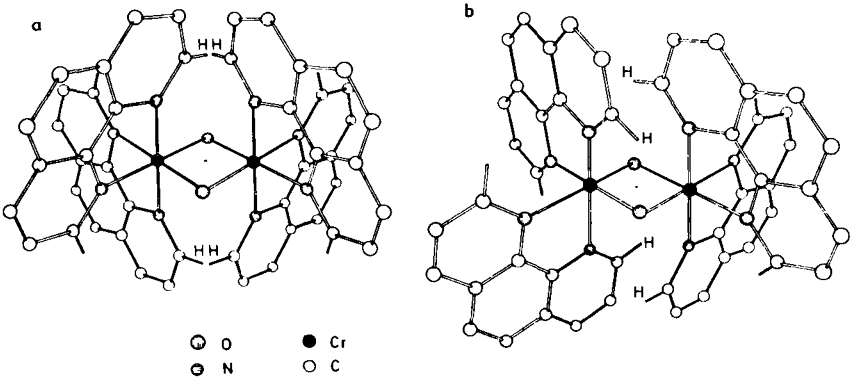


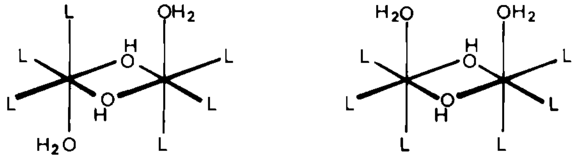
FIG. 8. Schematic drawing of the Δ,Λ and Λ,Λ forms of $(phen)_2Cr(OH)_2Cr(phen)_2^{4+}$. (a) Δ,Λ Isomer—the hydrogen atoms on different ligand molecules, HH, near the plane of symmetry, are seen to be very close; (b) Λ,Λ isomer—nonbonded hydrogen interactions are unimportant. Reprinted with permission from Josephsen, J., and Schäffer, C. E., *Acta Chem. Scand.* **24**, 2929 (1970).

empirical rule (derived originally for mononuclear species) that a negative major CD component in the first ligand absorption band is associated with configuration Δ (*184*).

A series of pyridyl-substituted bi-, tri-, and tetradentate amine complexes of chromium(III) has been studied by Michelsen and coworkers, and like the ethylenediamine complex, for example, these complexes may in principle occur in racemic (Δ,Δ and Λ,Λ) and meso (Δ,Λ) forms (*51, 85, 86, 111, 115, 116, 152, 157, 162*). However, the total number of possible isomers is considerably larger as a result of diastereoisomerism. Despite the large number of possible isomers, the hydrolysis reaction Eq. (1) apparently occurs with a high degree of stereoselectivity, and for each ligand only a few isomers are formed in reasonably high yield, and they are all of the types Δ,Δ and Λ,Λ. These selectivities are presumably a consequence of interactions between two pyridyl moieties attached either to one chromium(III) or to two different chromium(III) centers. The structures of some of these complexes have been established by single-crystal X-ray structure analyses (*84–86, 111*), but strong evidence for the proposed structures has also been provided by steric considerations, by qualitative analysis of the CD spectra, and by analysis of the cleavage products of hydrolysis in concentrated strong acids.

As mentioned above, several chromium(III) complexes containing amino acids as nonbridging ligands have been reported. In general only a very limited investigation of the chemistry of these complexes has been made, but several of the complexes have been characterized by single-crystal X-ray structure analysis. Despite the fact that the number of possible isomers (e.g., 24 with glycine) is very large, the isolated products appear in most cases to be pure, single isomers. This would seem to indicate a high degree of stereoselectivity, as substantiated by the observation that the reaction with glycine yields a Δ,Λ isomer which has the same structure as the complex formed with *S*-alanine (*71, 72, 78*). However, differences in the solubilities of the various isomers are likely to play an equally important role in this apparent stereospecificity e.g., with L-proline an isomer with configuration Δ,Δ can be isolated (*77*).

Hydrolysis of $ML_3(H_2O)_3^{3+}$ by reaction Eq. (1) gives dihydroxo-bridged species which may exist in several isomeric forms. For $(L)_3 = (NH_3)_3$ there are five possible isomers; if only facial coordination is considered then the number of isomers is reduced to two, the so-called cis and trans isomers (see Fig. 9). The ammonia, tame, and tacn chromium(III) complexes mentioned previously have all been isolated as their trans isomers. Similarly it has been found that



trans cis

FIG. 9. The so-called trans and cis isomers obtained by condensation of two facial $ML_3(H_2O)_3^{3+}$ cations.

$Rh(tacn)(H_2O)_3^{3+}$ reacts by Eq. (1) forming a trans isomer (*76*). Likewise, the analogous cobalt(III) complexes with $L_3 = (NH_3)_3$, dien, tach, and tacn are also exhaustively trans isomers (*88, 132, 174, 185–187*).

As well as yielding dihydroxo-bridged species, hydrolysis of *fac*-$ML_3(H_2O)_3^{3+}$ may give trihydroxy-bridged species by reaction Eq. (2). This behavior has been reported for chromium(III), cobalt(III), and rhodium(III), but not for iridium(III).

$$fac\text{-}ML_3(H_2O)(OH)_2^{+} + fac\text{-}ML_3(H_2O)_2(OH)^{2+} \rightleftharpoons L_3M(OH)_3ML_3^{3+} + 3H_2O \qquad (2)$$

Cobalt(III) complexes made by reaction Eq. (2) have been reported for $L_3 = (NH_3)_3$, dien, $(py)_3$, tacn, and tach (*99, 132, 174, 185, 186, 188*). For L_3 = dpt and metacn, trihydroxo-bridged cobalt(III) complexes have been prepared by oxidation (O_2 or H_2O_2) of aqueous cobalt(III) solutions in the presence of the amine (*95, 97*). The dpt complex has also been made by hydrolysis of $Co(dpt)_2^{3+}$ in aqueous solution (*95*).

Trihydroxo-bridged complexes of chromium(III) appear to be much more difficult to synthesize than their cobalt(III) analogs. As mentioned above, hydrolysis of *fac*-$Cr(NH_3)_3(H_2O)_3^{3+}$ yields predominantly dihydroxo-bridged species, and if any hydrolysis does occur by reaction Eq. (2), then the content of the trihydroxo-bridged species is at the very least considerably smaller (*40*) than clamined in an early report (*189*). Similarly, for L_3 = tame and tacn, the facial isomers of $CrL_3(H_2O)_3^{3+}$ do not appear to hydrolyze by reaction Eq. (2), but give dihydroxo-bridged species. To date, the only well-documented trihydroxo-bridged complexes of chromium(III) are $(metacn)Cr(OH)_3Cr(metacn)^{3+}$ and the corresponding tacd complex, which have both been obtained by reaction Eq. (2) (*97, 98*). The tacn and metacn rhodium(III) analogs have been obtained by reaction Eq. (2) (*76, 97*).

Finally it should be mentioned that several dinuclear trihydroxo-bridged η^5-pentamethylcyclopentadienylrhodium(III) and iridium(III) complexes have been characterized, as has also a dinuclear dihydroxo-bridged η^3-allylrhodium(III) species (*83, 89, 96, 190 192*).

2. *Higher Oligomers*

There are several examples of well-characterized tri- and tetranuclear hydroxo-bridged complexes of chromium(III) and cobalt(III). Penta- and hexanuclear aqua chromium(III) complexes have been prepared in solution, but their structure and properties are unknown. Oligomers of nuclearity higher than four have not been reported for cobalt(III), with the exception of some hetero-bridged heteronuclear species (*193, 194*). There appear to be no reports of rhodium(III) or iridium(III) complexes of nuclearity higher than two.

Most of the higher chromium(III) oligomers are made by hydrolytic condensation in aqueous solution. Condensation of mono- and dinuclear species gives trinuclear species and, as shown for the aqua chromium(III) system, tetranuclear species may be formed either by condensation of two dinuclear species or by condensation of mononuclear species with trinuclear species (*31*). As expected, these higher oligomers are obtained under more vigorous conditions than the dinuclear species described above, either by prolonged aging or by aging at higher temperature. As an example it can be mentioned that aging of an aqueous solution of *fac*-$Cr(tacn)(H_2O)_3^{3+}$ under mild conditions (25°C, 1 day) leads to formation of the dinuclear species *trans*-$(H_2O)(tacn)Cr(OH)_2Cr(tacn)(H_2O)^{4+}$ in high yield, but under more vigorous conditions (100°C, 3 days) such a solution forms the trinuclear complex $Cr_3(tacn)_3(OH)_5^{4+}$ (*50*). Optimal conditions may, as in this example, lead to a high yield of a specific isomer, but in general such aged solutions contain a large number of higher oligomers, and the isolation of the individual species usually involves separation by cation-exchange chromatography, possibly in combination with fractional crystallization procedures.

a. Chromium Ammine and Amine Oligomers. Andersen *et al.* have studied the equilibria between chromium(III) and nitrogen ligands such as ammonia and ethylenediamine in aqueous solution (*195, 196*). It was found that solutions in which equilibrium between the mononuclear species has been established can be prepared by employing the combined catalytic effects of chromium(II) and charcoal. Depending on the conditions, a variable content of polynuclear hydroxo-bridged complexes was also obtained, but equilibrium with respect to these species was not attained (*40, 42, 60, 87*).

Chromium(II) charcoal catalysis has been used to synthesize several new tri- and tetranuclear chromium(III) ammine species (*40*). Anaerobic charcoal-catalyzed oxidation of Cr(II) in aqueous ammonia/ammonium buffer solutions leads to evolution of hydrogen and the formation of a mixture of mononuclear and oligomeric chromium(III) ammine complexes. Under appropriate conditions a high content of polynuclear species is obtained and it is also possible to optimize the yield of certain species by using specific conditions. After quenching by removal of the catalysts, the desired polynuclear species was isolated either by direct precipitation from the product solution or by separation of the mixtures by cation-exchange chromatography in combination with fractional crystallization. Among the complexes which have been isolated by direct precipitation from such solutions is the so-called rhodoso ion, $Cr_4(NH_3)_{12}(OH)_6^{6+}$, which was first prepared by Jørgensen (*4*). The Cr(II) charcoal catalytic method is faster and more reliable than the original method, and gives a good yield in the form of the bromide salt, which can be crystallized directly from the hydrolysis mixture.

The trinuclear cation $Cr_3(NH_3)_{10}(OH)_4^{5+}$ and the tetranuclear cation $Cr\{(OH)_2Cr(NH_3)_4\}_3^{6+}$ have been prepared similarly by the Cr(II) charcoal catalytic method and were separated by cation-exchange chromatography (*40*). The trinuclear species was isolated as a bromide salt and has structure **5** in Fig. 1. The tetranuclear species $Cr\{(OH)_2Cr(NH_3)_4\}_3^{6+}$ has been shown to be a chromium ammonia analog of the so-called Werner's brown salt, $Co\{(OH)_2Co(en)_2\}_3^{6+}$ (structure **6** in Fig. 1) (*41*).

Polynuclear chromium(III) ethylenediamine complexes have been synthesized by methods similar to those applied for the ammine systems by using the combined catalytic effect of chromium(II) and charcoal on aqueous ethylenediamine buffer solutions (pH ~8) of chromium(III) (*40, 42, 60*). As mentioned above, the use of catalysts is important when equilibration between the mononuclear species is required, but it is unnecessary when the aim is to produce polynuclear species. In fact, identical polynuclear species are formed in approximately the same ratio when buffered chromium(III) solutions ($[Cr] = 0.1\ M$, $[en] = 0.3\ M$) without catalyst are kept for a few days at 40–50°C (*40*).

A trinuclear complex, $Cr_3(en)_5(OH)_4^{5+}$, and three tetranuclear complexes with the common formula $Cr_4(en)_6(OH)_6^{6+}$ have been isolated as salts and characterized. The structures of the trinuclear and one of the tetranuclear complexes have, however, not been established, although cleavage experiments and spectral properties suggest that they both have a linear structure; e.g., the most probable structure for the trinuclear species is structure **4a** in Fig. 1. X-Ray studies have shown that the remaining two tetranuclear species are the racemic cation $\Delta(\Delta\Lambda\Lambda)/\Lambda(\Lambda\Delta\Delta)\text{-Cr}\{(OH)_2Cr(en)_2\}_3{}^{6+}$ and the centrosymmetric cation $\Delta,\Lambda,\Delta,\Lambda\text{-lel}_6\text{-}(en)_2Cr(OH)_2Cr(en)(OH)_2Cr(en)(OH)_2Cr(en)_2{}^{6+}$, i.e., with structures **6** and **7a**, respectively, in Fig. 1. In addition to the trinuclear ammonia and tacn complexes mentioned above, it should be mentioned that analogous complexes (structure **5** in Fig. 1) have been reported for pyridyl-substituted amines (*51, 162*).

b. Oligomers of the Hexaaquachromium(III) Ion. Studies of the hydrolytic behavior of the hexaaqua chromium(III) ion were first reported by Niels Bjerrum in 1908 in his thesis "Studies on Basic Chromic Compounds. A Contribution to the Theory of Hydrolysis" (*14*). Bjerrum showed that aging of partially neutralized chromium(III) solutions leads to formation of hydroxo-bridged oligomers, and he was able to determine the composition and stability constants for some of these. The conclusions originally arrived at by Bjerrum have essentially been confirmed by several other groups (*25–31, 197 202*).

Hydrolysis of $Cr(H_2O)_6{}^{3+}$ yields a large number of polynuclear species. The most well-characterized species are the green monohydroxo-bridged species, $(H_2O)_5Cr(OH)Cr(H_2O)_5{}^{5+}$, and the blue dihydroxo-bridged species, $(H_2O)_4Cr(OH)_2Cr(H_2O)_4{}^{4+}$. Although neither of these cations has been isolated as crystalline salts, their respective mono- and dihydroxo-bridged binuclear structures have been established with great certainty by a variety of methods, including cation-exchange experiments (*29, 30*), ^{18}O-exchange experiments (*197*), magnetic measurements (*26*), cryoscopic molecular weight determination (*25*), and kinetic and thermodynamic studies (*26, 28, 31, 199, 200*). A report (*203*) to the effect that the blue dihydroxo-bridged species can be crystallized as a *meta-vanadate* $[VO_2(OH)_2{}^-]$ would seem to require reexamination before it can be concluded that the solid does in fact contain the dinuclear cation. In some recent studies of these species (*204–209*), structures such as $(H_2O)_4Cr(ClO_4)(OH)Cr(H_2O)_4{}^{4+}$ and $(H_2O)_5CrOCr(H_2O)_5{}^{4+}$ have been claimed, but these proposals appear to be in glaring conflict with the large body of evidence indicating mono- and dihydroxo-bridged structures, respectively.

In addition to binuclear species, trinuclear $Cr_3(OH)_4{}^{5+}$ and tetranuclear $Cr_4(OH)_6{}^{6+}$ cations (water ligands omitted) have been prepared in solution by separation of the components in the aged solution by cation-exchange chromatography (*31*). The trinuclear species is believed to occur as only one isomer, but the tetranuclear species occur as two forms which interconvert within ≤ 1 second at room temperature (*200*).

The two tetranuclear forms, which are not necessarily isomers and which might differ in the number of coordinated water molecules, are referred to in the following discussion as α-$Cr_4(OH)_6^{6+}$ and β-$Cr_4(OH)_6^{6+}$, corresponding to the stable and unstable forms, respectively, and $Cr_4(OH)_6^{6+}$ refers to an equilibrium mixture of both forms.

Hydrolysis of $Cr(H_2O)_6^{3+}$ gives tetranuclear species in only low yield, and a more convenient method for preparing these species is to partially neutralize solutions of the dinuclear species, yielding the tetranuclear species in high yield (21%) together with other species. Similarly a 1:1 mixture of $Cr(H_2O)_6^{3+}$ and $Cr_3(OH)_4^{5+}$ gives rise to a good yield of tetranuclear species, and it was shown that the yield of tetranuclear species decreases drastically (from 25 to 2%) if $Cr(H_2O)_6^{3+}$ is absent from the initial solution (*31*).

Bridge cleavage of the tetranuclear species in acidic solutions occurs, at least predominantly, with stepwise release of $Cr(H_2O)_6^{3+}$, as indicated in Eqs. (3)–(5), where the half-lives for $[H^+] = 1.0\ M$ at 25°C are (*31*)

$$Cr_4(OH)_6^{6+} \xrightarrow{t_{1/2} \approx 3\text{ hours}} Cr^{3+} + Cr_3(OH)_4^{5+} \qquad (3)$$

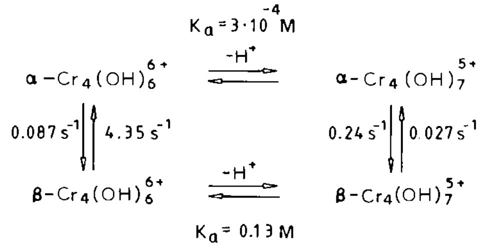
$$Cr_3(OH)_4^{5+} \xrightarrow{t_{1/2} = 21\text{ days}} Cr^{3+} + Cr_2(OH)^{5+} \qquad (4)$$

$$Cr_2(OH)^{5+} \xrightarrow{t_{1/2} \approx 7\text{ days}} 2Cr^{3+} \qquad (5)$$

It is interesting that the first step in the hydrolysis of the tetranuclear species gives a pure trinuclear species almost without interference from side reactions, such as, e.g., cleavage into two dinuclear species or into other isomers of the trinuclear species. This observation is in keeping with the observation that a mixture of trinuclear species and $Cr(H_2O)_6^{3+}$ at pH ~4 yields tetranuclear species in high yield. These results are further supported by Cr labeling experiments (*31*).

As mentioned, the tetranuclear species occurs in two forms which interconvert rapidly. These interconversion reactions have been studied spectrophotometrically in the pH range 0.3–4.0 (25°C) and the data have been interpreted in terms of the equilibria shown in Scheme 1.

The structures of the trinuclear species $Cr_3(OH)_4^{5+}$ and the two tetranuclear species α- and β-$Cr_4(OH)_6^{6+}$ have not been established. Linear as well as cyclic trimeric structures (structures **4a**, **4b**, and **5** in Fig. 1) have been considered (*27, 31*), as has another cyclic structure such as that shown in Fig. 10. However, the kinetic, thermodynamic, spectroscopic, and magnetic properties appear to provide no evidence to favor the one rather than the other (*27*). The number of possible



SCHEME 1. The α and β isomers of the two known tetranuclear aqua chromium(III) species interconvert rapidly. The values are for 25°C in 1 M (Na,H)ClO_4.

structures for the $Cr_4(OH)_6^{6+}$ species is quite large. Stüntzi and Marty have proposed cyclic structures which for the β isomer involve a hydroxide ligand coordinated to four chromium(III) ions (*31*). This proposal has been criticized in a recent note by L. Mønsted, O. Mønsted, and the present author (*118*). It was pointed out that the interpretation of the kinetic and thermodynamic properties does not require the postulation of unorthodox structures, and as an example it was shown that the trinuclear structure **4a** and linear tetranuclear structures such as structures **7b** and **7c** (Fig. 1) account for the properties of these species in a much more satisfactory way.

c. Cobalt(III) Oligomers. Only very few higher oligomers of cobalt(III) have been made by hydrolysis of mononuclear cobalt(III) aqua complexes. One of the few examples is provided by the hydrolysis of *cis*-$Co(NH_3)_4(H_2O)_2^{3+}$ in dilute ammonia solution, forming the

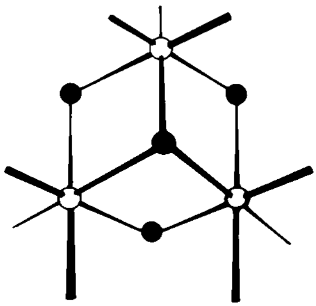


FIG. 10. A possible structure of the trinuclear aqua chromium(III) species $Cr_3(OH)_4^{5+}$. The metal ions and hydroxo bridges are indicated by ○ and ●, respectively. Another very plausible structure is **4a** in Fig. 1.

tetranuclear complex $Co\{(OH)_2Co(NH_3)_4\}_3^{6+}$ (*2, 9, 56, 156, 210*):

$$4cis\text{-}Co(NH_3)_4(H_2O)_2^{3+} + 2OH^- \longrightarrow Co\{(OH)_2Co(NH_3)_4\}_3^{6+} + 4NH_4^+ + 4H_2O \qquad (6)$$

This tetranuclear complex was first prepared by Jørgensen (*2*), and was resolved into optical isomers by Werner (*9*), who thereby disposed of the vitalist contention that organic carbon is an essential concomitant of optical activity. Werner named the complex "hexol" after the bridging ligands. The structure of this tetranuclear species has now been established by an X-ray crystal-structure analysis of the racemic salt (*52*). The complex racemizes fairly readily and rates of racemization depend heavily on pH; the first-order rate constants at pH 2.0, 7.0, and 8.1, are respectively, $k = 2 \times 10^{-6}$, 2×10^{-3}, and 4×10^{-2} sec^{-1} at 22°C. Tartrate and selenate decrease the rate of racemization, probably as a result of ion pairing between the hydroxo bridges and the anions (*56*).

Reaction Eq. (6) has been studied in the pH range 8–10 by the pH-stat method (*211*). The reaction was found to be first order in the mononuclear species, and the rate-determining step was proposed to involve a dissociation reaction of the *trans*-$Co(NH_3)_4(OH)_2^+$ ion.

Corresponding hexols containing aliphatic diamines have also been prepared, although not by the hydrolysis reaction Eq. (6) (see Section IV,C).

Heteronuclear complexes of the types $M(II)\{(OH)_2Co(tren)\}_2^{4+}$ and $M(II)\{(OH)_2Co(tren)\}_3^{5+}$ have been prepared by mixing aqueous solutions of M(II) and $Co(tren)(OH)_2^+$ (M = Co, Ni, Cu, Zn, and Cd). The stability constants were determined and some of the oligomers were isolated as crystalline perchlorate salts (*212*). The *cis*-$Co(en)_2(OH)_2^+$ ion reacts similarly (*213*).

B. SOLID-STATE REACTIONS

Dinuclear dihydroxo-bridged complexes can often be obtained from the parent mononuclear complexes by the solid-state reaction Eq. (7). This was first reported by Werner (*7, 11*) and Dubsky (*18*), and it is generally the most convenient method for the preparation of dihydroxo-bridged complexes of Cr(III), Co(III), Rh(III), and Ir(III) with $L_4 = (NH_3)_4$ or $(en)_2$ [and $(tn)_2$ in the case of chromium(III)] (*67, 131, 133, 214–219*). With the exception of the ammonia chromium(III) complex, these reactions are essentially quantitative and the rate of reaction follows the order chromium(III) > cobalt(III) > rhodium(III) $\gtrsim$

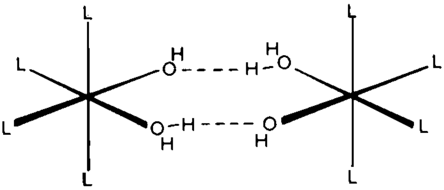


FIG. 11. Intermolecular hydrogen-bonded pairs of aqua hydroxo complexes have been found in several crystal structures and are probably always present in those salts of the type *cis*-$[ML_4(H_2O)(OH)]X_2$, which yield dinuclear dihydroxo-bridged complexes upon heating in the solid state.

iridium(III). With $L_4 = (en)_2$, the reaction for the chromium(III) complex (*220*) is complete within 15 minutes at 120°C, but at the same temperature the iridium(III) complex (*133*) requires about 14 hours (see Fig. 11).

$$2\mathit{cis}\text{-}[ML_4(H_2O)(OH)]X_2 \xrightarrow{\text{heat}} [L_4M(OH)_2ML_4]X_4 + 2H_2O \qquad (7)$$

The solid-state reactions of *cis*-$[Co(NH_3)_4(H_2O)(OH)]X_2$ ($X = Cl^-$, Br^-, NO_3^-, and $\frac{1}{2}S_2O_6^{2-}$) have been studied using differential thermal analysis and thermogravimetry (*221*–*223*). The reactions, which are all endothermic, are very sensitive to the anions and ΔH is in the region 8–40 kJ mol^{-1}. The activation energies also show a strong dependence on the anions, and for $X = Cl^-$, $\frac{1}{2}SO_4^{2-}$, Br^-, and $\frac{1}{2}S_2O_6^{2-}$, the values E_a = 84, 105, 180, and 205 kJ mol^{-1} have been reported. Thermal data have also been reported for a series of cobalt(III) complexes containing coordinated amino acid anions (*224*). ΔH values in the region 30–160 kJ mol^{-1} were found for the reactions of cationic and neutral aqua hydroxo mononuclear species, and anionic mononuclear

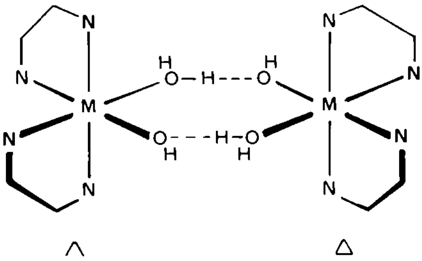


FIG. 12. Crystal packing of the cations in *cis*-$[M(en)_2(H_2O)(OH)]S_2O_6$ in the manner shown explains why heating of the solid salts for M = Co(III), Rh(III), Ir(III), or Cr(III) yields stereospecifically the meso (Δ,Λ) isomers of $(en)_2M(OH)_2M(en)_2^{4+}$.

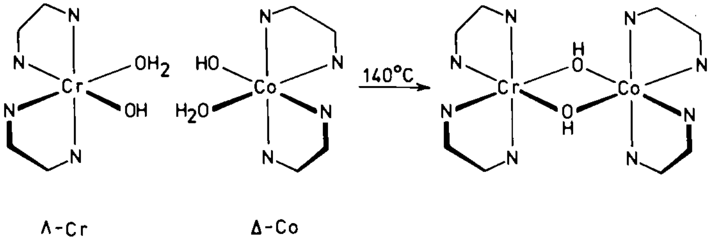


FIG. 13. In a syncrystallized mixture of Λ-*cis*-$Cr(en)_2(H_2O)(OH)^{2+}$ and Δ-*cis*-$Co(en)_2(H_2O)(OH)^{2+}$ (as the dithionate), the cations in the crystals are positioned with Λ opposite to Δ, as shown on the left, resulting in stereospecific formation of the heterodinuclear species $(-)_D$-Λ,Δ-$(en)_2Cr(OH)_2Co(en)_2^{4+}$ upon heating of the solid salt.

complexes yielded values between -20 and -80 kJ mol^{-1}. The activation energies varied from 200 to 400 kJ mol^{-1} with 330–380 kJ mol^{-1} as typical values. It was found that the effect of cations on the thermal condensation of anionic mononuclear species is smaller than the effect of anions on the condensation of cationic species.

It is probably a prerequisite for reaction Eq. (7) that the cations in the crystals of *cis*-$[ML_4(H_2O)(OH)]X_2$ pack in the fashion shown schematically in Fig. 11. This structure has been observed in a number of crystal structures and, as discussed at greater length in Section V, the pairs of cations in these structures are held together in the crystal by a strong hydrogen bond interaction, as indicated in the figure. With $L_4 = (en)_2$ reaction Eq. (7) is stereospecific and yields the meso (Δ,Λ) isomer quantitatively. This stereospecificity probably results from crystal packing with the Δ enantiomer opposite to the Λ enantiomer, as shown in Fig. 12. Indirect but strong evidence for crystal packing in this manner is provided by the fact that a cocrystallized 1:1 mixture of the dithionates of $(+)_D$-Λ-*cis*-$Cr(en)_2(H_2O)(OH)^{2+}$ and $(-)_D$-Δ-*cis*-$Co(en)_2(OH)(H_2O)^{2+}$ does not yield the dichromium or dicobalt complex upon heating, but instead yields stereospecifically the heterobinuclear diastereoisomer $(-)_D$-Λ,Δ-$[(en)_2Cr(OH)_2Co(en)_2](S_2O_6)_2$, as shown in Fig. 13 (*214, 215*). The fact that many species cannot be made by reaction Eq. (7) presumably reflects unfavorable packing in the crystals of the corresponding mononuclear aqua hydroxo complexes.

C. FORMATION BY OXIDATION REACTIONS

A variety of chromium(III) and cobalt(III) oligomers can be prepared by oxidation of an aqueous solution of the appropriate divalent metal-ion complex with oxidants such as O_2 and Tl^{3+}. The chromium(II) reactions with dioxygen are believed to involve the intermediate formation of chromium(IV). It is now well documented that the cobalt(II) reactions occur via the formation of peroxo-bridged dicobalt(III) complexes.

1. Chromium(III) Complexes

The so-called rhodo ion, $(NH_3)_5Cr(OH)Cr(NH_3)_5^{5+}$, is obtained by the oxidation of chromium(II) in an ammonia buffer (*3, 225–227*). The reaction is not quantitative and other unidentified products are formed, but the rhodo ion is the major component under optimal conditions.

Other oxidants such as ClO^-, BrO^-, and H_2O_2 have been investigated but do not lead to formation of the rhodo ion. H_2O_2 is a common product in the reduction of molecular oxygen, and the observation that this oxidant does not give the rhodo ion restricts the choice of possible mechanisms. Joyner and Wilmarth have studied the reaction (*226*) by using ^{18}O labeling followed by analysis of the percentage of ^{18}O among the bridging oxygen atoms in the rhodo ion. The proposed reaction sequence, Eqs. (8)–(12), explains the major results of the labeling experiments $[Cr = Cr(NH_3)_5]$:

$$2Cr(II) + {}^{18}O_2 \longrightarrow Cr(III)\ {}^{18}O_2\ Cr(III) \tag{8}$$

$$Cr(III)\ {}^{18}O_2\ Cr(III) + Cr(II) \xrightarrow{2H^+} Cr(III)\ {}^{18}OH\ Cr(III) + Cr(IV)(OH) \tag{9}$$

$$Cr(IV)({}^{18}OH) + H_2O \longrightarrow Cr(IV)(OH) + H_2{}^{18}O \tag{10}$$

$$Cr(IV)(OH) + Cr(II) \longrightarrow Cr(III)\ OH\ Cr(III) \tag{11}$$

$$Cr(IV)({}^{18}OH) + Cr(II) \longrightarrow Cr(III)\ {}^{18}OH\ Cr(III) \tag{12}$$

The oxidation of ammoniacal solutions of Cr(II) may be compared with reaction Eq. (13), for which there are no appreciable side reactions

$$2Cr(aq)^{2+} + \tfrac{1}{2}O_2 \longrightarrow (H_2O)_4Cr(OH)_2Cr(H_2O)_4{}^{4+} \tag{13}$$

(*30, 198*). The overall reaction rate is proportional to $[Cr(II)]^2[O_2]$, but at the same time it was found that the rate was proportional to the oxygen flow rate, and the results are not easily interpreted. The ^{18}O labeling experiments show that both of the oxygen atoms from O_2 are incorporated into the dinuclear species without exchanging with solvent during the oxidation (*197*). These observations have been interpreted in terms of the mechanism of Eqs. (14)–(16).

The blue dinuclear species in Eq. (13) can be obtained using oxidants other than O_2. It is obtained pure and in quantitative yield when the

$$2\mathrm{Cr(II)} + {}^{18}\mathrm{O}_2 \xrightarrow{\text{slow}} \mathrm{Cr(III)}\ {}^{18}\mathrm{O}_2\ \mathrm{Cr(III)} \tag{14}$$

$$\mathrm{Cr(III)}\ {}^{18}\mathrm{O}_2\text{-}\mathrm{Cr(III)} \xrightarrow{\text{fast}} 2\mathrm{Cr(IV)}({}^{18}\mathrm{O}) \tag{15}$$

$$\mathrm{Cr(IV)}({}^{18}\mathrm{O}) + \mathrm{Cr(II)} \xrightarrow{\text{fast}} \mathrm{Cr(III)}\ {}^{18}\mathrm{O}\ \mathrm{Cr(III)} \tag{16}$$

oxidation is performed with Tl^{3+}, and in lower yields when oxidation is carried out with ClO_3^- (60%), HClO (30%), $Cr_2O_7^{2-}$ (50%), or H_2O_2 (14%). One-electron oxidants such as Fe^{3+}, Cu^{2+}, Cl_2, or Br_2 do not give rise to polynuclear species (*30*).

A reaction sequence similar to that of Eqs. (14)–(16) has been observed for the reaction of chromium(II) porphyrins with oxygen (*228, 229*). Similarly, the green oxo-bridged complex $[\{Cr(NCS)(tpyea)\}_2O](BPh_4)_2$ has been prepared by the O_2 oxidation of $[Cr(NCS)(tpyea)](BPh_4)$ and its structure has been determined by single-crystal X-ray diffraction (*114*) [tpyea is the tetradentate ligand tris(2-pyrazal-1-ylethyl)amine]. An oxo-bridged salen dichromium(III) complex has been reported (*230*).

2. *Cobalt(III) Complexes*

The oxidation of aqueous solutions of cobalt(II) salts in the presence of ligands may give a variety of products depending on the conditions. Air oxidation of $Co(en)_2(H_2O)_2^{2+}$ in the presence of charcoal as catalyst yields $Co(en)_3^{3+}$, and without charcoal catalyst the reaction gives either the peroxo-bridged dicobalt(III) complex $(en)_2Co(OH)(O_2)Co(en)_2^{3+}$ or the tetranuclear complex $Co\{(OH)_2Co(en)_2\}_3^{6+}$, depending on the conditions.

The above μ-hydroxo–μ-peroxo complex represents an important class of complexes, and a series of $L_4Co(OH)(O_2)CoL_4^{3+}$ complexes has been prepared with other amines such as NH_3, tn, tren, and trien (*108, 231–244*); the structures of these have been established by X-ray crystal-structure analysis (*108, 109, 242, 243*). The kinetics of formation and the chemical properties of these dinuclear species have been studied in detail, as discussed in a recent review by Fallab and Mitchell (*119*).

The tetranuclear complex $Co\{(OH)_2Co(en)_2\}_3^{6+}$ was first prepared by Werner (*6*) and has subsequently been the subject of several studies (*53, 54, 57, 156, 245–247*). Its ammonia analog has already been mentioned in Section IV,A. As mentioned in Section II,B, the en tetranuclear species may exist in eight optically isomeric forms. All eight isomers are formed during the oxidation reaction and have been separated by column chromatography (*57*). The yields of the isomers decrease in the order Δ(ΛΛΛ) > Δ(ΔΛΛ) > Δ(ΔΔΛ) > Δ(ΔΔΔ). The X-ray crystal structures of salts of the racemates Δ(ΛΛΛ)/Λ(ΔΔΔ) and Δ(ΛΛΔ)/Λ(ΔΔΛ) have been reported (*53, 54, 245*). It is the latter of these racemates which was originally isolated as a nitrate by Werner, and which is now often referred to as Werner's brown salt.

Optical isomers of analogous tetranuclear species (hexols) containing other diamines have been reported for *meso*-2,3-bn (all eight possible optical isomers), R-pn (six isomers), and R,R-chxn (four isomers) (*58, 59*). As observed for the ammonia hexol, some diamine hexol isomers have been reported to mutarotate (*56, 58*).

Oxidation of cobalt(II) with O_2 or H_2O_2 may also yield di- or trihydroxo-bridged dinuclear complexes, some of which have already been mentioned in Section IV,A. Other examples may be found in the literature (*248–250*).

3. *Iridium(III) Complexes*

Electrochemical reduction of iridium(IV) aqua ions has been reported to give $(H_2O)_5Ir(OH)Ir(H_2O)_5^{5+}$ and $(H_2O)_4Ir(OH)_2Ir(H_2O)_4^{4+}$ (*251*).

D. Formation from Other Polynuclear Species

1. *Condensation of Smaller Oligomers*

Although it would be logical to assume that larger oligomers could be made in improved yield by starting with suitable smaller oligomers, this strategy has seldom been used preparatively. One of the few and successful examples is the preparation of the tetranuclear aqua chromium(III) species either by condensation of two dinuclear species or by condensation of Cr^{3+} with the trinuclear species (*31*).

2. *Substitution of the Nonbridging Ligands*

Hydrolysis of ammonia or amines is often observed, but only in a few cases have such reactions proved to be useful synthetically. Base hydrolysis (aqueous NH_3) of the so-called rhodo ion, $(NH_3)_5Cr(OH)Cr(NH_3)_5^{5+}$, yields the so-called cis hydroxo erythro ion, *cis*-$(NH_3)_5Cr(OH)Cr(NH_3)_4(OH)^{4+}$, and both this ion and its corresponding acid form, cis aqua erythro have been isolated as salts (*227, 252, 253*). The hydrolysis is complete within minutes, and unlike the hydrolysis of many other ammine chromium(III) complexes, is quite a clean reaction, at least in solutions of moderate alkalinity (*225*). The corresponding trans aqua isomer has been prepared by heating the solid

TABLE VIII

RATE CONSTANTS FOR THE HYDROLYSIS OF "RHODO" AND "ERYTHRO" IONS IN BASE AT $I = 0.1\ M$ AND 20°C[a]

Reactant	k (sec^{-1})
$(NH_3)_5Cr{-}O{-}Cr(NH_3)_5^{4+}$	0.016
cis-$(NH_3)_5Cr{-}O{-}Cr(NH_3)_4(en)^{4+}$	~0.01
cis-$(NH_3)_5Cr{-}O{-}Cr(NH_3)_4(NCS)^{3+}$	0.30
trans-$(NH_3)_5Cr{-}O{-}Cr(NH_3)_4Cl^{3+}$	0.54
cis-$(NH_3)_5Cr{-}O{-}Cr(NH_3)_4F^{3+}$	0.011[b]

[a] Reactions as shown in Eq. (17). From Refs. *24* and *256*.

[b] $(HO)(NH_3)_4Cr(OH)Cr(NH_3)_4F^{3+}$ is also formed.

chloride salt of cis aqua erythro, giving trans chloro erythro (*227, 252*), followed by Hg(II)-assisted hydrolysis of the latter to yield the trans aqua erythro ion, isolated as a perchlorate (*64, 252*).

Substitution reactions of the aqua erythro ion with other nucleophiles, usually under acidic conditions, have led to *cis*-$(NH_3)_5Cr(OH)$-$Cr(NH_3)_4X^{(5-n)+}$ species for $X^{n-} = NO_2^-$, F^-, SCN^-, and Cl^- (the last of these being isolated only in solution) (*24, 227, 254, 255*). Reaction of *cis*-$(NH_3)_5Cr(OH)Cr(NH_3)_4(SCN)^{4+}$ in ethylenediamine gives $(NH_3)_5$-$Cr(OH)Cr(NH_3)_4(NH_2(CH_2)_2NH_3)^{6+}$, which presumably has the cis configuration (*256*). The kinetics for the base hydrolysis reactions, Eq. (17), have been studied for $X^{n-} = SCN^-$ (cis), Cl^- (trans), F^- (cis), NH_3, and en (cis) (*24, 256, 257*) (Table VIII).

$$\begin{aligned} &(NH_3)_5Cr(OH)Cr(NH_3)_4X^{(5-n)+} + OH^- \xrightarrow{\text{fast}} \\ &\quad (NH_3)_5Cr{-}O{-}Cr(NH_3)_4X^{(4-n)+} + H_2O \xrightarrow{\text{slow}} \\ &\quad (NH_3)_5Cr(OH)Cr(NH_3)_4(OH)^{4+} + X^{n-} \end{aligned} \tag{17}$$

A kinetic study of the acid hydrolysis of the cis nitro erythro cation has been reported (*258*).

Replacement of the nonbridging ammine ligands in $(NH_3)_4Co(OH)$-$(NH_2)Co(NH_3)_4^{4+}$ has been reported to take place during acid hydrolysis (*259*), leading to $(H_2O)(NH_3)_4Co(NH_2)Co(NH_3)_3(H_2O)_2^{5+}$, and likewise the reaction with aqueous bicarbonate (*110*) gives $(NH_3)_4Co(OH)_2(NH_2)Co(CO_3)_2$. The latter complex reacts with acid, forming $(NH_3)_4Co(OH)(NH_2)Co(H_2O)_4^{4+}$.

3. *Hydroxo Bridge Cleavage or Formation*

Bridge cleavage of di- and trihydroxo-bridged complexes in acidic or basic solution provides a convenient method for the synthesis of the corresponding monohydroxo-bridged (*32–36, 133, 214–218*) and dihydroxo-bridged (*50, 76, 100, 132, 174, 185, 186, 188*) species, as exemplified by reaction Eqs. (18)–(20).

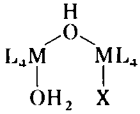
$$(NH_3)_4Rh(OH)_2Rh(NH_3)_4^{4+} + H_3O^+ \longrightarrow \textit{cis,cis}\text{-}(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(H_2O)^{5+} \qquad (18)$$

$$\Delta,\Lambda\text{-}(en)_2Cr(OH)_2Cr(en)_2^{4+} + OH^- \longrightarrow \Delta,\Lambda\text{-}(OH)(en)_2Cr(OH)Cr(en)_2(OH)^{3+} \qquad (19)$$

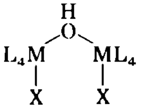
$$(NH_3)_3Co(OH)_3Co(NH_3)_3^{3+} + H_3O^+ \longrightarrow \textit{trans}\text{-}(H_2O)(NH_3)_3Co(OH)_2Co(NH_3)_3(H_2O)^{4+} \qquad (20)$$

The heterobinuclear complex Λ,Δ-$(H_2O)(en)_2Cr(OH)Co(en)_2(H_2O)^{5+}$ can be obtained similarly but has been characterized only in solution (*215*). $(H_2O)_5Cr(OH)Cr(H_2O)_5^{5+}$ has likewise been characterized only in solution, and can be made by acid hydrolysis of the dihydroxo-bridged complex (*26*).

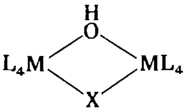
Reaction with nucleophiles other than water (or hydroxide) may lead to products of the types **I**, **II**, and **III**.



I



II



III

The products obtained in the bridge-cleavage reactions of the chromium(III), cobalt(III), rhodium(III), and iridium(III) complexes Δ,Λ-$(en)_2M(OH)_2M(en)_2^{4+}$ with different nucleophiles X^{n-} are summarized in Table IX. These reactions have been carried out under acidic conditions, except for $X^{n-} = OH^-$ (neutral or basic) and for $X = O_2^{2-}$ (neutral). These reactions are generally quantitative, and most of the products have been characterized by X-ray crystal-structure analysis. Two different pathways are possible. As illustrated in Scheme 2, the hydroxo-bridge cleavage and the entering of the nucleophile could occur simultaneously; alternatively, the initial reaction could be water-assisted hydroxo-bridge cleavage with subsequent substitution of OH_2 by X^{n-}. A pathway similar to that of reaction A (Scheme 2) has been demonstrated for the reaction of $(NH_3)_4Co(NH_2)(OH)Co(NH_3)_4^{4+}$ with a series of nucleophiles (see Section XII,A). For the dihydroxo-

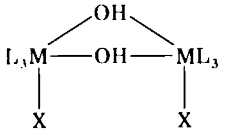
TABLE IX

PRODUCTS FORMED BY BRIDGE CLEAVAGE OF Δ,Λ-$(en)_2M(OH)_2M(en)_2^{4+}$ BY REACTION WITH VARIOUS NUCLEOPHILES X^{n-} [a]

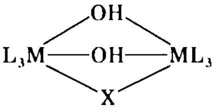
M	Structure I X^n	Structure II X^{n-}	Structure III X^{n-}
Cr(III)	H_2O, OH^- (*33*), CF_3COO^- (*261*)	OH^- (*33*), CF_3COO^- (*107*), Cl^- (*260*)	SO_4^{2-} (*262*); PO_4^{3-} (*105*); CF_3COO^- (*107*); $HCOO^-$, CH_3COO^-, and $RCH(NH_2)COO^-$ (*263*)
Co(III)	—	—	O_2^{2-} (*121*)
Rh(III)	H_2O, OH^- (*217*)	OH^- (*217*)	O_2^{2-} (*121*), PO_4^{3-} (*220*)
Ir(III)	H_2O, OH^- (*67*)	OH^- (*67*), Br^- (*264*)	—

[a] References are given in parentheses.

bridged complexes the reaction with H_2O is fast compared to the anation reactions studied, and pathway B cannot be ruled out. Cleavage of trihydroxo-bridged complexes in the presence of mono- or bidentate nucleophiles (other than water) usually gives dihydroxo-bridged complexes of types **IV** or **V**.

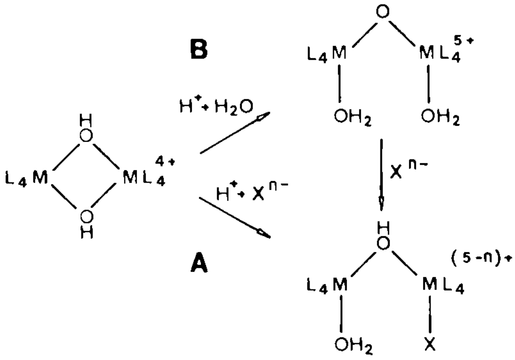


IV

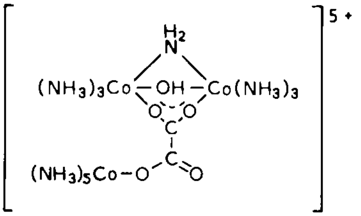


V

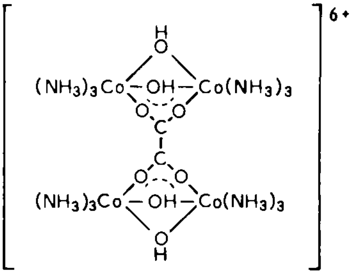
Starting from $(NH_3)_3Co(OH)_3Co(NH_3)_3^{3+}$, derivatives of type **IV** have been obtained for $X^{n-} = F^-$, N_3^-, and SCN^- (*132*) and of type **V** for $X^{n-} = SO_3^{2-}$ (*265*), NO_2^- (*266*), and a very large number of carbox-



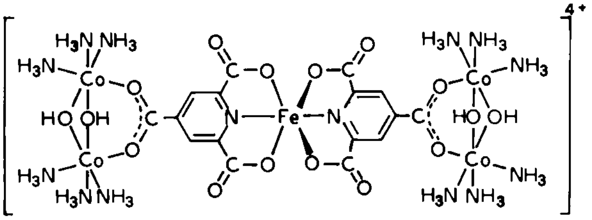
SCHEME 2. The reactions of dinuclear dihydroxo-bridged species with a nucleophile X^{n-} in acid solution may occur by pathway A or B.



VI



VII



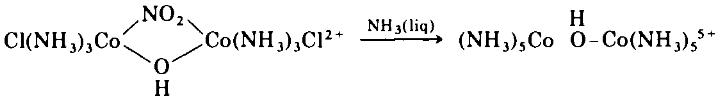
VIII

ylates (*193, 194, 265–282*). The bidentate coordination of both carboxylate functions in a dicarboxylate anion can lead to the formation of tri-, tetra-, and pentanuclear species, as exemplified by structures **VI**, **VII**, and **VIII**. The amido-bridged complex $(NH_3)_3Co(NH_2)(OH)_2$-$Co(NH_3)_3{}^{3+}$ reacts similarly, i.e., with hydroxo-bridge cleavage rather than with amido-bridge cleavage, as discussed in Section XII,A. The kinetics of reduction of $(NH_3)_3Co(OH)_2(X)Co(NH_3)_3{}^{(4-n)+}$ and $(NH_3)_3Co(NH_2)(OH)(X)Co(NH_3)_3{}^{(4-n)+}$, containing a variety of ligands X^{n-}, and of other related species have been studied thoroughly (*193, 194, 267–275, 283–299*).

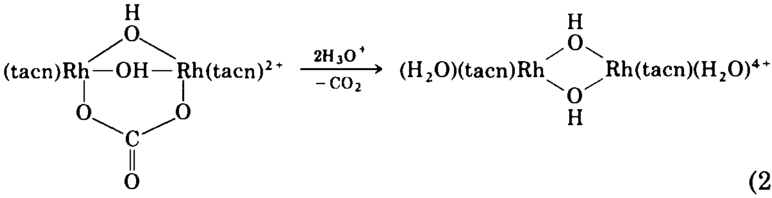
The reactions of hydroxo-bridged aqua chromium(III) oligomers with a variety of anions have been studied intensively because of their relevance to the use of chromium(III) in tanning (*300–317*). Partially neutralized chromic sulfate solutions are among the must widely used inorganic tanning agents. Such solutions contain a complex mixture of oligomeric chromium(III) species, which in the tanning process are believed to cross-link the polypeptide chains of collagen together by reactions with the carboxylate groups of acidic amino acids in the polypeptide chains. The composition of the active chromium(III) species is not known, but the size of the oligomer is believed to play an important role. Mononuclear chromium(III) species are too small to effect cross-linking, and the large oligomers (tetranuclear or larger) are not effective, perhaps because they are too large to penetrate the cavities in the collagen (*303*). Addition of inorganic or organic anions is often used to modify the tanning process, and these so-called masking (and demasking) agents are bound to the chromium(III) oligomers in either a terminal or a bridging fashion, thereby strongly influencing the nuclearity, the structure, and the reactivity of the oligomers (*305, 308, 311, 314*).

Studies of such reactions are very difficult and are seriously complicated by the fact that very few of the oligomers have been isolated or characterized. The most studied complexes are those containing sulfate, and of these the more well-characterized species (*315, 317*) appear to be $(H_2O)_4Cr(OH)(SO_4)Cr(H_2O)_4^{3+}$, $(H_2O)_4Cr(OH)(SO_4)Cr(H_2O)_3SO_4^{+}$, and $(H_2O)_3Cr(OH)(SO_4)_2Cr(H_2O)_3^{+}$, the last of which (*317*) has been isolated as a green chloride salt. Analogous amine complexes are well known, and X-ray crystal structures of Δ,Λ-$[(en)_2Cr(OH)(SO_4)Cr(en)_2]^{3+}$ and of $[(bispicam)Cr(OH)_2(SO_4)Cr(bispicam)]^{2+}$ have been reported (*51, 106, 262*).

Hydroxo-bridged complexes may be synthesized from hetero-bridged complexes, e.g., of the types M(OH)(X)M or $M(OH)_2(X)M$ by reactions involving cleavage of the X^{n-} bridge. Reactions shown in Eqs. (21) and (22) are examples (*100, 130*) of this type of process.

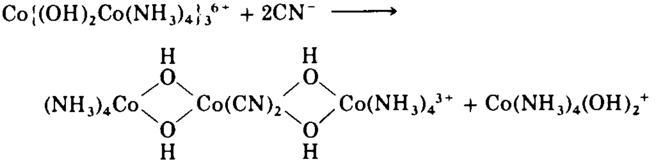


$$Cl(NH_3)_3Co\overset{NO_2}{\underset{\underset{H}{O}}{\langle\;\rangle}}Co(NH_3)_3Cl^{2+} \xrightarrow{NH_3(liq)} (NH_3)_5Co\;\overset{H}{O}\text{-}Co(NH_3)_5^{5+} \quad (21)$$



(22)

The tetranuclear cobalt(III) hexol reacts with cyanide (*318*) as shown in Eq. (23). The red trinuclear complex has been shown (*49*) by an X-ray



$$Co\{(OH)_2Co(NH_3)_4\}_3^{6+} + 2CN^- \longrightarrow (NH_3)_4Co(OH)_2Co(CN)_2(OH)_2Co(NH_3)_4^{3+} + Co(NH_3)_4(OH)_2^{+} \quad (23)$$

crystal-structure analysis of the racemic salt to contain cis-coordinated cyanide groups (structure **4a** in Fig. 1). Analogous reactions with hexols containing en, *R*-pn, and *S,S*-chxn have been reported. The optical isomers of the resulting trinuclear complexes have been separated and their absolute configuration determined on the basis of their circular dichroism and ^{13}C NMR spectra, and by characterization of the mononuclear complexes formed by cleavage in strong acid (*155*).

4. *Isomerization Reactions*

The cis/trans isomerization reaction, Eq. (24), has been applied in the preparation of salts of the cis isomers of the chromium(III) complexes with $L_3 = (NH_3)_3$ or tacn (*319*). For these species Eq. (24) equilibrium is shifted to the right, while the corresponding equilibria with the diaqua or dihydroxo species, respectively, are shifted to the left (Table X). The increased stability of the cis aqua hydroxo species can be explained in terms of intramolecular hydrogen bond formations (Section VI,C). As mentioned above, the corresponding cobalt(III) and rhodium(III) complexes have been isolated as salts only in the case of the *trans*-$(H_2O)L_3M(OH)_2ML_3(H_2O)^{4+}$ cations, but it seems very probable that their cis isomers could be prepared by reaction Eq. (24).

$$\textit{trans}\text{-}(H_2O)L_3M(OH)_2ML_3(OH)^{3+} \rightleftharpoons \textit{cis}\text{-}(H_2O)L_3M(OH)_2ML_3(OH)^{3+} \qquad (24)$$

The isomerization between meso and racemic isomers of $(OH)(en)_2Cr(OH)Cr(en)_2(OH)^{3+}$ has been used to synthesize the racemic isomer (*34, 35*). The equilibrium constant for Eq. (25) has been estimated to be $K = 4$ (45°C, 8 *M* ethylenediamine), which is significantly larger than the statistical value of unity.

$$\Delta,\Lambda\text{-}(OH)(en)_2Cr(OH)Cr(en)_2(OH)^{3+} \overset{K}{\rightleftharpoons} \Delta,\Delta/\Lambda,\Lambda\text{-}(OH)(en)_2Cr(OH)Cr(en)_2(OH)^{3+} \qquad (25)$$

Isomerization in the solid state has also been reported. One example is the preparation of *trans*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4Cl]Cl_4$ from *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(H_2O)]Cl_5$ (*252*). Solid-state isomerization

TABLE X

EQUILIBRIUM CONSTANTS FOR THE REACTION[a]

$$\textit{trans}\text{-}(X)L_3Cr(OH)_2CrL_3(Y)^{n+} \overset{K(D^{n+})}{\rightleftharpoons} \textit{cis}\text{-}(X)L_3Cr(OH)_2CrL_3(Y)^{n+}$$

L_3	$X = Y = H_2O$ $K(D^{4+})$	$X = H_2O$, $Y = OH^-$ $K(D^{3+})$	$X = Y = OH^-$ $K(D^{2+})$
$(NH_3)_3$	0.09(2)	8(2)	0.21(6)
tacn	0.037(3)	6.8(5)	0.19(2)

[a] At 25°C in 1 *M* $NaClO_4$ (*319*).

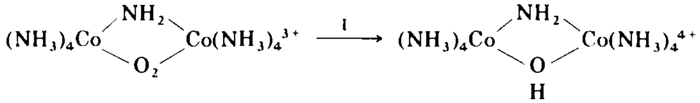
has also been reported for salts of the racemic isomers Δ,Δ/Λ,Λ-$(en)_2Cr(OH)_2Cr(en)_2^{4+}$ and Δ,Δ/Λ,Λ-$(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)^{4+}$. Heating of the solid salt Δ,Δ/Λ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2]Br_4 \cdot 4H_2O$ yields the corresponding meso complex, although in low yield (20%). When heated to 115°C, the solid salt Δ,Δ/Λ,Λ-$[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]Br_4 \cdot H_2O$ loses the water of crystallization, but neither formation of a dihydroxo-bridged complex, nor isomerization, occurs at this temperature. Heating at 140°C for 1 hour gave an almost quantitative (95%) conversion to the meso isomer of the dihydroxo-bridged complex. The very different yields in the two processes are somewhat surprising and might imply that two different mechanisms are operating (*34, 35*).

5. *Photochemical Reactions*

Photochemical reactions have not been studied to any great extent (*320–322*). Photochemical trans → cis isomerization of $(NH_3)_5Cr(OH)Cr(NH_3)_4X^{(5-n)+}$ ($X^{n-} = Cl^-$ or H_2O) has been reported (*320*). The partial photoresolution of $(ox)_2Cr(OH)_2Cr(ox)_2^{4-}$ has been reported (*322*).

6. *Redox Reactions*

Redox equilibria between μ-peroxo–μ-hydroxo dicobalt(III) complexes and their oxidized superoxo-bridged form have been discussed in a recent review article by Fallab and Mitchell (*119*). Corresponding dirhodium(III) complexes have recently been reported (*121–124*). Reduction of peroxo- (or superoxo)-bridged dicobalt(III) complexes provides a method for inserting a hydroxo bridge, as shown in reaction Eq. (26) (*323*).



$$(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}O_2)Co(NH_3)_4^{3+} \xrightarrow{I} (NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(NH_3)_4^{4+} \quad (26)$$

V. Stability Constants

A. DETERMINATION OF STABILITY CONSTANTS

The simplest and probably the most fundamental reaction, since it initiates all oligomerization reactions, is the condensation of two appropriate metal ions to give a dinuclear monohydroxo-bridged species, M(OH)M. However, the singly bridged species is seldom very stable and further condensation generally takes place, either through intramolecular bridge formation to give, e.g., $M(OH)_2M$, or through further oligomerization. Formation constants are often given in terms of concentration equilibrium constants Q_{xy} defined by Eq. (27).

$$xM(OH_2)_n^{z+} \underset{}{\overset{Q_{xy}}{\rightleftharpoons}} M_x(OH)_y(OH_2)_{nx-my}^{(xz-y)+} + yH^+ + (m-1)yH_2O \qquad (27)$$

This equation shows that not only a high metal-ion concentration, but also a high pH, often favors the formation of higher polynuclear species, since y generally increases more rapidly than x. For many aqua metal ions, however, the precipitation of insoluble hydroxides sets an upper pH limit, so that in practice it is possible to study the oligomerization reactions only within a narrow pH region defined by the magnitude of the first acid dissociation constant of the monomeric aqua ion and the pH at which insoluble hydroxide formation occurs.

A wide variety of methods has been used in studies of oligomerization reactions. The most important quantitative method is potentiometric measurement of pH as a function of the total metal concentration and of the concentration of the analytical excess of acid or base. Other quantitative methods which are often used are potentiometric determination of metal ion concentration, calorimetry, spectrophotometry, and ion exchange. These, together with a number of other techniques, have recently been discussed thoroughly by Baes (*22*).

In the case of inert systems such as cobalt(III) and chromium(III) it is possible, at least in principle, to separate the different species by means of ion-exchange chromatography. It is thus possible to characterize the polynuclear species much better than in the case of labile systems, and their equilibrium concentrations can be determined by direct measurement. The majority of chromium(III) and cobalt(III) oligomers reported are ammine and amine complexes. The N ligators reduce the number of possible skeletons by blocking ligand positions, which in certain respects facilitates the study of such amine complexes. Also, they reduce the number of water ligands, thereby greatly simplifying studies of the acid–base properties of such complexes. The drawback in connection with the study of amine complexes is that the number of isomers which can be formed for a given bridge skeleton may be quite large, as discussed in the previous sections. Another problem is that hydrolysis of the amine ligands may take place on the same time scale as the oligomerization reaction studies, and this complication appears to be more pronounced for chromium(III) than for cobalt(III), rhodium(III), and iridium(III) ammine systems. The hydrolysis of *cis*-$Cr(en)_2(H_2O)_2^{3+}$ is a typical example. The reaction gives dinuclear mono- and dihydroxo-bridged species of the types $(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)^{4+}$ and $(en)_2Cr(OH)_2Cr(en)_2^{4+}$, of which both meso (Δ,Λ) and racemic (Δ,Δ-Λ,Λ) isomers are known (*33, 35*). Quantitative studies, however, are complicated by the fact that hydrolysis of the ethylenediamine ligands takes place at the same time as the condensation processes, leading to the formation of mono- and dinuclear species with less than two ethylenediamine ligands per chromium, together with polynuclear complexes of nuclearity higher than two (*42, 324*). The resulting solution thus contains a complex mixture of known and unidentified species, and attempts to achieve equilibrium conditions have so far failed.

One way to overcome the above problem would be to suppress hydrolysis of the amine ligands by working with an appropriate amine buffer medium. This strategy has been used with great success by Andersen *et al.* to obtain quantitative equilibrium data for the formation of mononuclear amine complexes (*195, 196*). Andersen *et al.* have also studied the formation of polynuclear complexes under similar conditions, but equilibrium was not attained with respect to these species (*40, 42, 60, 87*). The fact, however, that both thermal hydrolysis and charcoal/chromium(II)-catalyzed hydrolysis in such an amine buffer medium give the same polynuclear species in almost identical ratios would seem to indicate that some degree of equilibration had been achieved. It therefore seems likely that these methods could, in principle, be modified so as to also be applicable for equilibrium studies. Quite a different approach would be to study complexes with macrocyclic amines such as cyclam, which are known to have a reduced tendency to hydrolysis. However, such systems have not as yet been studied in detail.

B. Monohydroxo-Bridged Species

Condensation to monohydroxo-bridged complexes is often described by Eq. (28), for which the equilibrium constants K_d are related to those defined by Eq. (27) by $K_d = Q_{21}/Q_{11}$, where Q_{11} is the first acid dissociation constant of the mononuclear aqua ion.

$$ML_5(H_2O)^{n+} + ML_5(OH)^{(n-1)+} \overset{K_d}{\rightleftharpoons} L_5M(OH)ML_5^{(2n-1)+} + H_2O \qquad (28)$$

The few constants K_d which have been reported for chromium(III) and rhodium(III) are listed in Table XI and are compared with those

TABLE XI

Equilibrium Constants $K_d = Q_{21}/Q_{11}$ for Eq. (28) at 25°C

Dinuclear ion	K_d (M^{-1})	Ionic strength (M)	Reference
$(NH_3)_5Co(OH)Co(NH_3)_5^{5+}$	$\ll 1$	—	*174*
$(NH_3)_5Rh(OH)Rh(NH_3)_5^{5+}$	$\ll 1$	—	*220*
$(H_2O)_5Cr(OH)Cr(H_2O)_5^{5+}$	$\sim 10^{-0.8}$	1.0–2.0	—[a]
$(H_2O)(en)_2Rh(OH)Rh(en)_2(H_2O)^{5+}$	$\sim 10^{-2.5}$	1.0	*325*[b]
$(H_2O)_5Cr(OH)Cr(H_2O)_4(OH)^{4+}$	$\sim 10^{1.9}$	1.0–2.0	—[a]
$(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+}$	$\sim 10^{1.4}$	1.0	*325*[b]
$(OH)(en)_2Rh(OH)Rh(en)_2(OH)^{3+}$	$\sim 10^{0.5}$	1.0	*325*[b]
$Zn_2(OH)^{3+}$	$10^{1.8}$	3.0	*22*
$Cd_2(OH)^{3+}$	$10^{1.1}$	3.0	*22*
$Hg_2(OH)^{3+}$	$10^{0.9}$	3.0	*22*
$Pb_2(OH)^{3+}$	$10^{1.7}$	2.0	*22*

[a] Calculated from data given in Tables XIII, XIX, and XXVIII and from $Q_{11} = 10^{-4.29}$ M (1 M $NaClO_4$) from Ref. *31*.

[b] Approximate values for Δ,Λ isomer (see text).

published for aqua ions of other metals. The values in Table XI demonstrate that K_d increases as the charge on the mononuclear cations decreases, and this is in agreement with the trends that one would expect on the basis of purely electrostatic considerations. However, other factors such as intra- and intermolecular interactions may also influence the equilibrium, as discussed below.

Dinuclear complexes of the type *cis,cis*-$(H_2O)L_4M(OH)ML_4(OH)^{4+}$ may be stabilized by intramolecular hydrogen bond formation of the α type, as mentioned briefly in Section II,B and as further corroborated in the next section. The same kind of stabilization is not possible in dinuclear complexes of the type $L_5M(OH)ML_5^{5+}$ ($L = H_2O$ or NH_3). The significantly greater stability of the $(H_2O)L_4M(OH)ML_4(OH)^{4+}$ species relative to the $L_5M(OH)ML_5^{5+}$ species (a factor of 10^3–10^4) is therefore most likely due, in addition to charge effects, to a strong intramolecular hydrogen bond stabilization of the former species. Similarly, the greater stability of the $(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+}$ ion relative to its deprotonated form is the reverse of that expected on the basis of electrostatic effects and is explicable by hydrogen bond stabilization of the former species.

Intermolecular hydrogen bond formation between the mononuclear species in aqueous solution has been proposed by Ardon and Bino,

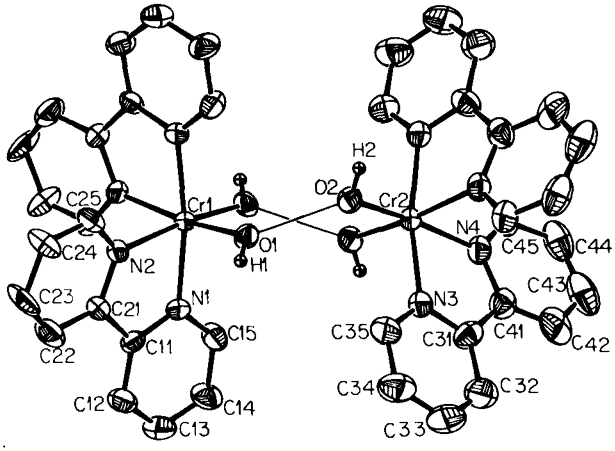


FIG. 14. Structure of *cis*-$[Cr(bipy)_2(H_2O)(OH)]^{2+}$. Reprinted with permission from Ardon, M., and Bino, A., *Inorg. Chem.* **24**, 1343 (1985). Copyright (1986) American Chemical Society.

essentially on the basis of crystal-structure studies (*326–330*). Formation of cation pairs of the type shown in Figs. 11 and 14 has been observed in a large number of crystal structures of salts of the type *cis*-$[ML_4(H_2O)(OH)]X_2$. A similar kind of interaction has been observed in, e.g., the crystal structure of the salt *trans*-$[Co(en)_2(H_2O)(OH)](ClO_4)_2$, which forms an infinite chain of Co–OH---H---HO–Co units. The intermolecular hydrogen bond distances quoted in Table XII show that these bonds are strong with an O–O distance varying from 2.41 to 2.59 Å. It should be noted that Ardon and Bino use a different

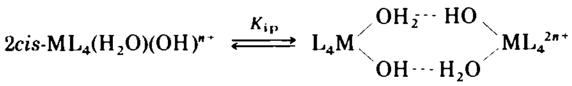
TABLE XII

STRUCTURAL DATA FOR INTERMOLECULAR HYDROGEN-BONDED CATION PAIRS

Compound	$O_1 \cdots O_2$ (Å)	$M_1 \cdots M_2$ (Å)	Reference
cis-$[Cr(pic)_2(H_2O)(OH)]S_2O_6$	2.586(6)	6.18	*333*
$[Co(tren)(H_2O)(OH)](NO_3)_2 \cdot H_2O$	2.450(4)	4.82	*326*
cis-$[Cr(bipy)_2(H_2O)(OH)]I_2 \cdot H_2O$	2.446(5)	5.03	*331*
cis-$[Cr(bipy)_2(H_2O)(OH)](NO_3)_2$	2.442(4)	4.96	*326*
trans-$[Co(en)_2(H_2O)(OH)](ClO_4)_2$	2.441(2)	5.72	*331*
trans-$[Co(en)_2(NO_2)(H_2O)]$, *trans*-$[Co(en)_2(NO_2)(OH)](ClO_4)_3 \cdot 2H_2O$	2.412(9)	5.67	*326*
trans-$[Co(en)_2(NCS)(H_2O)]$, *trans*-$[Co(en)_2(NCS)(OH)](CF_3SO_3)_3 \cdot H_2O$	2.415(6)	5.77	*326*

terminology for these cation pairs: they refer to the hydrogen-bonded cation pair as a dimer and describe the H–O–H---OH$^-$ entity as an $H_3O_2^-$ ligand. However, the fact that the O–O distance of the $H_3O_2^-$ entity varies more than is usually observed for ligands has made the present author reluctant to adopt this terminology.

Evidence for the formation of such hydrogen-bonded cation pairs in solution has been obtained by three-phase vapor tensiometry studies on solutions of *cis*-$Cr(bipy)_2(H_2O)(OH)^{2+}$ in a saturated solution of barium nitrate (the total molality of chromium species was 0.1–0.2 *m*) (*326, 330*). It was shown that the equilibrium of Eq. (29) in concentrated solutions lies considerably to the right, and it was estimated that $K_{ip} \sim 1\ M^{-1}$.



$$2cis\text{-}ML_4(H_2O)(OH)^{n+} \overset{K_{ip}}{\rightleftharpoons} L_4M\begin{matrix} OH_2\cdots HO \\ OH\cdots H_2O \end{matrix}ML_4^{2n+} \qquad (29)$$

It is noted that the formation of such hydrogen-bonded cation pairs corresponds well to results obtained in a study of the behavior of freshly precipitated chromic hydroxide (*199*).

It is readily seen that a large value of K_{ip} would imply that the ratio [dinuclear]:[mononuclear] becomes constant and independent of the total metal-ion concentration. The observation that K_d for Eq. (28) is a true constant, which does not vary within a reasonably large metal-ion concentration range, is therefore indirect evidence that K_{ip} is small, and this seems to be the case for the chromium(III) and rhodium(III) complexes listed in Table XI.

It may thus be concluded that variations in K_d can to a large extent be rationalized in terms of charge effects, but that intramolecular hydrogen bond interactions (α type) may contribute significantly to stabilization of the dinuclear species. Intermolecular hydrogen bond interactions may stabilize the mononuclear species, but in the case of +2 charged cations such interactions are measurable only in very concentrated solutions. The possible kinetic consequences of these inter- and intramolecular hydrogen bond interactions are discussed in Sections VII and VIII.

C. Dihydroxo-Bridged Species

The formation of dihydroxo-bridged species may be considered to take place via stepwise formation of a monohydroxo-bridged species with subsequent intramolecular bridge formation. Thermodynamic

TABLE XIII

Equilibrium Constants $K_d = Q_{22}/(Q_{11})^2$ for Eq. (31)

Mononuclear species	K_d (M^{-1})	Temperature (°C)	Ionic strength (M)	Reference
$Sc(OH)^{2+}$	$10^{4.2}$	25	1.0	*22*
$Y(OH)^{2+}$	$10^{4.0}$	25	3.0	*22*
$Al(OH)^{2+}$	$10^{3.0}$	25	1.0	*22*
$Cr(OH)^{2+}$	$10^{3.6}$	25	1.0	*22, 31*[a]
$Cr(nta)(H_2O)(OH)^-$	$10^{3.28}$	25	1.0	*171*
$Co(tach)(H_2O)_2(OH)^{2+}$	$10^{3.5}$	20	0.1	*174*
cis-$Co(NH_3)_2(NO_2)_2(H_2O)(OH)$	$10^{2.2}$	20	0.1	*174*
$Co(tren)(H_2O)(OH)^{2+}$	<10	20	0.1	*174*
fac-$Co(NH_3)_3(H_2O)_2(OH)^{2+}$	>1	20	0.1	*174*
fac-$Co(bamp)(H_2O)_2(OH)^{2+}$	$\ll 1$	20	0.1	*174*
cis-$Co(en)_2(H_2O)(OH)^{2+}$	$\ll 1$	20	0.1	*332*

[a] Calculated from $Q_{22}(\text{av}) = 10^{-5.0}$ M (Table XIV) and $Q_{11} = 10^{-4.29}$ M (*31*).

data for reaction Eq. (30) are known for a number of systems and are discussed in Section IX.

$$(H_2O)L_4M(OH)ML_4(OH)^{n+} \rightleftharpoons L_4M(OH)_2ML_4^{n+} + H_2O \tag{30}$$

Condensation to give dihydroxo-bridged species is often described by Eq. (31), which is related to Eq. (27) by $K_d = Q_{22}/(Q_{11})^2$. The cation $(H_2O)_4Cr(OH)_2Cr(H_2O)_4^{4+}$ and the anion $(nta)Cr(OH)_2Cr(nta)^{2-}$ are so far the only chromium(III) complexes for which K_d has been determined. A number of amine Co(III) complexes have been shown to hydrolyze according to Eq. (31), but only in a few instances has it been possible to determine the equilibrium constant K_d.

$$2cis\text{-}ML_4(H_2O)(OH)^{(n-1)+} \xrightleftharpoons{K_d} L_4M(OH)_2ML_4^{(2n-2)+} + 2H_2O \tag{31}$$

From the values given in Table XIII it is noted that K_d is apparently much more sensitive to variation of the nonbridging ligands than to variation of the metal ion. It is seen that K_d for all the aqua metal ions lies within a relatively narrow range of about $10^{3.5}$ M^{-1}. In contrast, chromium(III) and cobalt(III) amine complexes have K_d values which vary by at least five orders of magnitude.

D. Trihydroxo-Bridged Species

Although condensation of $ML_3(H_2O)_2(OH)^{2+}$ and $ML_3(H_2O)(OH)_2^+$ to trihydroxo-bridged species is known for chromium(III), cobalt(III), and rhodium(III), the equilibrium constants have been determined only for the tach cobalt(III) system, which has $K_d = 10^{9.4}\ M^{-1}$ [Eq. (2)] (*174*).

E. THE AQUA CHROMIUM(III) SYSTEM

Stability constants for higher oligomers have, until now, been reported only for the aqua chromium(III) system. In addition to Bjerrum's classical study of this system (*14*), stability data for this very complicated system have been reported by several independent groups (*26, 27, 28, 200*). The Q_{xy} values given in Table XIV show some deviation between the values reported by different authors, and it should further be noted that Q_{46} applies to a mixture of at least two tetranuclear species (see Section IV). The stability constants K_n for the stepwise polymerization process, Eq. (32), have been determined as $K_2 \approx 1 \times 10^5\ M^{-1}$, $K_3 \approx 6 \times 10^6\ M^{-1}$, and $K_4 \approx 2 \times 10^5\ M^{-1}$. The change in free energy is therefore approximately the same when $Cr(H_2O)_4(OH)_2^+$ is added successively to form di-, tri-, and tetranuclear species, respectively, and this regular trend may indicate structural similarity between the different polynuclear species, as discussed in Section IV. It should be noted, however, that the trinuclear species is significantly more stable than both the di- and tetranuclear species. A similar

$$Cr_{n-1}(OH)_{2n-4}^{(n+1)+} + Cr(OH)_2^+ \xrightleftharpoons{K_n} Cr_n(OH)_{2n-2}^{(n+2)+} \qquad (32)$$

TABLE XIV

EQUILIBRIUM DATA FOR THE REACTION[a]

$$x\text{Cr}^{3+} \xrightleftharpoons{Q_{xy}} \text{Cr}_x(\text{OH})_y^{(3x-y)+} + y\text{H}^+$$

$Cr_x(OH)_y^{(3x-y)+}$	$-\log Q_{xy}$[c]	ΔH_{xy}[b] (kJ mol^{-1})	ΔS_{xy}[b] (J mol^{-1} K^{-1})
$Cr_2(OH)_2^{4+}$	5.34,[d] 5.1,[e] 4.9[b]	53[f]	84[f]
$Cr_3(OH)_4^{5+}$	8.3,[e] 7.95[b]	96[g]	314[g]
$Cr_4(OH)_6^{6+}$	≤14.1[d]	—	—

[a] At $I = 1.0\ M$ and 25°C.

[b] From Ref. *22*, extrapolated on the basis of data given in Refs. *28* and *334*.

[c] $Q_{xy} = [H^+]^y[Cr_x(OH)_y^{(3x-y)+}]/[Cr^{3+}]^x$.

[d] From Ref. *31*.

[e] From Ref. *31*, extrapolated on the basis of data given in Refs. *26* and *27*.

[f] From Ref. *26*.

[g] From Ref. *27*.

increased stability of trinuclear relative to dinuclear species has been observed for the tacn system, where heating of an aqueous solution of *trans*-$(H_2O)(tacn)Cr(OH)_2Cr(tacn)(H_2O)^{4+}$ under reflux yields a trinuclear species in high yield (*50*).

VI. Acid–Base Equilibria

The acid–base properties of the polynuclear complexes are closely connected with the reactivity of these compounds, this being primarily a question of the acid–base properties of terminally coordinated water or hydroxide and bridging hydroxide. The protolytic properties of water and hydroxide ligand are influenced by the nature of the other ligands, by the overall charge, by the medium, and by the central ion in the same way as is known for mononuclear species. However, for both ligands the acid–base properties can be predicted only in a few cases on the basis of the properties of the corresponding mononuclear species. In most cases, other properties specific to the polynuclear compounds are of importance, particularly the formation of intramolecular hydrogen bonds, and the effect of these properties on the acid strength of terminally coordinated water in particular can be very pronounced.

A. BRIDGING HYDROXIDE

The bridging hydroxo ligand is a weak acid as well as an extremely weak base. The acid properties are by far the best investigated, and acid dissociation constants have been reported for singly and doubly bridged dinuclear complexes containing one or two hydroxo bridges (cf. Tables XV and XVI).

TABLE XV

ACID STRENGTH OF BRIDGING HYDROXIDE IN SINGLY BRIDGED CHROMIUM(III) COMPLEXES AT 20°C

Complex	pK_a	Medium	Reference
cis-$(NH_3)_5Cr(OH)Cr(NH_3)_4(enH)^{6+}$	6.36[a]	0.1 *M* KCl	*256*
$(NH_3)_5Cr(OH)Cr(NH_3)_5^{5+}$	7.63	0.12 *M* $NaClO_4$	*24*
trans-$(NH_3)_5Cr(OH)Cr(NH_3)_4(OH)^{4+}$	~9	1 *M* $NaClO_4$	*129*
cis-$(NH_3)_5Cr(OH)Cr(NH_3)_4NCS^{4+}$	10.62	0.11 *M* $NaClO_4$	*24*
trans-$(NH_3)_5Cr(OH)Cr(NH_3)_4Cl^{4+}$	11.37	0.2 *M* NaCl	*24*
cis-$(NH_3)_5Cr(OH)Cr(NH_3)_4F^{4+}$	13.4	1.0 *M* (KCl, NaOH)	*24*
cis-$(NH_3)_5Cr(OH)Cr(NH_3)_4(OH)^{4+}$	>16	0.14 *M* $NaClO_4$	*24*

[a] The coordinated $NH_2CH_2CH_2NH_3^+$ ligand has a pK_a = 8.42 (*256*).

TABLE XVI

ACID STRENGTH OF BRIDGING HYDROXIDE IN $L_4Cr(OH)_2CrL_4^{4+}$ SPECIES AT 25°C AND $I = 1.0\ M$

L_4[a]	Configuration	pK_{a1}	pK_{a2}	Reference
$(NH_3)_4$	—	~12	—	*220*
$(en)_2$	Δ,Λ	~12	>14	*33*
$(tn)_2$	—	~12	—	*216*
$(mepic)_2$	Δ,Δ(α,α)(*RR,RR*)	10.7	—	*111*[a]
bispicen	Δ,Δ(α,α)(*RR,RR*)	9.3	—	*152*[a]
bispicpn	Δ,Δ(α,α)	~9	>14	*152*
$(bipy)_2$	Δ,Δ	7.60	11.9	*37*[a]
$(phen)_2$	Δ,Δ	7.40	11.8	*37*[a]
nta[b]	—	8.7	9.8	*171*

[a] pK_a measured for the racemic salt.

[b] $(nta)Cr(OH)_2Cr(nta)^{2-}$

1. *Monohydroxo-Bridged Species*

The species must studied in this context are the so-called rhodo ion, $(NH_3)_5Cr(OH)Cr(NH_3)_5^{5+}$, and its derivatives *cis-* and *trans-* $(NH_3)_5Cr(OH)Cr(NH_3)_4X^{(5-n)+}$, the so-called aniono erythro ions. In strong base these ions deprotonate, giving oxo-bridged blue cations, as shown in Eq. (33) and (34).

$$(NH_3)_5Cr(OH)Cr(NH_3)_5^{5+} \rightleftharpoons (NH_3)_5CrOCr(NH_3)_5^{4+} + H^+ \qquad (33)$$

$$(NH_3)_5Cr(OH)Cr(NH_3)_4X^{(5-n)+} \rightleftharpoons (NH_3)_5CrOCr(NH_3)_4X^{(4-n)+} + H^+ \qquad (34)$$

In Eq. (34) the configuration may be either cis or trans and X can be, for example, OH^-, Cl^-, F^-, SCN^-, or $^-NH_2CH_2CH_2NH_3^+$ (cf. Table XV). The blue species are unstable, and one cis ammonia ligand in the basic rhodo ion and the X groups in the basic erythro ions are hydrolyzed rapidly in the basic solutions. The K_a values have therefore been determined by a rapid-flow technique in combination with potentiometric or spectrophotometric measurements (*24*).

The basic rhodo ion has been isolated as a salt and its crystal structure has been reported (Table V), but the instability and lability of the other oxo-bridged species have prevented their isolation as salts.

The rhodo ion is the only +5 charged species in this series and it has a significantly higher acidity than expected. From the pK_a values of H_3O^+ ($pK_a \sim -1.7$) and of $Cr(NH_3)_5(H_2O)^{3+}$ ($pK_a \sim 5.2$) it is anticipated that $(NH_3)_5Cr(OH)Cr(NH_3)_5^{5+}$ should have $pK_a \sim 12$. This is very much higher than the observed value of ~8. The increased acidity is a consequence of π bond formation between chromium(III) and the oxide ligand in the linear oxo-bridged form, i.e., stabilization of the base form by donation of electrons from oxygen to chromium(III).

The cation *cis*-$(NH_3)_5Cr(OH)Cr(NH_3)_4(NH_2CH_2CH_2NH_3)^{6+}$ is formally a +6 charged species, but since the charge of the ammonium group is remote from the hydroxo bridge, it is reasonable that the acidity of the latter is comparable to that for the +5 charged rhodo ion.

The lower acidities of the +4 charged erythro ions relative to that of the +5 charge rhodo ion are to some extent explicable on the basis of charge effects. However, if one considers the variation of pK_a with X^- for the erythro cations of the same charge, $(NH_3)_5Cr(OH)$-$Cr(NH_3)_4X^{4+}$, it is clear that the very large variation in pK_a cannot be explained in terms of simple inductive effects. The substitution of Cl^- by OH^- in *trans*-$(NH_3)_5Cr(OH)Cr(NH_3)_4Cl^{4+}$ reduces the acid strength by more than 2 pK units, while a similar substitution in $Cr(H_2O)_5Cl^{2+}$ causes a change in pK_a of only 0.4 units (*24*). Differences in π bond stabilization resulting from differences in the properties of the nonbridging ligands could be responsible for the large variations observed, but no quantitative considerations of this issue have been reported. In any case, it is not easy to find an explanation for the very large difference (>7 pK units) between the pK_a values of the two isomers of the $(NH_3)_5Cr(OH)Cr(NH_3)_4(OH)^{4+}$ ion.

A number of +3 charged singly bridged species of the type $(HO)L_4M(OH)ML_4(OH)^{3+}$ have been reported for chromium(III), rhodium(III), and iridium(III), all of them having pK_a > 14 (*33, 35, 67, 133*).

2. *Dihydroxo-Bridged Species*

Dihydroxo-bridged complexes may deprotonate to form μ-hydroxo–μ-oxo and di-μ-oxo species, as shown in Eqs. (35) and (36).

$$L_4M(OH)_2ML_4^{n+} \xrightleftharpoons{K_{a1}} L_4M(OH)(O)ML_4^{(n-1)+} + H^+ \tag{35}$$

$$L_4M(OH)(O)ML_4^{(n-1)+} \xrightleftharpoons{K_{a2}} L_4M(O)_2ML_4^{(n-2)+} + H^+ \tag{36}$$

Nearly all the reported studies have been on chromium(III) complexes (*cf.* Table XVI). The chromium(III) complexes $L_4Cr(OH)_2CrL_4^{4+}$ with ammonia or aliphatic diamines (en and tn) deprotonate in strongly basic solutions to form blue μ-hydroxo–μ-oxo species, which in some cases have been isolated as stable and crystalline salts, e.g., Δ,Λ-

$[(en)_2Cr(OH)(O)Cr(en)_2](ClO_4)_3 \cdot 2H_2O$ (*33*). Deprotonation to yield a di-μ-oxo bridged species has not been observed. Studies of these basic forms are made difficult by the fact that they rapidly undergo bridge cleavage to form the singly bridged species, e.g., Δ,Λ-$(OH)(en)_2Cr(OH)Cr(en)_2(OH)^{3+}$. In the case of the ammonia complex, hydrolysis of the ammonia ligands further complicates the issue.

A number of dinuclear species with bi- or tetradentate ligands containing heteroaromatic nitrogen ligators show acid properties similar to those of the ammine and diamine analogs, and they appear to be much more robust (or more stable) in basic media with respect to bridge cleavage than the latter. The chromium(III) complexes with 1,10-phen and 2,2′-bipy deprotonate in basic solution, forming yellow μ-hydroxo–μ-oxo species and brown di-μ-oxo species (*37, 336*), and these basic forms have been isolated as crystalline salts (*37, 161*) and their magnetic properties studied (*335*). Similar acid properties have also been reported for the chromium(III) complexes with pyridyl-substituted amines (mepic, bispicen, or bispicpn) (*111, 152*).

From the pK_a values listed in Table XVI it can be seen that pK_{a1} decreases as the number of heteroaromatic N donors increases: values are $pK_{a1} \sim 12$ when all N donors are aliphatic, $pK_{a1} \sim 10$ when there is an equal number of aliphatic and heteroaromatic N donors, and $pK_{a1} \sim 7.5$ when all N donors are heteroaromatic. A similar trend has been observed for the mononuclear species *cis*-$CrL_4(H_2O)_2{}^{3+}$, which for $L_4 = (en)_2$ and $(phen)_2$ show $pK_{a1} = 4.75$ (*337*) and 3.4 (*181*), respectively.

The difference between the first and the second pK_a values for the dihydroxo-bridged complexes is more than 4 pK units, which is significantly larger than the differences observed in the corresponding mononuclear species, which is about 2 pK units. The large difference for the dinuclear species is contrary to the effect expected on the basis of electrostatic consideration, since the charge is distributed among two metal centers in the binuclear species. The larger separation of the pK_a values may reflect that a large bridging angle and thereby good π bonding can be achieved more easily for an oxo bridge in a mono-deprotonated complex than in a doubly deprotonated complex.

It is interesting that the acid strength of the $(nta)Cr(OH)_2Cr(nta)^{2-}$ ion is comparable to that of the tetrapositive 1, 10-phen complex, for example, a fact which is in keeping with the above suggestion that factors other than the overall charge strongly influence the acid strength of these complexes.

The few and rather preliminary pK_a values for dihydroxo-bridged rhodium(III) and iridium(III) complexes which have been measured indicate that these are weaker acids than the chromium(III) species

(*67, 133, 217*). This is consistent with trends observed for the mononuclear species and with the reduced tendency toward π bonding of the metal ions with filled d_π orbitals.

A number of hetero-bridged complexes of the type $(en)_2Cr(OH)(X)Cr(en)_2^{(5-n)+}$ for $X^{n-} = SO_4^{2-}$ or $RCOO^-$ have been studied and they all exhibit $pK_{a1} \sim 12$. The observation that the +3 charged sulfato complex is more acidic than the +3 charged μ-hydroxo–μ-oxo analog ($pK_a > 14$) reflects the greater flexibility of the former ring system, implying that the Cr–O–Cr angle in the deprotonated sulfato complex can attain a larger value than is possible in the di-μ-oxo complex (*33, 262, 263*).

3. *Trihydroxo-Bridged Species*

Only a few trihydroxo-bridged complexes have been studied: $(tacd)Cr(OH)_3Cr(tacd)^{3+}$ has $pK_a = 12.9$ (25°C, $I = 0.4\ M$) (98) and $(tach)Co(OH)_3Co(tach)^{3+}$ has $pK_a \sim 14$ (*186*).

B. BRIDGING WATER

The hydroxo bridge possesses very weak basic properties, but there has been no report of any direct evidence for the formation of aqua-bridged complexes. From an extrapolation of the pK_a values of water ($pK_a \sim 15.7$) and of $Cr(NH_3)_5(H_2O)^{3+}$ ($pK_a \sim 5.2$) it is anticipated that an aqua-bridged complex such as $(NH_3)_5Cr(OH_2)Cr(NH_3)_5^{6+}$ should have a pK_a in the region of -5. Spectroscopic studies support this proposal, but from the available data only an upper limit of about -1 can be estimated (*33, 35, 36, 67, 133, 217*). From the kinetic data presented in the following sections it is concluded that the aqua-bridged species are unstable and labile with respect to bridge cleavage, which explains why such species have not been isolated as salts. In this context, however, it is of interest to mention that X-ray crystal structures of aqua-bridged species with copper(II), nickel(II), cadmium(II), cobalt(II), and ruthenium(II) have been reported (*338–345*).

C. TERMINALLY COORDINATED WATER

The acid strength of the terminally coordinated water ligands in many polynuclear complexes is strongly influenced by intramolecular hydrogen bond interaction. The main issue of the last part of this section will be a discussion of such interactions, although other

TABLE XVII

ACID STRENGTH OF WATER LIGANDS IN DINUCLEAR COMPLEXES WITH NEGLIGIBLE INTRAMOLECULAR HYDROGEN BOND INTERACTION AT 25°C AND $I = 1.0\ M$

Complex	pK_{a1}	pK_{a2}	ΔpK_a	Reference
cis-$(NH_3)_5Cr(OH)Cr(NH_3)_4(H_2O)^{5+}$	3.5[a]	—	—	*347*
trans-$(NH_3)_5Cr(OH)Cr(NH_3)_4(H_2O)^{5+}$	≈4.5	—	—	*129*
trans-$(H_2O)(NH_3)_3Cr(OH)_2Cr(NH_3)_3(H_2O)^{4+}$	6.15	7.48	1.33	*319*
trans-$(H_2O)(tacn)Cr(OH)_2Cr(tacn)(H_2O)^{4+}$	5.08	7.25	2.17	*319*

[a] $pK_a = 2.8$ at 20°C in 0.14 M $NaClO_4$ (*24*).

factors such as the charge on the complex ion and the nature of the other ligands need also to be considered. The influence of the latter is best illustrated by first considering some of the few polynuclear complexes in which intramolecular hydrogen bond interactions must be expected to play a minor role.

1. *Comparison with Mononuclear Species*

The acid strength of terminally coordinated water in polynuclear species is influenced by the charge, and the effect may be compared with that in mononuclear species (Tables XVII and XVIII). Since the charge

TABLE XVIII

ACID DISSOCIATION CONSTANTS FOR MONONUCLEAR AQUA COMPLEXES AT 25°C IN 1.0 M $(Na,H)ClO_4$

Complex	pK_{a1}	pK_{a2}	ΔpK(monomer) $= pK_{a2} - pK_{a1}$	Reference
trans-$Cr(NH_3)_4(H_2O)_2^{3+}$	4.38	7.78	3.40	*337*
cis-$Cr(NH_3)_4(H_2O)_2^{3+}$	4.96	7.53	2.57	*337*
cis-$Cr(en)_2(H_2O)_2^{3+}$	4.75	7.35	2.60	*337*
fac-$Cr(NH_3)_3(H_2O)_3^{3+}$	5.00	7.27	2.27	*347*
$Cr(tacn)(H_2O)_3^{3+}$	4.47	6.64	2.17	*347*
cis-$Co(NH_3)_4(H_2O)_2^{3+}$	5.69[a]	7.99[a]	2.30	*174*
cis-$Co(en)_2(H_2O)_2^{3+}$	6.06[b]	8.19[b]	2.13	*332*
cis-$Rh(NH_3)_4(H_2O)_2^{3+}$	6.40	8.32	1.92	*346*
cis-$Rh(en)_2(H_2O)_2^{3+}$	6.34	8.24	1.90	*217*
cis-$Ir(en)_2(H_2O)_2^{3+}$	6.29	8.10	1.81	*348*
$Ir(H_2O)_6^{3+}$	4.37	5.2	0.8	*349*

[a] 0.1 M $NaClO_4$, 20°C.

[b] 1 M $NaNO_3$.

on the polynuclear species is distributed among several metal centers, it would seem reasonable when making such comparisons to consider the average charge per metal center rather than the total charge. The *trans*-$(H_2O)(NH_3)_3Cr(OH)_2Cr(NH_3)_3(H_2O)^{4+}$ cation is a significantly stronger acid than *cis*-$Cr(NH_3)_4(OH)(H_2O)^{2+}$:$pK_{a1} = 6.2$ and 7.5, respectively [here, and in the following discussion, the minor statistical corrections which ought to be made due to the presence of different numbers of water (hydroxide) ligands have been ignored]. Similarly, *cis*-$(NH_3)_5Cr(OH)Cr(NH_3)_4(H_2O)^{5+}$ has $pK_a = 3.5$, which is significantly lower than the average value $\frac{1}{2}(pK_{a1} + pK_{a2}) = 6.25$ for the *cis*-$Cr(NH_3)_4(H_2O)_2{}^{3+}$ ion. The same is found if *trans*-$(NH_3)_5Cr(OH)Cr(NH_3)_4(H_2O)^{5+}$ is compared with the trans diaqua mononuclear species. These few examples indicate that the acid strength of a water ligand in a polynuclear species is greater than that in the corresponding mononuclear species, of charge equal to the average charge per metal center in the polynuclear species.

The difference between the two pK_a values for *trans*-$(H_2O)(NH_3)_3$-$Cr(OH)_2Cr(NH_3)_3(H_2O)^{4+}$ is 1.3, which is significantly less than the difference of 2.6 observed for *cis*-$Cr(NH_3)_4(H_2O)_2{}^{3+}$. This is in accordance with the fact that the water ligands are separated more in the dinuclear cation than in the mononuclear cation.

The influence of the other ligands, as long as they do not participate in intramolecular hydrogen bonds, is expected to be the same as that observed in the corresponding mononuclear species. The number of complexes for which this can be examined is small, but the pK_a values for the trans isomers of $(H_2O)L_3Cr(OH)_3CrL_3(H_2O)^{4+}$ with $L_3 = (NH_3)_3$ or tacn do indeed show that the complex with the more bulky amine is the stronger acid, as observed for the mononuclear complexes (Tables XVII and XVIII).

The difference in acid strength of the cis and trans isomers of $(NH_3)_5Cr(OH)Cr(NH_3)_4(H_2O)^{5+}$ may be explained as an effect of the ligand trans to water. A comparison with the effect of trans ligand on the water ligand acidity observed for mononuclear ammine and amine complexes of chromium(III) or rhodium(III) (*346*) leads to the sequence $\mu(OH) < OH \sim NH_3 < H_2O$ for increasing acidity due to the trans ligand.

2. *Hydrogen Bond Interactions*

a. Monohydroxo-Bridged Species. Chromium(III), rhodium(III), and iridium(III) complexes of the type *cis,cis*-$(H_2O)L_4M(OH)ML_4$-$(H_2O)^{5+}$ are known for $L_4 = (NH_3)_4$, $(en)_2$, $(NH_3)_3(H_2O)$, or $(H_2O)_4$.

TABLE XIX

Acid Strength of Water Ligands in Monohydroxo-Bridged Complexes Affected by Intramolecular Hydrogen Bonds at 25°C in 1.0 M (Na,H)ClO_4

Complex ion	pK_{a1}	pK_{a2}	ΔpK(dinuclear) $= pK_{a2} - pK_{a1}$	Reference
$(H_2O)_5Cr(OH)Cr(H_2O)_5{}^{5+}$	1.6	—	—	*28*[a]
cis,cis-$(H_2O)(NH_3)_4Cr(OH)Cr(NH_3)_4(H_2O)^{5+}$	1.75	7.50	5.75	*36*
Δ,Λ-$(H_2O)(en)_2Cr(OH)Cr(en)_2(H_2O)^{5+}$	0.48	7.94[b]	7.27[b]	*33, 36*
$\Delta,\Delta/\Lambda,\Lambda$-$(H_2O)(en)_2Cr(OH)Cr(en)_2(H_2O)^{5+}$	0.54	6.87[c]	6.30[c]	*35*
Δ,Λ-$(H_2O)(en)_2Cr(OH)Co(en)_2(H_2O)^{5+}$	1.31	~8	~6.7	*36, 214, 215*
fac-$(H_2O)_2(NH_3)_3Cr(OH)Cr(NH_3)_3(H_2O)_2{}^{5+}$	1.5	5.52	4.0	*319*
cis,cis-$(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(H_2O)^{5+}$	3.41	8.80	5.39	*133*
Δ,Λ-$(H_2O)(en)_2Rh(OH)Rh(en)_2(H_2O)^{5+}$	2.37	9.13	6.76	*217*
Δ,Λ-$(H_2O)(en)_2Ir(OH)Ir(en)_2(H_2O)^{5+}$	1.91	9.04	7.13	*67*
$(H_2O)_5Ir(OH)Ir(H_2O)_5{}^{5+}$	0.8[d]	—	—	*251*

[a] Determined from kinetic data, 2 M (Li,H)ClO_4. The $pK_a \approx 1.3$–1.6 has recently been reported in an independent study (*350*).

[b] At 0.8°C; $pK_{a1} = 0.67$ at this temperature.

[c] At 20°C; $pK_{a1} = 0.57$ at this temperature.

[d] 2 M (Li,H)ClO_4.

A common and very important feature for all these species is that the first and second acid dissociation constants are significantly larger and smaller, respectively, than predicted from the behavior of the corresponding mononuclear species, following the lines of reasoning given above (Tables XVIII and XIX). This may be illustrated by comparing the difference $\Delta pK(\text{dinuclear}) = pK_{a2} - pK_{a1} = 7.3$ for Δ,Λ-$(H_2O)(en)_2Cr(OH)Cr(en)_2(H_2O)^{5+}$ with the difference $\Delta pK(\text{mononuclear}) = pK_{a2} - pK_{a1} = 2.6$ for the corresponding mononuclear species *cis*-$Cr(en)_2(H_2O)_2{}^{3+}$. The observation that $\Delta pK(\text{dinuclear}) \gg \Delta pK(\text{mononuclear})$ is the opposite of what would be expected from the fact that the protolytic groups are further apart in the dinuclear ion than in the mononuclear ion. The large value for ΔpK(dinuclear) reflects an unexpectedly large stabilization of the aquahydroxo cation relative to its corresponding acid or base forms. Similar strong stabilization of the aqua hydroxo species has been observed for a series of analogous chromium(III), rhodium(III), and iridium(III) complexes (cf. Table XIX). This increased stability of the aqua hydroxo cation has been explained as arising from intramolecular hydrogen bond formation between the hydroxide ligand bound at one metal center and the water ligand bound at the other, as

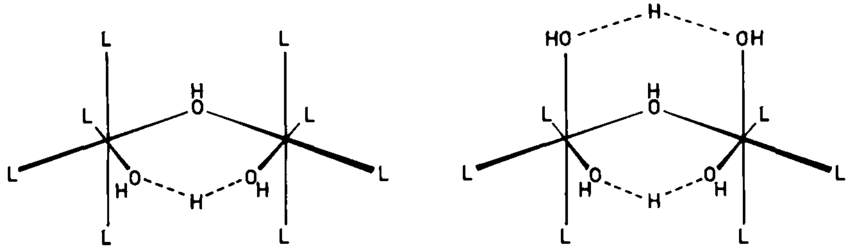


FIG. 15. Intramolecular hydrogen bond stabilization of monohydroxo-bridged complexes.

shown in Fig. 15 (*33, 35, 36, 67, 133, 217*). Crystallographic evidence for this kind of hydrogen bond formation (α type) has been discussed in Section II,B.

For the complex *fac,fac*-$(H_2O)_2(NH_3)_3Cr(OH)Cr(NH_3)_3(H_2O)_2{}^{5+}$ the first acid dissociation constant clearly shows that the singly deprotonated species must be hydrogen bond stabilized (Table XIX). However, the fact that the difference between the first and the second acid dissociation constants for this system is relatively small is consistent with stabilization also of the doubly deprotonated species (by two intramolecular hydrogen bonds) as shown in Fig. 15. A similar effect is expected for the cations $(H_2O)_5Cr(OH)Cr(H_2O)_5{}^{5+}$ and $(H_2O)_5Ir(OH)Ir(H_2O)_5{}^{5+}$.

b. Dihydroxo-Bridged Species. Intramolecular hydrogen-bond stabilization also explains the significant difference between the cis and trans isomers of the ions $(H_2O)L_3Cr(OH)_2CrL_3(OH_2)^{4+}$ (see Fig. 16).

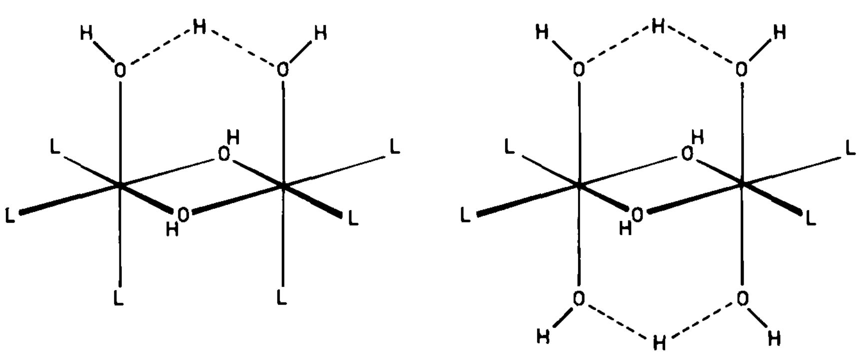


FIG. 16. Intramolecular hydrogen bond stabilization of dihydroxo-bridged complexes.

TABLE XX

ACID STRENGTH OF WATER LIGANDS IN CATIONS OF THE TYPE $(H_2O)L_3Cr(OH)_2CrL_3(H_2O)^{4+}$ AFFECTED BY INTRAMOLECULAR HYDROGEN BONDS AT 25°C IN 1.0 M (Na,H)ClO$_4$

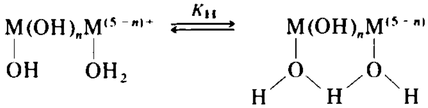
L_3	pK_{a1} (cis isomer)	pK_{a2} (cis isomer)	ΔpK^a (cis isomer)	ΔpK^b (trans isomer)	Reference
$(NH_3)_3$	4.19	9.05	4.86	1.33	*319*
(tacn)	2.82	8.8	5.98	2.17	*319*
	pK_{a1}	pK_{a2}	ΔpK	—	—
$(H_2O)_3$	3.68	6.04	2.36	—	*31*

[a] $\Delta pK = pK_{a2} - pK_{a1}$.
[b] See also Table XVII.

From the data in Tables XVII and XX it is seen that for both the ligands NH_3 and tacn ΔpK(cis) $\gg$ ΔpK(trans) and that this is due to an increase in K_{a1} as well as a decrease in K_{a2} for the cis isomer relative to the trans isomer.

A similar effect may explain the rather high strength of $(H_2O)_4Cr(OH)_2Cr(H_2O)_4{}^{4+}$, but in this system the doubly deprotonated cation may also be stabilized by two identical intramolecular hydrogen bonds (Fig. 16), which explains the significantly smaller ΔpK value (cf. Table XX) for this system than for *cis*-$(H_2O)L_3Cr(OH)_2CrL_3(H_2O)^{4+}$.

c. Quantitative Considerations. For the monohydroxo-bridged complexes of the type *cis,cis*-$(H_2O)L_4M(OH)ML_4(H_2O)^{5+}$ and the dihydroxo-bridged complexes of the type *cis*-$(H_2O)L_3M(OH)_2$-$ML_3(H_2O)^{4+}$ (L_3 and L_4 refer to ammine or amine ligands) it is possible to obtain an estimate for the magnitude of the hydrogen bond stabilization, i.e., the equilibrium constant K_H for Eq. (37).



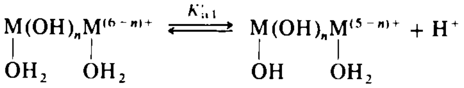
$$\underset{\substack{| \qquad\quad |\\ OH \quad OH_2}}{M(OH)_nM^{(5-n)+}} \overset{K_H}{\rightleftharpoons} \underset{\substack{| \qquad\quad |\\ H-O\cdots H\cdots O-H}}{M(OH)_nM^{(5-n)+}} \tag{37}$$

The observed acid dissociation constants K_{a1} and K_{a2} may then be expressed by Eqs. (38) and (39), where K'_{a1} and K'_{a2} are the microscopic

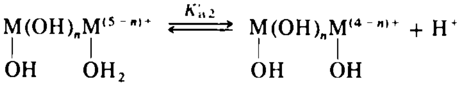
$$K_{a1} = K'_{a1}(1 + K_H) \tag{38}$$

$$K_{a2} = K'_{a2}/(1 + K_H) \tag{39}$$

equilibrium constants for the equilibria, Eqs. (40) and (41), between the non-hydrogen-bonded species.



$$\underset{OH_2}{\mathrm{M}}(\mathrm{OH})_n\underset{OH_2}{\mathrm{M}}^{(6-n)+} \xrightleftharpoons{K'_{a1}} \underset{OH}{\mathrm{M}}(\mathrm{OH})_n\underset{OH_2}{\mathrm{M}}^{(5-n)+} + \mathrm{H}^+ \qquad (40)$$



$$\underset{OH}{\mathrm{M}}(\mathrm{OH})_n\underset{OH_2}{\mathrm{M}}^{(5-n)+} \xrightleftharpoons{K'_{a2}} \underset{OH}{\mathrm{M}}(\mathrm{OH})_n\underset{OH}{\mathrm{M}}^{(4-n)+} + \mathrm{H}^+ \qquad (41)$$

Since $K_H \gg 1$, Eqs. (38) and (39) may be combined to give Eq. (42) and

$$\log K_H = \tfrac{1}{2}[\Delta pK_a(\text{dinuclear}) - \Delta pK'_a(\text{dinuclear})] \qquad (42)$$

K_H can be calculated if $\Delta pK'_a$(dinuclear) is known. The microscopic equilibrium constants K'_a cannot be determined directly, but a good estimate for $\Delta pK'_a$(dinuclear) = $pK'_{a2} - pK'_{a1}$ can be obtained. Following the discussion above, the difference between the pK_a values for *trans*-$(H_2O)L_3Cr(OH)_2CrL_3(H_2O)^{4+}$ ions can be taken as a reliable estimate for $\Delta pK'_a$(dinuclear). This gives $\Delta pK'_a = 2.2$ for the tacn chromium(III) complex and $\Delta pK'_a = 1.3$ for the ammine and ethylenediamine complexes of chromium(III) (Table XVII). The corresponding values for the ammine and ethylenediamine complexes of rhodium(III) and iridium(III) are probably slightly smaller, as suggested by the data for the mononuclear species; ΔpK_a(mononuclear) for chromium(III) is about 0.7 pK units greater than for rhodium(III) and iridium(III) (TableXVIII). If this difference (0.7) is assumed to apply to the dinuclear complexes, the value $\Delta pK'_a$(dinuclear) = 0.6 is then obtained for rhodium(III) and iridium(III). These estimated $\Delta pK'_a$(dinuclear) values yield the K_H values quoted in Table XXI.

TABLE XXI

HYDROGEN BOND STABILIZATION OF $(H_2O)L_{5-n}M(OH)_nML_{5-n}(OH)^{(5-n)+}$ SPECIES AT 25°C IN 1.0 *M* (Na,H)ClO$_4$[a]

Complex ion	K_H[Cr(III)]	K_H[Rh(III)]	K_H[Ir(III)]
cis,cis-$(H_2O)(NH_3)_4M(OH)M(NH_3)_4(OH)^{4+}$	$10^{2.2}$	$10^{2.4}$	—
Δ,Λ-$(H_2O)(en)_2M(OH)M(en)_2(OH)^{4+}$	$10^{3.0}$[b]	$10^{3.1}$	$10^{3.3}$
cis-$(H_2O)(NH_3)_3M(OH)_2M(NH_3)_3(OH)^{3+}$	$10^{1.8}$	—	—
cis-$(H_2O)(tacn)M(OH)_2M(tacn)(OH)^{3+}$	$10^{1.9}$	—	—

[a] K_H is defined in Eq. (37); see the text.

[b] Estimated on the basis of ΔpK_a at 0°C and $\Delta pK'_a$ at 25°C.

TABLE XXII

THERMODYNAMIC PARAMETERS FOR THE EQUILIBRIUM[a]

$$(H_2O)L_4M(OH)ML_4(H_2O)^{5+} \underset{}{\overset{K_{a1}}{\rightleftharpoons}} (H_2O)L_4M(OH)ML_4(OH)^{4+} + H^+$$

	$L_4 = (NH_3)_4$		$L_4 = (en)_2$[b]		
M	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	Reference
Cr(III)	49(6)	129(20)	12(3)	30(9)	*33, 36*
Rh(III)	53(2)	111(5)	28(4)	49(13)	*133, 217*
Ir(III)	—	—	11(7)	−1(22)	*67*

[a] At 1 *M* (Na,H)ClO$_4$.

[b] Δ,Λ isomers.

The K_H values in Table XXI show some obvious and very reasonable trends. For the monohydroxo-bridged complexes it is seen that K_H is very sensitive to changes in the first coordination sphere, but is practically insensitive to the nature of the metal centers, i.e., $\log K_H(NH_3) \sim 2.3$ and $\log K_H(en) \sim 3.1$, independent of the metal ion. The observation that $K_H(en) > K_H(NH_3)$ is qualitatively supported by the enthalpy and entropy changes associated with the first acid dissociation equilibrium (Table XXII). Increased hydrogen bond stabilization should contribute negatively to both $\Delta H^0(K_{a1})$ and $\Delta S^0(K_{a1})$, which is consistent with the observation for both chromium(III) and rhodium(III) that it is the ammine complexes which have the highest $\Delta H^0(K_{a1})$ and $\Delta S^0(K_{a1})$ values. The greater acid strength of the ethylenediamine systems is then due to a decrease of ΔH^0, which is greater than the decrease of ΔS^0. The $\Delta H^0(K_{a1})$ and $\Delta S^0(K_{a1})$ parameters for the iridium(III) complex are, within the uncertainty limits, similar to those for the ethylenediamine complexes of chromium(III) and rhodium(III), which is consistent with the finding that K_H is almost identical for all three complexes.

The dihydroxo-bridged chromium(III) complexes are, not unexpectedly, significantly less hydrogen bond stabilized than the more flexible monohydroxo-bridged species. The variation of K_H with the nature of the nonbridging ligands which is observed for the monohydroxo-bridged species is not apparent for the dihydroxo-bridged chromium(III) species, and this may be due to the inherently rigid conformation in the latter.

From Eqs. (38) and (39) together with the K_H values in Table XXI the microscopic equilibrium constants K'_{a1} and K'_{a2} can be calculated.

For the Δ,Λ-$(H_2O)(en)_2M(OH)M(en)_2(H_2O)^{5+}$ ions this gives the values $pK'_{a1} = 3.5$, 5.5, and 5.2 for chromium(III), rhodium(III), and iridium(III), respectively. It is noted that the K'_{a1} varies in the order $Cr(III) \gg Ir(III) \sim Rh(III)$, as observed for K_{a1} for the mononuclear diaqua complexes. It is also quite reasonable that the value $pK'_{a1} = 3.5$ for the chromium(III) complex is equal to $pK_a = 3.5$ for the equally charged cis aqua erythro ion.

3. Higher Polynuclear Species

The few data available for tri- and tetranuclear species can be rationalized along the lines given above with the additional prospect of β-type hydrogen bonds being involved, i.e., interaction between the hydroxo bridges and the nonbridging ligands (see also Section II,B). The latter type of interaction has been proposed to be responsible for the enhanced acid strength ($pK_a \leq 1$) of the trinuclear chromium(III) complex $Cr_3(tacn)_3(OH)_4(H_2O)^{5+}$ (*50*).

The acid dissociation constants for tri- and tetranuclear aqua chromium(III) species are summarized in Table XXIII. The structures of these species are not known. If, however, it is assumed that they have linear structures, such as structures **4a**, **7b**, and **7c** shown in Fig. 1, then the observed acid strengths can be rationalized in terms of α -and β-type hydrogen bond interactions, as discussed recently (*118*).

TABLE XXIII

ACID DISSOCIATION CONSTANTS FOR AQUA CHROMIUM(III) OLIGOMERS AT 25°C IN 1.0 *M* (Na,H)ClO$_4$

Complex	pK_{a1}	pK_{a2}	pK_{a3}	Reference
Cr_2OH^{5+}	1.6[a]	—	—	*28*
$Cr_2(OH)_2{}^{4+}$	3.68	6.04	—	*31*
$Cr_3(OH)_4{}^{5+}$	4.35	5.63	6.0	*31*
$Cr_4(OH)_6{}^{6+}$	2.55[b]	5.08[b]	—	*31*[b]
α-$Cr_4(OH)_6{}^{6+}$	3.53	—	—	*200*
β-$Cr_4(OH)_6{}^{6+}$	0.89	—	—	*200*

[a] Determined from kinetic data; in 2 *M* (Li,H)ClO$_4$ a $pK_a \approx$ 1.3–1.6 has recently been reported in an independent study (*350*).

[b] Apparent dissociation constants for an equilibrium mixture of the α and β isomer; see also Section IV,A.

VII. Kinetics for the Condensation Reaction of Mononuclear Species to Give Dinuclear Species

The condensation of two mononuclear aqua species to form a monohydroxo-bridged dinuclear species is of fundamental interest, since it is the first step in polymerization reactions [Eq. (43)]. However,

$$ML_5(H_2O)^{n+} + ML_5(OH)^{(n-1)+} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} L_5M(OH)ML_5^{(2n-1)+} + H_2O \qquad (43)$$

kinetic studies of the forward reaction in Eq. (43) are generally complicated by subsequent (often faster) bridge-formation reactions to give di- or trihydroxy-bridged species, or by further condensation to higher polynuclear species, and this probably explains the scarcity of kinetic data for reactions of this type.

From simple electrostatic considerations it is expected that the rate of condensation will depend strongly on the charge of the mononuclear species. This is qualitatively confirmed by the observation that condensation of the neutral species $Co(NH_3)_2(NO_2)_2(OH_2)(OH)$ is much faster than condensation of +2 charged species such as $Co(tach)(H_2O)_2(OH)^{2+}$ or $Co(tren)(H_2O)(OH)^{2+}$ (*174*).

The kinetics of the condensation of the $Cr(H_2O)_6{}^{3+}$ ion and its corresponding deprotonated species have been studied in the pH region 3.5–5.0 [25°C, $I = 1.0$ M ($NaClO_4$)] (*201*). The study of this reaction is complicated by the formation of higher oligomers. Chromatographic analysis of the products as a function of time established the dinuclear species to be the main product for the first 5% of reaction, and the initial-rate kinetics of condensation were studied by a pH-stat technique. The observed pH dependence of the rate was interpreted in terms of the second-order rate constants defined by Eq. (44), and values for

$$Cr(OH)_p{}^{(3-p)+} + Cr(OH)_q{}^{(3-q)+} \xrightarrow{k_{p,q}} Cr(OH)Cr(OH)_s{}^{(5-s)+} \qquad (44)$$

k_{11}, k_{12}, and k_{22} were determined (Table XXIV). In the pH range studied the k_{00} and k_{10} processes do not contribute significantly to the rate, but k_{10} can be estimated from equilibrium data together with the rate constant for the cleavage of $(H_2O)_5Cr(OH)Cr(H_2O)_5{}^{5+}$. The condensation constants seem to be unexpectedly large. Thus the smallest rate constant, k_{10}, is 140 times larger than the bimolecular rate constant, k_{H_2O}, for water exchange of Cr^{3+} ($k_{H_2O} = k_{ex}/[H_2O] = 4.3 \times 10^{-8}$ M^{-1} s^{-1}) (*351*). A rather regular increase by a factor of ~30–200 is found for each deprotonation step in the series k_{10}, k_{11}, k_{12},

TABLE XXIV

KINETIC DATA FOR SOME DIMERIZATION REACTIONS AT 25°C

		k (M^{-1} sec^{-1})		
Reactants	$k_{p,q}$	M = Cr(H_2O)$_4$[a]	M = Rh(en)$_2$[b,c]	M = Co(*trans*[14]diene)[d]
$M(OH_2)_2^{3+} + M(OH_2)_2^{3+}$	k_{00}	—	$\approx 5 \times 10^{-14}$	—
$M(OH_2)(OH)^{2+} + M(OH_2)_2^{3+}$	k_{10}	6×10^{-6}	$\approx 1 \times 10^{-8}$	—
$M(OH_2)(OH)^{2+} + M(OH_2)(OH)^{2+}$	k_{11}	$2.0(4) \times 10^{-4}$	$\approx 6 \times 10^{-5}$	2.4×10^{-2}
$M(OH)_2^{+} + M(OH_2)(OH)^{2+}$	k_{12}	$3.8(10) \times 10^{-2}$	—	—
$M(OH)_2^{+} + M(OH)_2^{+}$	k_{22}	1.8(2)	—	—

[a] From Ref. *201*.

[b] From Ref. *325*.

[c] k_{00}, k_{10}, and k_{11} correspond to k_{-5}, k_{-4}, and k_{-3}, respectively, in Scheme 5, and refer to the formation of Δ,Λ isomers of the dinuclear species.

[d] From Ref. *352*.

and k_{22}. These increments correspond well to the increase in reactivity for water exchange found on going from Cr^{3+} to $Cr(OH)^{2+}$, $k_{ex}(Cr(OH)^{2+})/k_{ex}(Cr^{3+}) = 75$ (*351*).

Kinetic data for the formation of dinuclear species from *cis*-$Rh(en)_2(H_2O)_2{}^{3+}$ and the corresponding deprotonated species are also given in Table XXIV. These values have been calculated from the kinetic data for the cleavage reaction, k_r, in Eq. (43) (see Section VIII), together with the relevant equilibrium constants. The bimolecular rate constants for these rhodium(III) species show trends similar to those for the aqua chromium(III) ions. The significantly reduced activity of two *cis*-$Rh(en)_2(H_2O)_2{}^{3+}$ ions with respect to condensation probably reflects the fact that the nucleophile in this case is a coordinated water ligand, whereas in the other reactions it can be a coordinated hydroxide ligand. Alternatively, the enhanced reactivity of the latter species may be the result of the labilizing effect of coordinated hydroxide.

The kinetics for the dimerization of *trans*-Co(*trans*-[14]diene)$(H_2O)(OH)^{2+}$ have been reported (*352*). The product was not isolated, nor identified, but a structure such as *trans,trans*-$(H_2O)L_4Co(OH)CoL_4(OH)^{4+}$ would seem likely. The rate constant for the dimerization reaction is given in Table XXIV.

Grant and Hamm have studied the kinetics of the reaction Eq. (45) (*353*). In dilute solution the reaction is second order, as expected from Eq. (45), but with increasing concentration the order decreases until it

$$2\textit{cis}\text{-}Cr(C_2O_4)_2(H_2O)(OH)^{2-} \longrightarrow (C_2O_4)_2Cr(OH)_2Cr(C_2O_4)_2{}^{4-} + 2H_2O \quad (45)$$

becomes first order for chromium(III) concentrations above ~0.01 *M*. As pointed out by Ardon and Bino, this behavior can be explained in terms of cation-pair formation [Eq. (29)] if K_{ip} is large (*326*).

VIII. Cleavage of Polynuclear into Mononuclear Species

A. CLEAVAGE IN STRONG ACIDS

Hydrolysis of polynuclear hydroxo-bridged chromium(III) complexes in concentrated solutions of strong acid yields the corresponding mononuclear species. Such cleavage reactions are fast in comparison with the hydrolysis in dilute acid and proceed with retention of configuration of the mononuclear entities. A few representative examples are shown in Eqs. (46)–(49) (*40, 42, 161, 252*).

$$(NH_3)_5Cr(OH)Cr(NH_3)_5{}^{5+} + H_3O^+ \longrightarrow 2Cr(NH_3)_5(H_2O)^{3+} \tag{46}$$

$$\Delta,\Lambda\text{-}(en)_2Cr(OH)_2Cr(en)_2{}^{4+} + 2H_3O^+ \longrightarrow 2\mathit{cis}\text{-}Cr(en)_2(H_2O)_2{}^{3+} \tag{47}$$

$$Cr_3(NH_3)_{10}(OH)_4{}^{5+} + 4H_3O^+ \longrightarrow \mathit{cis}\text{-}Cr(NH_3)_4(H_2O)_2{}^{3+} + 2\mathit{fac}\text{-}Cr(NH_3)_3(H_2O)_3{}^{3+} \tag{48}$$

$$(-)_{589}\text{-}\Delta,\Delta\text{-}(phen)_2Cr(OH)_2Cr(phen)_2{}^{4+} + 4HBr \longrightarrow 2(-)_{589}\text{-}\Delta\text{-}\mathit{cis}\text{-}Cr(phen)_2Br_2{}^{+} + 2H_3O^+ \tag{49}$$

Analysis of the products of these cleavage reactions has often served as proof of the structures of the polynuclear species. Cleavage of hydroxo-bridged complexes of nuclearity higher than two will in most cases yield at least two different mononuclear species. Identification of these species and determination of the relative ratio in which they are formed reduce the number of possible bridged skeletons greatly, and the studies of polynuclear ammine and amine chromium(III) made by Andersen *et al.* (mentioned in Section IV) provide many examples of this, one of which is shown in Eq. (48) above (see also Section II,A).

Cleavage reactions have also been utilized as a convenient method for the synthesis of "parent" mononuclear species. An example would be the acid cleavage of optically active dinuclear dihydroxo-bridged 1,10-phen and 2,2′-bipy chromium(III) species, providing a facile synthetic route to optically pure $(-)_{589}$ enantiomers of *cis*-$Cr(phen)_2X_2{}^{(3-2n)+}$ or *cis*-$Cr(bipy)_2X_2{}^{(3-2n)+}$ ($X^{n-} = H_2O$, Cl^-, and Br^-) (*161*).

Similar cleavage reactions have been reported for hydroxo-bridged Co(III) complexes, and the product analyses have been taken as evidence for the proposed structures. However, the greater tendency of cobalt(III) than of chromium(III) to undergo isomerization and redox reactions limits to some extent the applicability of such reactions in terms of structural analyses and synthetic methods. These difficulties can be illustrated by the results obtained for the acid hydrolysis of $(py)_3Co(OH)_3Co(py)_3{}^{3+}$. Cleavage in 12 *M* HCl yields the mer isomer and not, as would have been expected, the fac isomer of $Co(py)_3Cl_3$. Cleavage in 12 *M* $HClO_4$ probably yields $Co(py)_3(H_2O)_3{}^{3+}$, but the formation of other species [including Co(II) species] hampered a further study of this reaction (*188*).

The cleavage of polynuclear hydroxo-bridged rhodium(III) and iridium(III) complexes into the corresponding mononuclear fragments has been reported in only a few instances, but the well-established tendency of mononuclear complexes of these metal ions to undergo substitution reactions with retention of configuration indicates the possibility of analytical and synthetic applications such as described above for chromium(III).

B. Kinetics of the Cleavage of Dinuclear Monohydroxo-Bridged Complexes

1. *Acid Hydrolysis*

In the majority of the kinetic studies reported $HClO_4$–$NaClO_4$ media have been employed. The acid cleavage process can be described by Eq. (50), but in the presence of additional nucleophiles other than water, i.e., either anionic ($X^{n-} = Cl^-$, SCN^-, SO_4^{2-}, etc.) or neutral (X = DMSO, CH_3CN, etc.), there is competition between Eq. (50) and the reaction shown in Eq. (51). The presence of anionic nucleophiles may either increase or decrease (relative to ClO_4^-) the rate of cleavage by the formation of ion doublet and triplets.

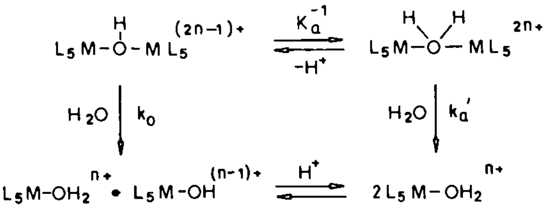
$$L_5M(OH)ML_5^{5+} + H^+ + H_2O \longrightarrow 2ML_5(H_2O)^{3+} \tag{50}$$

$$L_5M(OH)ML_5^{5+} + H^+ + X^{n-} \longrightarrow ML_5(H_2O)^{3+} + ML_5X^{(3-n)+} \tag{51}$$

The cleavage reaction, Eq. (50), may proceed by an uncatalyzed path (k_0) and/or by an acid-catalyzed path ($k_a = k'_a/K_a$), as shown in Scheme 3.

The acid-catalyzed path is proposed to involve a labile aqua-bridged intermediate which is a strong acid with $K_a \gg 1$, and the observed rate constant for the acid-catalyzed path is thereby a composite term: $k_a = k'_a/K_a$.

It seems to be a general feature that the acid-catalyzed path plays a more dominant role in the reactions of cobalt(III) and rhodium(III) than in those of chromium(III). A rationalization for this could be that the latter species do not readily protonate, in keeping with the observation that chromium(III) aqua complexes are significantly more acidic than cobalt(III) or rhodium(III) aqua complexes (Table XVIII).



SCHEME 3. Acid cleavage of dinuclear monohydroxo-bridged species may occur uncatalyzed (k_0) and acid-catalyzed ($k_a = k'_a/K_a$).

a. Chromium(III) Complexes. The cleavage of the rhodo ion, $(NH_3)_5Cr(OH)Cr(NH_3)_5{}^{5+}$, and of the cis or trans isomers of the erythro ions, $(NH_3)_5Cr(OH)Cr(NH_3)_4X^{(5-n)+}$, $(X^{n-} = H_2O, Cl^-, SCN^-$, or $F^-)$ has been studied using acidic perchlorate media. The rhodo ion yields $Cr(NH_3)_5(H_2O)^{3+}$, whereas the erythro ions yield both $Cr(NH_3)_5(H_2O)^{3+}$ and the respective cis or trans isomers of $Cr(NH_3)_4(H_2O)X^{(3-n)+}$. The kinetic data are consistent with a contribution from the uncatalyzed path (k_0 in Scheme 3) alone, and yield the parameter values listed in Table XXV. Bond rupture in the unsymmetric species is assumed to occur at the $Cr(NH_3)_4X$ fragment, since, when trans chloroerythro is cleaved in the presence of Cl^- or Br^-, the halide is incorporated into the tetraammine fragment while the pentaammine fragment remains as $Cr(NH_3)_5(H_2O)^{3+}$ (*252*). The cleavage of the cis aquaerythro ion in the presence of Cl^- and Br^-, respectively, has been studied (*254*), and both systems follow the rate law $-d[\text{dinuclear}]/dt = (k_1 + k_2[X])[\text{dinuclear}]$, where $X = Cl^-$ or Br^-. In the reaction with chloride the products are $Cr(NH_3)_5(H_2O)^{3+}$ and *cis*-$Cr(NH_3)_4Cl(H_2O)^{2+}$, and the formation of cis chloroerythro as an active intermediate was proposed. In contrast to this, the products in the bromide reaction are $Cr(NH_3)_5(H_2O)^{3+}$ and *cis*-$Cr(NH_3)_4(H_2O)_2{}^{3+}$. The enhancement of the cleavage rate by bromide has been explained in terms of ion-pair formation.

TABLE XXV

KINETIC DATA FOR THE CLEAVAGE REACTIONS OF MONOHYDROXO-BRIDGED CHROMIUM(III) COMPLEXES AT 25°C IN 1.0 *M* (Na,H)ClO$_4$

Complex	$10^5 \times k_0$ (sec^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	Reference
$(NH_3)_5Cr(OH)Cr(NH_3)_5{}^{5+}$	1.03	113(1)	40(3)	*252, 254*[a]
trans-$(NH_3)_5Cr(OH)Cr(NH_3)_4(H_2O)^{5+}$	0.83	113(2)	37(6)	*354*
cis-$(NH_3)_5Cr(OH)Cr(NH_3)_4(H_2O)^{5+}$	0.24	105(3)	−1(8)	*252, 254*[a]
$(H_2O)_5Cr(OH)Cr(H_2O)_5{}^{5+}$	0.1	107(10)	0(30)	*28*[b]
cis-$(NH_3)_5Cr(OH)Cr(NH_3)_4Cl^{4+}$		Faster than *trans*-Cl		*252*
trans-$(NH_3)_5Cr(OH)Cr(NH_3)_4Cl^{4+}$	1.47	115(1)	50(4)	*252, 254*[a]
cis-$(NH_3)_5Cr(OH)Cr(NH_3)_4F^{4+}$	1.21	97(3)	−14(3)	*254*
cis-$(NH_3)_5Cr(OH)Cr(NH_3)_4(NCS)^{4+}$	0.21	71(6)	−116(18)	*254*

[a] There are some discrepancies between the calculated activation parameters originally published in Ref. *252* and some parameters later recalculated in Ref. *254*. The data given here are from Ref. *254*.

[b] These data are for approximately 2 *M* HClO$_4$. Values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ have been calculated from the rate constants at 25, 35.5, and 45°C given in Ref. *28*, and $\Delta H^{\ddagger}$ deviates by a factor of ~2 from the value quoted in this reference.

The mechanistic aspects of the variation of the activation parameters with the nature of the substitutent X in $(NH_3)_5Cr(OH)Cr(NH_3)_4X^{n+}$ have been discussed previously (*254, 354*), but the paucity of data for ions of the same geometry and the same charge renders discussion difficult.

Cleavage of $(H_2O)_5Cr(OH)Cr(H_2O)_5{}^{5+}$ in various media has been investigated by Connick and co-workers, and only an uncatalyzed path (k_0) was observed (Table XXV). The activation parameters are very similar to those for *cis*-$(NH_3)_5Cr(OH)Cr(NH_3)_4(H_2O)^{5+}$, which is a very reasonable result. It should be noted that there is no agreement between Connick's results quoted in Table XXV and data from some recent studies by Holwerda and co-workers (*204–208*). According to Holwerda the cleavage of the dinuclear aqua species in 1 *M* $HClO_4$ is approximately 10^3 times faster than was found by Connick, and it is also claimed (*204*) that $(H_2O)_5Cr(OH)Cr(H_2O)_5{}^{5+}$ deprotonates to form an oxo-bridged ion even in 1 *M* $HClO_4$. This would require that the acid strength of the hydroxo bridge in $(H_2O)_5Cr(OH)Cr(H_2O)_5{}^{5+}$ should be at least 10^8 times greater than that observed in the related rhodo ion, $(NH_3)_5Cr(OH)Cr(NH_3)_5{}^{5+}$ ($pK_a = 7.6$), and would seem to be a very surprising result.

Cleavage of Δ,Λ-$(en)_2Cr(OH)_2Cr(en)_2{}^{4+}$ in concentrated strong acids (e.g., 12 *M* $HClO_4$) proceeds in two kinetically well-separated steps. The first and fast step ($t_{1/2} \sim 40$ seconds at 25°C) yields Δ,Λ-$(H_2O)(en)_2Cr(OH)Cr(en)_2(H_2O)^{5+}$, which then undergoes bridge cleavage much more slowly ($t_{1/2} \sim 3$ hours at 25°C) to yield *cis*-$Cr(en)_2(H_2O)_2{}^{3+}$ quantitatively (*33, 42*). The kinetics for the first bridge cleavage have been studied for ionic strength 1.0 *M*, as described in Section IX. Kinetic studies of the second bridge cleavage are seriously complicated by the occurrence of side reactions at lower acidities. A spectrophotometric study of the second bridge-cleavage reaction at lower acidities ($[H^+] = 0.02–1.0$ *M* at $I = 1.0$ *M*) has been reported (*324*), and the observed rate constants in this study were obtained on the basis of the assumption that the only side reaction occurring is subsequent hydrolysis of the product *cis*-$Cr(en)_2(H_2O)_2{}^{3+}$ to $Cr(en)(H_2O)_4{}^{3+}$. This is, however, in conflict with a more recent report that the hydrolysis of Δ,Λ-$(en)_2Cr(OH)_2Cr(en)_2{}^{4+}$ (and of its parent monohydroxo-bridged species) in 1 *M* $HClO_4$ yields a complex mixture of new polynuclear species, *cis*-$Cr(en)_2(H_2O)_2{}^{3+}$ and mononuclear species with fewer than four nitrogens coordinated per chromium (*42*). It therefore seems uncertain to which reaction(s) the observed rate constant should be related, and a more detailed analysis of the products seems to be called for.

The cleavage is accelerated in the presence of nitrate and a rate law of the form $k_{obs} = a + b[NO_3^-] + c[H^+][NO_3^-]$ has been reported (*324*). The acceleration is probably due to rapid formation of a labile nitrate complex, e.g., $(H_2O)(en)_2Cr(OH)Cr(en)_2(NO_3)^{4+}$, but it does not seem possible on the basis of the present data to establish an unambiguous reaction scheme.

b. Cobalt(III) Complexes. The cleavage of $(NH_3)_5Co(OH)$-$Co(NH_3)_5{}^{5+}$ in perchlorate media has been studied several times (*130, 355–358*). In neutral or alkaline medium the reaction is complicated by the formation of products other than $Co(NH_3)_5(H_2O)^{3+}$ and $Co(NH_3)_5(OH)^{2+}$; these products apparently result from loss of ammonia in the binuclear species since the aqua or hydroxo products are known to be comparatively stable under these conditions (*130, 356*). In acidic media and in the absence of complexing ligands the only cleavage product is $Co(NH_3)_5(H_2O)^{3+}$. Wharton and Sykes (*355*) have studied the kinetics in 2 *M* $LiClO_4$ in the $[H^+]$ region $10^{-4} \leq [H^+] \leq 2$ *M* and the results were interpreted in terms of uncatalyzed (k_0) and acid-catalyzed (k_a) bridge-cleavage reactions (Scheme 3). Kinetic data for lower ionic strength support this reaction scheme (Table XXVI). However, the observation that k_0 shows a greater ionic strength dependence than does k_a is somewhat surprising. The aqua-bridged intermediate is a strong acid, and an estimated value of $K_a > 50$ *M* was

TABLE XXVI

KINETIC PARAMETERS FOR CLEAVAGE OF $(NH_3)_5Co(OH)Co(NH_3)_5{}^{5+}$ IN VARIOUS MEDIA AT 25°C

Medium	k_0 (sec^{-1})	k_a (M^{-1} sec^{-1})	Reference
2 *M* $LiClO_4$	$7.58(10) \times 10^{-3}$ [a,b]	$5.37(7) \times 10^{-3}$ [a]	*355*
1 *M* $NaClO_4$	4.0×10^{-3}	6.2×10^{-3}	*356*
0.2 *M* $NaClO_4$	$\approx 2.2 \times 10^{-3}$		*130*[c]
CH_3CN–water ($X_{CH_3CN} = 0.5$)	2.3×10^{-3}	4.05×10^{-4}	*356*[d]
DMSO–water ($X_{DMSO} = 0.25$)	$\leq 3 \times 10^{-5}$	1.11×10^{-4}	*356*[d]
DMSO–water ($X_{DMSO} = 0.20$)	1.8×10^{-4}	1.35×10^{-3}	*356*[d]

[a] $\Delta H^\ddagger(k_0) = 84(3)$ kJ mol^{-1}, $\Delta S^\ddagger(k_0) = -4(9)$ J mol^{-1} K^{-1}; $\Delta H^\ddagger(k_a) = 50(3)$ kJ mol^{-1}, $\Delta S^\ddagger(k_a) = -120(1)$ J mol^{-1} K^{-1}.

[b] $k_0 = 6.0 \times 10^{-3}$ sec^{-1} in 2 *M* $NaClO_4$ (*355*).

[c] Calculated from the value $k_0 = 0.65 \times 10^{-3}$ sec^{-1} at 15°C from Ref. *130*, using $E_a = 86.6$ kJ mol^{-1} for 2 *M* $LiClO_4$ taken from Ref. *355*.

[d] k_a in sec^{-1} kg mol^{-1}

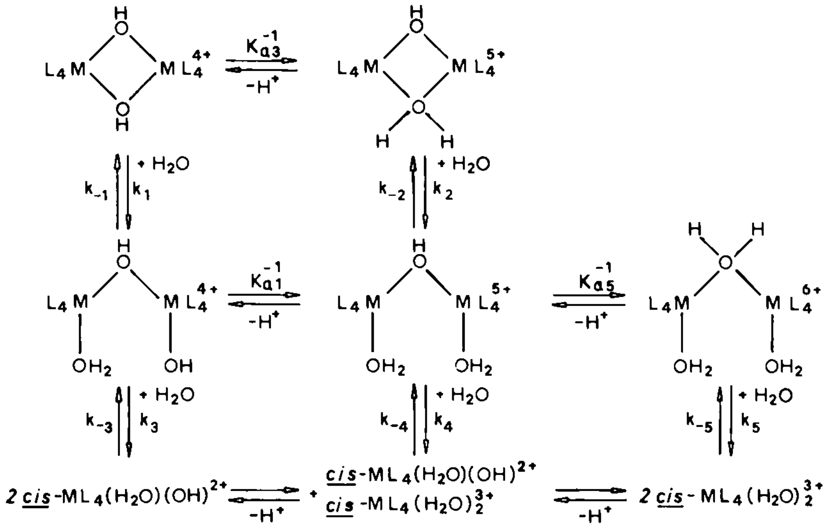
obtained (*355*). Since k_a is a composite term, the corresponding activation energies are also composite: $\Delta H^{\ddagger}(k_a) = \Delta H^{\ddagger}(k'_a) - \Delta H^0(K_a)$ and $\Delta S^{\ddagger}(k_a) = \Delta S^{\ddagger}(k'_a) - \Delta S^0(K_a)$. Since the aqua bridged species is a strong acid, $\Delta H^0(K_a)$ is probably negative. This implies that $\Delta H^{\ddagger}(k'_a) <$ 50 kJ mol^{-1}, in keeping with the presumed poor bridging-ligand properties of a water molecule.

Cleavage in aqueous solution in the presence of other anions, Y^-, has been studied for $Y^- = NO_3^-$, SCN^-, Cl^-, and $CH_3SO_3^-$ (*355–358*). In all these reactions variable amount of $Co(NH_3)_5Y^{2+}$ are produced together with the aqua complex, and extensive competition studies have been reported for the uncatalyzed as well as for the acid-catalyzed cleavage reaction. The results of these competition experiments are in keeping with an essentially dissociative mechanism for bridge cleavage.

The kinetic data reveal a complex dependence on the anion concentration and the hydrogen-ion concentration and have been interpreted on the basis of ion-pair and ion-triplet formation. The uncatalyzed path (k_0) has been shown to involve $(NH_3)_5Co(OH)Co(NH_3)_5^{5+}$ ($= M^{5+}$) and the ion pair $M \times Y^{4+}$, and it was proposed that the ion pair $M \times Y^{4+}$ scavenges Y^- from solution and not from the second coordination sphere (*357*). It was shown that the reactive intermediates are quite selective for anions (as well as being selective for the N terminus of NCS^-, the ratio for N-bound:S-bound being approximately 4), and this has been interpreted as arising from a genuine, coordinately unsaturated intermediate. The acid-catalyzed path has been interpreted in terms of the formation of protonated unaggregated reactant, MH^{6+}, and small concentrations of the protonated ion pairs and ion triplets $MH \times Y^{5+}$ and $MH \times Y_2^{4+}$ (*355, 356*).

c. Rhodium(III) Complexes. Acid cleavage of the monohydroxo-bridged species Δ,Λ-$(H_2O)(en)_2Rh(OH)Rh(en)_2X^{n+}$ ($X = H_2O$ or OH^-) has been studied in the $[H^+]$ region 10^{-5}–1.0 *M* (*325*). Since equilibration of the monohydroxo-bridged species with the parent dihydroxo-bridged species takes place much faster than cleavage into mononuclear species, it was necessary to take account of these equilibria in the calculations, as shown in Scheme 4. The kinetic experiments were conducted at low complex concentrations [[Rh(III)] = 2 × [dinuclear] + [mononuclear] $\sim 10^{-4}$ *M*] so that the influence of the condensation reactions (k_{-3}, etc.) could be disregarded ($K_d = k_{-3}/k_3 \sim 25$, as discussed in Section V,B). The observed rate constants were found to obey Eq. (52) derived from Scheme 4. Since the equilibrium constants K_{a1} and

$$k_{obs} = \frac{k_3K_{a1} + k_4[H^+] + (k_5/K_{a5})[H^+]^2}{K_{a1}/K_1 + K_{a1} + [H^+]} \qquad (52)$$



SCHEME 4. Complete reaction scheme for the formation and cleavage of dinuclear dihydroxo-bridged species in acidic solution.

K_1 have been determined in an independent study (see Section IX), it was possible to determine the rate constants k_3 and k_4 (k_0 in Scheme 3) and the ratio k_5/K_{a5} ($k_a = k'_a/K_a$ in Scheme 3), given in Table XXVII. The fact that $\Delta H^\ddagger(k_0)$ is much larger than $\Delta H^\ddagger(k_a)$ for the cleavage of the diaqua complex may be rationalized as discussed above for the cobalt(III) species. The rate constant for the uncatalyzed bridged cleavage of the aqua hydroxo species, $\Delta,\Lambda\text{-}(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+}$, k_0, is about 20 times smaller than that for cleavage of the diaqua species, $\Delta,\Lambda\text{-}(H_2O)(en)_2Rh(OH)Rh(en)_2(H_2O)^{5+}$, which is in keeping with their respective thermodynamic stabilities (Table XI). As discussed in Sections V and VI, the increased thermodynamic stability of the aqua hydroxo species can be explained on the basis of intramolecular hydrogen bond formation (Fig. 15; Table XXI). The kinetic consequences of this hydrogen bond interaction are strongly dependent on the structure of the transition state, i.e., on whether the hydrogen bond persists or is broken in the transition state, as shown in Scheme 5. Cleavage of the hydrogen bond prior to the formation of the transition state would provide a good explanation for the increased kinetic stability. The experimental results thus indicate the non-hydrogen-bonded transition state structure II in Scheme 5. It should be noted that this is not consistent with the proposal (*326*) that the reactive species for the reverse reaction is a cation pair with intermolecular

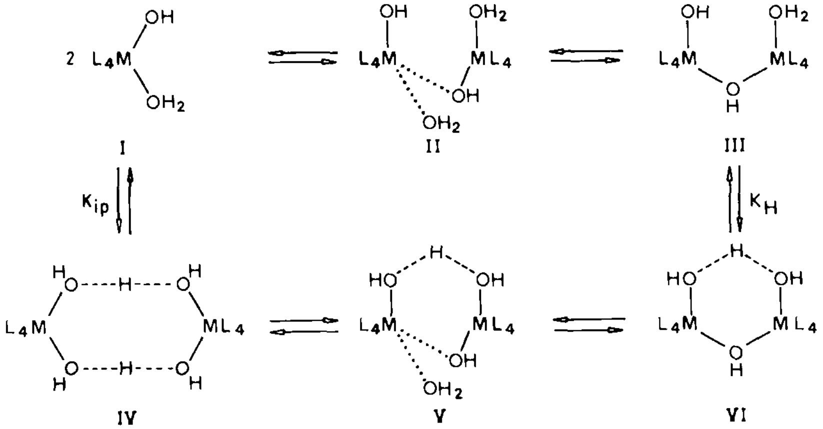
TABLE XXVII

KINETIC DATA FOR UNCATALYZED AND ACID-CATALYZED CLEAVAGE OF MONOHYDROXY-BRIDGED RHODIUM(III) COMPLEXES AT 25°C IN 1.0 M (Na,H)ClO$_4$[a,b]

	Uncatalyzed path			Acid-catalyzed path			
Compound	$10^6 \times k_0$ (sec^{-1})	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ (J mol^{-1} K^{-1})	$10^5 \times k_a$ (M^{-1} sec^{-1})	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ (J mol^{-1} K^{-1})	Reference
$(H_2O)(en)_2Rh(OH)Rh(en)_2(H_2O)^{5+}$	3.82	116(3)	40(10)	3.48	78(4)	−68(14)	*325*
$(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+}$	0.23	107(2)	−12(6)	—	—	—	*325*
$(H_2O)_2(tacn)Rh(OH)Rh(tacn)(H_2O)_2^{5+}$	1.4	81(15)	−86(48)	3.4	68(2)	−102(8)	*100*

[a] k_0 equal to k_3 or k_4 and k_a equal to k_5/K_{a5} in Scheme 4.

[b] As discussed in the text, the data for the tacn system are based on a tentative interpretation (*325*).



SCHEME 5. Stabilization of dinuclear species in aqueous solution by intramolecular hydrogen-bond formation (VI) is well established. Stabilization of the mononuclear species in aqueous solution by intermolecular hydrogen bonds (IV) may be important in some systems. Interconversion between mononuclear and dinuclear species may occur via non-hydrogen-bonded and hydrogen-bonded transition states, respectively, as schematically shown in II and V. Dashed lines denote hydrogen bonds; dotted lines denote bond making and bond breaking.

hydrogen bonding (Fig. 11), since such a species would lead to a hydrogen-bonded transition state structure (structure V in Scheme 5).

Acid hydrolysis of the dihydroxo-bridged complex *trans*-$(H_2O)(tacn)Rh(OH)_2Rh(tacn)(H_2O)^{4+}$ yields mononuclear triaqua complex (*100*). Only one reaction step was observed for $[H^+] = 0.2–1.0$ *M*, the rate expression being of the form $k_{obs} = a + b[H^+]$. If it is assumed that the first bridge cleavage is faster than the second, as has been found for the corresponding tetraammine and bis(ethylenediamine) complexes, the observed $[H^+]$ dependence can be interpreted in terms of Scheme 4, which for large $[H^+]$ leads to the approximate expression $k_{obs} = k_4 + (k_5/K_{a5})[H^+]$. Values for k_4 and k_5/K_{a5} are listed in Table XXVII.

2. *Base Hydrolysis*

Studies of the hydroxo-bridge cleavage in basic solution are often complicated by hydrolysis of the nonbridging ligands, and few kinetic studies have been made. The kinetics of hydrolysis of the $(en)_2Co(OH)_2Co(en)_2^{4+}$ ion in basic solution indicate two consecutive steps, and different mechanisms involving cleavage of the presumed intermediate $(H_2O)(en)_2Co(OH)Co(en)_2(OH)^{4+}$ (or its deprotonated form) have been considered (*359*). Base hydrolysis in the presence of carbonate has been proposed to involve cleavage of the presumed intermediate $(H_2O)(en)_2Co(OH)Co(en)_2(HCO_3)^{4+}$ (*360*).

3. *Chromium(II)-Catalyzed Hydrolysis*

The Cr^{2+}-catalyzed hydrolysis reaction, Eq. (53), has been studied for 1 *M* $HClO_4$ medium (*361*). The reaction is followed by a much slower reaction in which Cr^{2+}-catalyzed hydrolysis of $(NH_3)_5Cr(H_2O)^{3+}$ takes place. The kinetic data for Eq. (53) are consistent with a rate law of the

$$(NH_3)_5Cr(OH)Cr(NH_3)_4Cl^{4+} + 5H_3O^+ \xrightarrow{Cr^{2+}}$$
$$(NH_3)_5Cr(H_2O)^{3+} + 4NH_4^+ + (H_2O)_5CrCl^{2+} \qquad (53)$$

form $k_{obs} = k[Cr^{2+}][\text{dinuclear}]$, with $k = 3.0\ M^{-1}\ sec^{-1}$ at 25°C and $E_a = 39\ kJ\ mol^{-1}$. The form of the rate law and the occurrence of $Cr(H_2O)_5Cl^{2+}$ as a reaction product suggest that the rate-determining step in the chromium(II)-catalyzed reaction is an electron-transfer process in which the chloride ion serves as a bridging ligand.

4. *Photochemical Hydrolysis*

The photochemical (254 nm) hydrolysis of $(NH_3)_5Cr(OH)Cr(NH_3)_5^{5+}$ to $Cr(NH_3)_5(H_2O)^{3+}$ has been reported (*321*).

IX. Equilibria between Mono- and Dihydroxo-Bridged Dinuclear Complexes of Chromium(III), Rhodium(III), and Iridium(III)

A. GENERAL REMARKS

The equilibrium Eq. (54) has been studied for a series of chromium(III), rhodium(III), and iridium(III) complexes. Nearly all

$$L_4M(OH)_2ML_4^{4+} + H_2O \overset{K_1}{\rightleftharpoons} (H_2O)L_4M(OH)ML_4OH^{4+} \qquad (54)$$

the species studied contain ammonia or ethylenediamine ligands and mono- and dihydroxo-bridged cations have been isolated and characterized as crystalline salts, as described in Section IV. For these ammine and ethylenediamine complexes the equilibration reaction, Eq. (54), is relatively fast, so it has been possible to study the kinetics and thermodynamics of the process without interference from other

TABLE XXVIII

Equilibrium between Mono- and Dihydroxo-Bridged Species at 25°C in 1.0 M (Na,H)ClO$_4$[a]

M(III)	L$_4$	K_I	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	Reference
Cr(III)	Δ,Λ-(en)$_2$	0.75(2)	−3.1(9)	−13(3)	*33, 36*
Cr(III)	$\Delta,\Delta/\Lambda,\Lambda$-(en)$_2$	0.22(3)	−2(4)	−19(13)	*35, 36*
Cr(III)/Co(III)	Δ,Λ-(en)$_2$	4	—	—	*36, 215*
Cr(III)	(NH$_3$)$_4$	0.318(11)	6(4)	11(14)	*36*
Cr(III)	(H$_2$O)$_4$	0.02	—	—	*28*
Cr(III)	$\Delta,\Delta/\Lambda,\Lambda$-(phen)$_2$	$\ll 1$	—	—	*336*
Rh(III)	Δ,Λ-(en)$_2$	11.2(5)	−14(3)	−28(8)	*217*
Rh(III)	(NH$_3$)$_4$	3.03(4)	2(1)	15(4)	*133*
Ir(III)	Δ,Λ-(en)$_2$	5.7(8)	−2(5)	10(15)	*67*

[a] See Scheme 6.

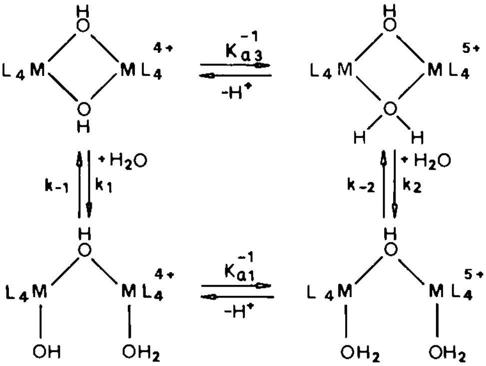
reactions such as hydrolysis of the N-donor ligands or cleavage of the monohydroxo-bridged species to give mononuclear species.

Thermodynamic data for the equilibrium Eq. (54) have been obtained by spectrophotometric and potentiometric (pH) measurements (cf. Table XXVIII). The K_I values lie in the region 1–10, the only significant exceptions being the small values for the aqua and 1,10-phenanthroline chromium(III) systems. The enthalpy changes are small, as anticipated for reactions which involve bond breaking and bond making of similar kinds of bonds.

Most of the kinetic studies made have been spectrophotometric and have employed acidic or neutral solutions. For the ammine and ethylenediamine complexes pseudo first-order rate constants were obtained for solutions initially containing either monohydroxo-bridged species [k_{obs}(M)] or dihydroxo-bridged species [k_{obs}(D)]. It was found that $k_{\text{obs}}(M) = k_{\text{obs}}(\text{D})$, which is consistent with reversible first-order kinetics.

The [H$^+$] dependence of k_{obs} has been interpreted in terms of an acid-catalyzed and an uncatalyzed reaction path, as shown in Scheme 6. The acid-catalyzed path has been proposed to involve protonation of one hydroxo bridge to give a labile aqua-bridged intermediate. The aqua-bridged complexes have in no case been identified, but spectroscopic results indicate that such species are very strong acids with $K_{a3} \gg 1$. The kinetic parameters calculated from the rate expression, Eq. (55), are

$$k_{\text{calc}} = k_1 + \frac{[\text{H}^+]K_1 k_{-2}}{K_{a1}} + \frac{K_{a1}K_1^{-1}k_1 + [\text{H}^+]k_{-2}}{K_{a1} + [\text{H}^+]} \tag{55}$$



SCHEME 6. Reaction scheme for the equilibria between dinuclear mono- and dihydroxo-bridged species of chromium(III), rhodium(III), and iridium(III).

given in Tables XXIX–XXXII. As mentioned previously, the parameters K_{a1} and K_1 have been determined independently of the kinetic measurements by spectrophotometry or potentiometry (Tables XIX and XXVIII). The kinetic parameters for uncatalyzed bridge cleavage and formation (k_1 and k_{-1}) have been determined for each of the ammine and ethylenediamine complexes of chromium(III), rhodium(III), and iridium(III), whereas the parameters for the acid-catalyzed path (k_2/K_{a3} and k_{-2}) have been determined only for some of these systems. In the meso and racemic Cr(III) ethylenediamine systems and in the mixed CrCo ethylenediamine system the contribution from the acid-catalyzed path is insignificant even in 1 *M* $HClO_4$, and only an upper limit value for the rate constants has been determined (see Tables XXXI and XXXII).

A kinetic study of the aqua chromium(III) system has also been interpreted in terms of Scheme 6. In this system the parameters K_{a1} and K_1 are not known with great precision and consequently the rate constants are somewhat uncertain and have not been taken into account in the discussion below. The following values have been reported for 25°C [2 *M* $(H^+,Li)ClO_4$]: $k_1 = 1.5 \times 10^{-5}$ sec^{-1}, $k_{-1} = 8 \times 10^{-4}$ sec^{-1}, $k_2/K_{a3} = 9 \times 10^{-5}$ M^{-1} sec^{-1}, and $k_{-2} = 1.2 \times 10^{-4}$ sec^{-1} (*28*). It should be noted that these values are similar to those observed for the chromium(III) ammonia system (Tables XXIX–XXXII).

The kinetics for the acid hydrolysis of Δ,Δ/Λ,Λ-$(phen)_2Cr(OH)_2Cr(phen)_2^{4+}$ revealed that the formation of cis diaqua mononuclear species proceeds in one step without significant buildup of monohydroxo-bridged intermediates (*336*). The rate law observed is $k_{obs} = a + b[H^+]$ at low acidities ($[H^+] = 0.01–0.05$ *M*) and $k_{obs} = b[H^+]$ at

TABLE XXIX

UNCATALYZED CLEAVAGE OF $L_4M(OH)_2ML_4^{4+}$ SPECIES AT 25°C IN 1.0 M (Na,H)ClO$_4$

M(III)	L_4	$10^4 \times k_1$ (sec^{-1})	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ (J mol^{-1} K^{-1})	Reference
Cr(III)/Co(III)	Δ,Λ-(en)$_2$	69(9) [138(17)]	78(3)	−25(12) [−20(12)]	*36, 215*[a]
Cr(III)	Δ,Λ-(en)$_2$	69(5)	80(2)	−18(7)	*33, 36*
Cr(III)	Δ,Δ/Λ,Λ-(en)$_2$	46.1(19)	85(1)	−4(5)	*35, 36*
Cr(III)	$(NH_3)_4$	1.21(2)	87(2)	−29(5)	*36*
Cr(III)	Δ,Δ/Λ,Λ-(phen)$_2$	0.69(3)	99(3)	7(11)	*336*[b]
Rh(III)	Δ,Λ-(en)$_2$	4.56(11)	86(3)	−19(8)	*217*
Rh(III)	$(NH_3)_4$	0.426(18)	91(5)	−24(16)	*133*
Ir(III)	Δ,Λ-(en)$_2$	0.0148(11)	113(2)	22(6)	*67*

[a] Δ,Λ-(en)$_2$Cr(OH)$_2$Co(en)$_2^{4+}$. If it is assumed that the bridge cleavage in the mixed system occurs essentially with Cr–O bond breaking, the k_1 value should be corrected with a statistical factor of 2 when compared with the remaining complexes. This then gives the values in square brackets.

[b] 0.1 M (Na,H)NO$_3$.

TABLE XXX

ACID-CATALYZED BRIDGE CLEAVAGE OF $L_4M(OH)_2ML_4^{4+}$ SPECIES AT 25°C IN 1.0 M (Na,H)ClO$_4$

M(III)	L_4	k_2/K_{a3} (M^{-1} sec^{-1})	$\Delta H^{\ddagger}(k_2) - \Delta H^0(K_{a3})$ (kJ mol^{-1})	$\Delta S^{\ddagger}(k_2) - \Delta S^0(K_{a3})$ (J mol^{-1} K^{-1})	Reference
Cr(III)	Δ,Λ-(en)$_2$	$<3.5 \times 10^{-4}$	—	—	*33*[a]
Cr(III)	$(NH_3)_4$	$4.9(5) \times 10^{-5}$	82(11)	−53(35)	*36*
Rh(III)	Δ,Λ-(en)$_2$	$1.34(3) \times 10^{-1}$	58(2)	−68(7)	*217*
Rh(III)	$(NH_3)_4$	$7.4(2) \times 10^{-2}$	58(3)	−72(9)	*133*
Ir(III)	Δ,Λ-(en)$_2$	$2.40(5) \times 10^{-4}$	69(2)	−84(6)	*67*

[a] Estimated from data in Ref. *33*.

high acidities ($[H^+] = 0.1$–1.0 M). The rate at which the dinuclear species exchange ^{18}O was found to be independent of $[H^+]$ over the range $[H^+] = 0.01$–0.1 M [0.1 M (Na,H)NO$_3$] and the exchange is fast compared with the cleavage reaction, viz. $k_{\text{exchange}}/k_{\text{cleavage}} = 38$ at 60°C and $[H^+] = 0.1$ M. Experiments involving cleavage in D_2O indicated that there is a rapid prequilibrium entailing protonation prior to the rate-determining step. These observations suggest that rapid equilibration between mono- and dihydroxo-bridged species takes place prior to the rate-determining bridge cleavage of the monohydroxo-bridged species (Scheme 4). The observations that the monohydroxo-bridged species never attains a high concentrations and that the dihydroxo-bridged complex exchanges ^{18}O rapidly provide strong evidence that $K_1 \ll 1$, from which it then follows that $k_1 = 4k_{ex}$ (Table XXIX). The fact that the ^{18}O exchange rate is independent of $[H^+]$ rules out the possibility that bridge cleavage proceeds by an acid-catalyzed pathway to any significant extent, i.e., $[H^+]k_2/K_{a3} \ll k_1$. Then $[H^+]$ dependence of k_{obs} can be interpreted in terms of Scheme 4, but it is not possible to determine any values for the individual parameters as long as neither K_1 nor K_{a1} is known.

Preliminary kinetic data for the cleavage of $(tn)_2Cr(OH)_2Cr(tn)_2^{4+}$ have been reported: $k_1 + k_{-1} = 6(1) \times 10^{-4}$ sec^{-1} at 25°C (*216*). Cleavage of the *trans*-$(H_2O)(NH_3)_3Cr(OH)_2Cr(NH_3)_3(H_2O)^{4+}$ ion (Fig. 9) has been studied qualitatively. In 4 M HClO$_4$, cleavage of the first bridge is much faster than that of the second bridge and the product *fac,fac*-$(H_2O)_2(NH_3)_3Cr(OH)Cr(NH_3)_3(H_2O)_2^{5+}$ has been isolated. It was shown that the monohydroxo-bridged complex at pH 2 reforms the dihydroxo-bridged species (*87*).

The kinetic parameters for the bridge cleavage and formation reactions show a number of trends which in some cases parallel those

TABLE XXXI

BRIDGE FORMATION OF $(H_2O)L_4M(OH)ML_4(OH)^{4+}$ SPECIES AT 25°C IN 1.0 *M* $(Na,H)ClO_4$

M(III)	L_4	k_{-1} (sec^{-1})	$\Delta H^‡$ (kJ mol^{-1})	$\Delta S^‡$ (J mol^{-1} K^{-1})	K_{a1}[a] (*M*)	Reference
Cr(III)	$\Delta,\Delta/\Lambda,\Lambda$-$(en)_2$	$2.07(8) \times 10^{-2}$	87(1)	15(5)	0.29	*35, 36*
Cr(III)	Δ,Λ-$(en)_2$	$0.93(7) \times 10^{-2}$	84(2)	−1(7)	0.33	*33, 36*
Cr(III)/Co(III)	Δ,Λ-$(en)_2$	$0.18(2) \times 10^{-2}$	78(3)	−37(12)	5×10^{-2}[b]	*36, 215*
Cr(III)	$(NH_3)_4$	$3.80(4) \times 10^{-4}$	81(2)	−40(5)	1.8×10^{-2}	*36*
Rh(III)	Δ,Λ-$(en)_2$	$4.07(10) \times 10^{-5}$	101(3)	9(9)	4.2×10^{-3}	*217*
Rh(III)	$(NH_3)_4$	$1.41(6) \times 10^{-5}$	89(5)	−39(16)	3.9×10^{-4}	*133*
Ir(III)	Δ,Λ-$(en)_2$	$2.58(35) \times 10^{-7}$	114(4)	13(14)	1.2×10^{-2}	*67*

[a] K_{a1} is the acid dissociation constant for the $(H_2O)L_4M(OH)ML_4(H_2O)^{5+}$ ion.

[b] Measured at 0.8°C.

TABLE XXXII

BRIDGE FORMATION OF $(H_2O)L_4M(OH)ML_4(H_2O)^{5+}$ SPECIES AT 25°C IN 1.0 M (Na,H)ClO$_4$

M(III)	L_4	k_{-2} (sec^{-1})	$\Delta H^‡$ (kJ mol^{-1})	$\Delta S^‡$ (J mol^{-1} K^{-1})	Reference
Cr(III)	Δ,Λ-(en)$_2$	$<2 \times 10^{-4}$	—	—	*33*[a]
Cr(III)	$(NH_3)_4$	$2.7(3) \times 10^{-6}$	123(11)	63(35)	*36*
Rh(III)	Δ,Λ-(en)$_2$	$5.1(1) \times 10^{-5}$	100(2)	9(7)	*217*
Rh(III)	$(NH_3)_4$	$9.6(3) \times 10^{-6}$	109(3)	24(11)	*133*
Ir(III)	Δ,Λ (en)$_2$	$5.1(8) \times 10^{-7}$	81(8)	−94(27)	*67*

[a] Estimated from data given in Ref. *33*.

observed for the corresponding mononuclear species. Other trends are due to effects specific for the polynuclear species, and in particular intramolecular hydrogen bond interactions are important factors in relation to the bridge-formation reactions. The most important of these trends are summarized in the following discussion.

B. UNCATALYZED CLEAVAGE

From the data in Table XXIX it can be seen that the rate constant, k_1, for the bridge-cleavage reaction of different dihydroxo-bridged chromium(III) complexes decreases in the ligand order *meso*-en > *racemic*-en > NH_3 > 1,10-phen, and that this order is accompanied by an increase in $\Delta H^‡$. The data for the heteronuclear complex, Λ,Δ-$(en)_2Cr(OH)_2Co(en)_2{}^{4+}$, place this complex in the above sequence close to the corresponding dichromium complex with respect to both k_1 and $\Delta H^‡$, which might suggest that the k_1 path in the CrCo complex essentially involves Cr–O bond cleavage.

A comparison of the activation parameters $\Delta H^‡(k_1)$ for the ammonia and ethylenediamine (meso isomer) complexes shows that $\Delta H^‡(NH_3) > \Delta H^‡(en)$ for both chromium(III) and rhodium(III), and that $\Delta H^‡(Ir) > \Delta H^‡(Rh) > \Delta H^‡(Cr)$ for both NH_3 and en. These trends are in keeping with the data for substitution reactions of the corresponding mononuclear complexes (*364*).

Although it is tempting to suggest that the variations in k_1 could be the result of differing degrees of strain in the M_2O_2 ring system, it is not possible to establish such a relationship on the basis of available crystal data since the observed variations in the M–O–M angles for different cations are equal to the variations found for salts of the same cation with different anions. As an example, it could be mentioned that the Cr–O–Cr angles found in the chloride salts of the NH_3, en, and 1,10-phen chromium(III) complexes, respectively, are 99.9, 102.4, and 102.7°, whereas the Cr–O–Cr angles in different salts of the Δ,Λ-$(en)_2Cr(OH)_2Cr(en)_2^{4+}$ cation vary from 100.0 to 103.4° (*38,69, 70, 91–93*).

C. ACID-CATALYZED CLEAVAGE

Only values for the ratio k_2/K_{a3} have been determined and the activation parameters are therefore composite terms, $\Delta H^{\ddagger}(k_2) - \Delta H^0(K_{a3})$ and $\Delta S^{\ddagger}(k_2) - \Delta S^0(K_{a3})$. For all three metal ions it is found that the aqua-bridged complexes are very strong acids, implying that the $\Delta H^0(K_{a3})$ values are undoubtedly all negative. It therefore follows that the values for $\Delta H^{\ddagger}(k_2) - \Delta H^0(K_{a3})$ represent upper limits to the values of $\Delta H^{\ddagger}(k_2)$. The small $\Delta H^{\ddagger}(k_2)$ reflect the fact that water is a poor bridging group, and similar low $\Delta H^{\ddagger}$ values are found for the acid-catalyzed bridge cleavage of trihydroxo-bridged complexes (see Section XI).

The quantity $(k_2/K_{a3})/k_1$ gives the ratio between the rate of acid-catalyzed bridge cleavage at $[H^+] = 1$ *M* and the rate of uncatalyzed bridge cleavage. For the ammonia systems this ratio is 1700 and 0.4, respectively, for rhodium(III) and chromium(III). For the meso ethylenediamine systems the ratio is 300, 160, and less than 0.05, respectively, for rhodium(III), iridium(III), and chromium(III). The considerably enhanced relative efficiency of the acid-catalyzed path in iridium(III) and rhodium(III) compared with chromium(III) could be due to the differences in K_{a3}, which would be qualitatively in keeping with the greater acidity of mononuclear chromium(III) complexes compared to complexes of iridium(III) and rhodium(III) (Table XVIII). Also, the observation that for both chromium(III) and rhodium(III) the ratio $(k_2/K_{a3})/k_1$ is greater for NH_3 than for ethylenediamine can be explained qualitatively along the same lines.

D. BRIDGE FORMATION

The bridge-formation reactions k_{-1} are strongly influenced by the intramolecular hydrogen bond interactions which have been discussed in Section VI (Figs. 15 and 16, and Table XXI). For the chromium(III) complexes (and the mixed CrCo complex) it is found that k_{-1} decreases in the order *racemic*-$(en)_2 >$ *meso*-$(en)_2 >$ *meso*-$(en)_2(CrCo) > (NH_3)_4$, which is also the order of decreasing acid strength (K_{a1}) of the corresponding diaqua monohydroxo-bridged species (Table XXXI). For the rhodium(III) systems the order of decreasing k_{-1} and K_{a1} is $(en)_2 > (NH_3)_4$. This correlation has been explained in terms of intramolecular hydrogen bond stabilization of the aquahydroxo species. The hydrogen-bond-stabilized conformation resembles the transition state structure more than other conformations and should therefore contribute to k_{-1} by an enhancement of $\Delta S^\ddagger$. On the other hand, the intramolecular hydrogen bond has to be broken and this bond breaking will contribute to k_{-1} in terms of increasing $\Delta H^\ddagger$. It is therefore anticipated that increasing hydrogen bond stabilization, i.e., increasing K_{a1}, should be associated with increasing $\Delta S^\ddagger$ and increasing $\Delta H^\ddagger$. This is seen to be in good agreement with the experimental results for both chromium(III) and rhodium(III). The fact that it is found that increasing hydrogen bond stabilization is associated with increasing k_{-1} values is seen to be due to an increase larger in $T\Delta S^\ddagger$ than in $\Delta H^\ddagger$.

The values for k_{-1} may be compared with those for k_{-2} (Tables XXXI and XXXII). For the chromium(III) species $k_{-2} \ll k_{-1}$ for each of the systems studied. Since coordinated water is undoubtedly a much poorer nucleophile than coordinated hydroxide, this is in keeping with an essentially associative mechanism for both the k_{-1} and the k_{-2} pathways. For the rhodium(III) and iridium(III) species it is found that k_{-1} is roughly equal to k_{-2}, which is in keeping with an essentially dissociative mechanism. This may be illustrated further by comparing the activation parameters. Comparison of the activation parameters for bridge cleavage of the ammine complexes of chromium(III) and rhodium(III) with the kinetic data for water exchange (k_{ex}) of the corresponding mononuclear diaqua complexes shows the sequences $\Delta H^\ddagger(k_{-1}) < \Delta H^\ddagger(k_{ex}) < \Delta H^\ddagger(k_{-2})$ and $\Delta S^\ddagger(k_{-1}) < \Delta S^\ddagger(k_{ex}) < \Delta S^\ddagger(k_{-2})$ for both of the metal centers (Table XXXIII). The large separation in the $\Delta H^\ddagger$ values for the chromium(III) reactions is evidence for a high degree of associative behavior and this is in keeping with the properties of mononuclear tetraamminechromium(III) complexes. The sequence further confirms the expected order, $Cr{-}OH > H_2O > Cr{-}OH_2$, of decreasing nucleophilic character. It is seen that the nucleophilicity of water decreases tremendously on coordination, as reflected by a very large $\Delta H^\ddagger(k_{-2})$ value. However, despite this, k_{-2} is a factor of only 20 less than the rate of water exchange, this being due to a proximity effect, i.e., a very large $\Delta S^\ddagger(k_{-2})$ value. The observation that the $\Delta H^\ddagger$ values for rhodium(III) are much less separated indicates that these

TABLE XXXIII

KINETIC PARAMETERS FOR BRIDGE-FORMATION AND WATER-EXCHANGE REACTIONS OF AMMINE COMPLEXES AT 25°C IN 1.0 *M* (Na,H)ClO$_4$[a]

	Rhodium(III)			Chromium(III)		
	$10^6 \times k$ (sec^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	$10^6 \times k$ (sec^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})
k_{-1}	14.1	89	−39	380	81	−40
k_{ex}	7.5	105	11	59	95	−7
k_{-2}	9.6	109	24	2.7	123	63

[a] k_{-1} and k_{-2} are the rate constants for the formation of $(NH_3)_4M(OH)_2M(NH_3)_4^{4+}$ as defined in Scheme 6 (*36, 133*). Values of k_{ex} represent the statistically corrected rate constants for exchange of one water in *cis*-$M(NH_3)_4(H_2O)_2^{3+}$ for M = Rh(III) or Cr(III) (*362, 363*).

reactions are less associative than those of chromium(III), a conclusion which is in keeping with results for mononuclear ammine systems (*364*).

The activation parameters for the ethylenediamine complexes of rhodium(III) and iridium(III) are also in keeping with an essentially dissociative mechanism. The observation that $\Delta H^{\ddagger}(k_{-1})$ is *larger* than $\Delta H^{\ddagger}(k_{-2})$ for iridium(III) has been rationalized in terms of stabilization of the aquahydroxo species by intramolecular hydrogen bond formation. Similarly, the observation for the rhodium(III) system that $\Delta H^{\ddagger}(k_{-1}) < \Delta H^{\ddagger}(k_{-2})$ for ammonia, whereas $\Delta H^{\ddagger}(k_{-1}) \sim \Delta H^{\ddagger}(k_{-2})$ for ethylenediamine may, in part, by rationalized in terms of the observed differences in the degree of intramolecular hydrogen bond stabilization of the aqua hydroxo species in the two systems [$K_H(\text{en}) > K_H(NH_3)$; see Table XXI].

E. BASE-CATALYZED BRIDGE CLEAVAGE

Detailed studies of the base hydrolysis of the dihydroxo-bridged species have not been reported. The hydrolysis of Δ,Λ-$(\text{en})_2Rh(OH)_2Rh(\text{en})_2^{4+}$ to give Δ,Λ-$(HO)(\text{en})_2Rh(OH)Rh(\text{en})_2(OH)^{3+}$ has been reported to be five times faster at pH 12 than the uncatalyzed (k_1) bridge-cleavage reaction. The dihydroxo-bridged species is a weak acid (pK_a > 12) and the mechanism could either involve cleavage via formation of an oxo-bridged species or via direct attack by hydroxide (*217*).

X. Kinetics of the Hydrolysis of Dihydroxo-Bridged Cobalt(III) Complexes

The kinetics of the acid hydrolysis of dihydroxo-bridged cobalt(III) complexes have been studied for both cationic and anionic species. The stoichiometry of the hydrolysis reaction for cationic complexes can be expressed by Eq. (56). The equilibrium lies completely to the right at low pH (typically less than 3) and the reverse process in Eq. (56) can normally be disregarded. For all the systems studied to date the observed rate laws can be interpreted in terms of Scheme 4.

$$L_4Co(OH)_2CoL_4^{2n+} + 2H_2O + 2H^+ \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2\mathit{cis}\text{-}CoL_4(H_2O)_2^{(n+1)+} \qquad (56)$$

A major problem in the chemistry of the cobalt(III) species has been the fact that, although reaction Eq. (56) has to proceed in two steps, only one reaction stage is normally observed. The species which apparently follow first-order kinetics are $L_4Co(OH)_2CoL_4^{4+}$ for $L_4 = (NH_3)_4$, $(NH_3)_3(H_2O)$, $(en)_2$, and $(dien)(H_2O)$ (*132, 186, 187, 365, 366*); a so-called induction period has usually been observed for these reactions. In a few other cases, however, hydrolysis has been reported to follow consecutive first-order kinetics (*177, 359*). In none of the systems studied so far has it been possible to isolate the monohydroxo-bridged intermediate, and in the absence of additional information on the properties of this intermediate, unambiguous interpretation of the kinetic data is not possible. The following discussion should be read with this in mind.

Hoffman and Taube have studied the acid hydrolysis of $(NH_3)_4Co(OH)_2Co(NH_3)_4^{4+}$ spectrophotometrically in the $[H^+]$ range 0.05–1.0 *M* (*365*). The cleavage was found to follow first-order kinetics and k_{obs} showed an $[H^+]$ dependence of the form

$$k_{obs} = a[H^+]/(1 + b[H^+]) \qquad (57)$$

Additional studies of the reduction of the dinuclear species by Eu^{2+} and Cr^{2+} revealed the rate law, Eq. (58). The *c* term corresponds to direct

$$-d(\ln \text{dimer})/dt = a[H^+] + c[M^{2+}] \qquad (58)$$

attack by the reducing agents on the complex ion, and, as expected, the values of *c* for the two reducing agents are different. The parameter *a* has the same value for the two reducing agents and is identical with the parameter in Eq. (57). The latter connection between the two processes is explained if Cr^{2+} and Eu^{2+} are assumed to scavenge the monohydroxo-bridged intermediate efficiently, which in terms of Scheme 4 implies that $a = k_2/K_{a3}$. A rate expression for the hydrolysis reaction which is consistent with the reduction kinetics was then proposed by applying the steady-state approximation for the monohydroxo-bridged intermediate. Assuming that $k_3K_{a1} > [H^+]k_4 + [H^+]^2k_5/K_{a5}$ and $k_3 > k_{-1}$, this gives an expression, Eq. (59), which for large $[H^+]$

$$k_{obs} = \frac{k_1 + (k_2/K_{a3})[H^+]}{1 + k_{-2}[H^+]/(k_3K_{a1})} \tag{59}$$

may be reduced to Eq. (60), in which the $[H^+]$ dependence is the same as for the observed rate law, Eq. (57). This leads to the values $k_2/K_{a3} = 1.2 \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$ and $k_{-2}/(k_3K_{a1}) = 0.57\ M^{-1}$ (25°C, $I = 1.0\ M$).

$$k_{obs} = \frac{(k_2/K_{a3})[H^+]}{1 + k_{-2}[H^+]/(k_3K_{a1})} \tag{60}$$

It has been reported, however, that the length of the induction period has an $[H^+]$ dependence which does not agree with this interpretation, although the full mechanistic implications have not yet been evaluated (*369*).

The acid hydrolysis of $(en)_2Co(OH)_2Co(en)_2{}^{4+}$ has been studied several times, but with very conflicting results (*359*, *366–368*). Rasmussen and Bjerrum studied the reaction at low acidities ($[H^+] = 0.004–0.1\ M$) and found a pseudo first-order rate expression of the form given in Eq. (61) (*367*).

$$k_{obs} = a + b[H^+] \tag{61}$$

DeMaine and Hunt studied the reaction by spectrophotometry and by pH-stat measurements, but covering a wider $[H^+]$ range ($10^{-4}–1.0\ M$), and found a pseudo first-order rate expression of the form in Eq. (62)

$$k_{obs} = k_0 + \frac{a[H^+]}{1 + b[H^+]} \approx \frac{k_0 + a[H^+]}{1 + b[H^+]} \tag{62}$$

(*366*). It should be noted that although Eq. (62) approaches Eq. (61) at low acidities, the observed rate constants found in the two studies are not in agreement.

A very different result has been reported by El-Awady and Hugus, who studied the hydrolysis in acidic and basic solutions by spectrophotometry and by pH-stat measurements, respectively. According to these authors, the spectral changes occurring during the acid hydrolysis ($[H^+] = 10^{-3}$–10^{-1} M) are best interpreted in terms of two consecutive first-order reactions (*359*).

An unambiguous interpretation of these conflicting results is quite impossible, not only because there is disagreement as to whether the kinetics are simple first order or consecutive first order, but also because it appears to be possible to interpret each of the rate laws in terms of different mechanisms. However, with the kinetic results for the ammine system in mind it seems reasonable to use the approximate expression Eq. (59) to interpret DeMaine and Hunt's data (*366*), and this approach leads to the values $k_1 = 1.4 \times 10^{-5}$ sec^{-1}, $k_2/K_{a3} = 2.7 \times 10^{-3}$ M^{-1} sec^{-1}, and $k_{-2}/(k_3K_{a1}) = 0.50$ M (25°C, $I = 1.0$ M). An alternative and quite different interpretation would be that a fast preequilibrium between mono- and dihydroxo-bridged species precedes a much slower bridge cleavage of the singly bridged species. This leads to Eq. (52), which for $k_4 > k_5[H^+]/K_{a5}$ reduces to an expression which has an $[H^+]$ dependence of the observed form.

The hydrolysis has also been studied in chloride media. After an induction period, the reaction was found to follow pseudo first-order kinetics with $k_{obs} = k_{Cl}[H^+][Cl^-]$, where $k_{Cl} = 2.8 \times 10^{-2}$ M^{-2} sec^{-1} at 25°C and $I = 1.0$ M ($E_a = 61$ kJ mol^{-1}). Evidence for a chloride-containing intermediate was obtained and its structure could be either $Cl(en)_2Co(OH)Co(en)_2(H_2O)^{4+}$ or $(en)_2Co(OH)(Cl)Co(en)_2^{4+}$ (*366*).

The base hydrolysis of $(en)_2Co(OH)_2Co(en)_2^{4+}$ studied by the pH-stat method (pH 9.3–10.4) revealed two consecutive first-order reactions which could, however, be interpreted in terms of quite different reaction schemes (*359*).

Schwarzenbach and colleagues have studied the reaction, Eq. (56), for $L_4 = (NH_3)_3(H_2O)$ and (dien)(H_2O) (*186*). Only one reaction stage was observed and the observed rate constants showed an $[H^+]$ dependence as in Eq. (57). The cleavage of the ammine complex has also been studied by Lindhard and Siebert (*132*) and by Jentsch *et al.* (*187*), and in contrast to the results of Schwarzenbach, a rate expression of the form $k_{obs} = a + b[H^+]$ was observed in both studies. Jentsch *et al.* proposed slow bridge cleavage of the dibridged species followed by fast cleavage of the second bridge. This is contradictory to the proposal given by Schwarzenbach, who proposed the second bridge cleavage to be the slower.

The anionic oxalato complex $(ox)_2Co(OH)_2Co(ox)_2^{4-}$ hydrolyzes completely in acidic aqueous solution to *cis*-$Co(ox)_2(H_2O)_2^-$, but kinetic studies are complicated by decomposition of the mononuclear species to give cobalt(II) and CO_2 (*370*). The hydrolysis has been studied in a variety of buffer solutions (formate, acetate, and chloroacetate), and an increase in rate with increasing buffer concentration was observed for each buffer system. The limiting rates were identical for the different buffers at a given pH, and have been interpreted as being equal to $k_2/K_{a3} = 4.1\ M^{-1}\ \text{sec}^{-1}$ (25°C). The observation that k_2/K_{a3} for the anionic oxalato complex is 10^3 times larger than the value observed for the cationic ammine complex is qualitatively in agreement with the expected variation in K_{a3} due to the difference in charge.

The kinetics of the acid hydrolysis of $(nta)Co(OH)_2Co(nta)^{2-}$ have been reported in two independent studies (*177, 178*). At $[H^+] \geq 10^{-2}\ M$, the hydrolysis yields mononuclear $Co(nta)(H_2O)_2$ quantitatively and proceeds in two kinetically well-separated steps, a fast step ($t_{1/2} \sim$ 0.04 second at pH 0) followed by a much slower step (about 10^2 times slower under similar conditions). The occurrence of two steps has, however, been interpreted quite differently in the two studies. Thacker and Higginson assumed that their samples contained one of the two possible isomers contaminated with small amounts of the other isomer and it was suggested that the "rapid" and "slow" reactions correspond to hydrolysis of the two isomeric forms (*178*).

The proposal of Thacker and Higginson has been questioned by Meloon and Harris (*177*), who found that a pure potassium salt can be made and that this compound exhibits the same kinetic properties as originally reported for the "impure" compound. Meloon and Harris therefore assumed that the kinetic data should be interpreted in terms of consecutive cleavage of the two bridges in one of the two possible isomers. A comparison of the kinetic data obtained in the two studies is complicated by different choices of media. Meloon and Harris interpreted the occurrence of $[H^+]^2$ terms in the rate expressions by assuming that the rate-determining step in both paths involves protonation of the hydroxo bridge to give a μ-aqua complex which then undergoes *acid-catalyzed* bridge cleavage. This interpretation would imply [Eq. (4) in Ref. *177*] that the μ-aqua complex, $(nta)Co(OH)(OH_2)$-$Co(nta)^-$, has $K_a = 0.02\ M$ (25°C, 2 M $NaNO_3$), which would appear to be an unusually low value (see Section VI,B). Furthermore, this value for K_a seems to be in conflict with the observation made in the same study that the dihydroxo-bridged complex does not exhibit basic properties when titrated with dilute acid.

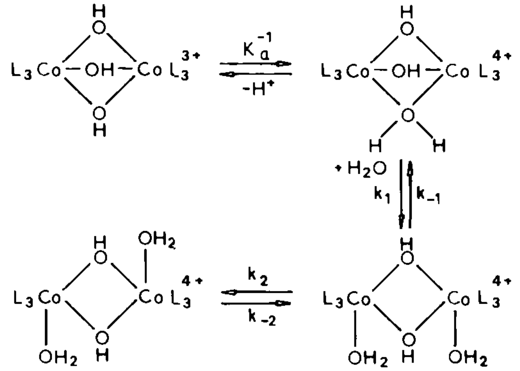
XI. Equilibria between Tri- and Dihydroxo-Bridged Complexes

A. COBALT(III)

The kinetics for acid hydrolysis of $L_3Co(OH)_3CoL_3^{3+}$ ions have been reported for $L_3 = (NH_3)_3$, dien, tach, and tacn (*132, 185–187, 371*). The ammonia system has been studied in detail (*132, 186, 187, 371*), and it is now generally accepted that the kinetic data should be interpreted in terms of Scheme 7.

The main features of this reaction scheme are a fast, acid-catalyzed bridge-cleavage and -formation reaction, followed by a slower, but still fast, isomerization reaction between the cis and trans diaqua isomers of the dihydroxo-bridged species. The thermodynamic and kinetic data are listed in Table XXXIV. The aqua-bridged intermediate is assumed to be a very strong acid ($K_a \gg 1$) and it has therefore been possible only to determine the ratio k_1/K_a. Since $\Delta H^0(K_a)$ is probably negative, the low value for $\Delta H^\ddagger(k_1) - \Delta H^0(K_a)$ shows that $\Delta H^\ddagger(k_1) < 47$ kJ mol^{-1} and emphasizes the fact that water acts as a poor bridging ligand.

The kinetics of the acid cleavage of the trihydroxobridged complexes with the tridentate amines dien and tach have also been studied (*186*). These systems are very similar to the ammonia system, and the kinetic and thermodynamic data are therefore likely to be interpretable in the same way (Table XXXV). The cleavage of the NH_3, dien, and tach complexes in chloride media has also been studied (*186*). These reactions were found to give dihydroxo-bridged species in two



SCHEME 7. The acid cleavage of dinuclear trihydroxo-bridged species is normally followed by a fast cis–trans isomerization process.

TABLE XXXIV

CLEAVAGE OF $(NH_3)_3Co(OH)_3Co(NH_3)_3^{3+}$ AT 25°C IN 1.0 M (Li,H)ClO$_4$[a]

Constant	Values	$\Delta H^\ddagger$ or ΔH^0 (kJ mol^{-1})	$\Delta S^\ddagger$ or ΔS^0 (J mol^{-1} K^{-1})
k_1/K_a	4.22 M^{-1} sec^{-1}	47(8)	−77(28)
k_{-1}	1.80 sec^{-1}	73(7)	3(21)
K_1/K_a	2.34 M^{-1}	−26(11)	−80(35)
k_2	0.186 sec^{-1}	98(11)	69(37)
k_{-2}	0.00662 sec^{-1}	95(6)	32(18)
K_2	27.9	2.5(13)	38(41)

[a] See Scheme 7. From Refs. *187* and *371*.

kinetically well-separated steps, but substitution by chloride in the dihydroxo-bridged species complicated the study.

Acid hydrolysis of $(tacn)Co(OH)_3Co(tacn)^{3+}$ yields *trans*-$(H_2O)(tacn)Co(OH)_2Co(tacn)(H_2O)^{4+}$, as confirmed by an X-ray crystal-structure analysis of the perchlorate salt (*185*). The kinetics of the equilibration reactions in Scheme 7 showed only one step for which the observed rate law $k_{obs} = k_r + k_f[H^+]$ was interpreted in terms of a rapid bridge-cleavage equilibration reaction followed by a rate-determining isomerization reaction (*185*). This interpretation, which was preferred to the alternative mechanism involving a rate-determining bridge-cleavage reaction, gave the values for $k_2K_1/K_a = k_f$ and $k_{-2} = k_r$ shown in Table XXXV. Deuterium isotope effects on the kinetic parameters have also been measured, and they support the proposed mechanism. The reduction of the tacn complex by Cr(II) was found to follow a rate law of the form $k_{obs} = a + b[H^+] + c[H^+][Cr(II)]$ (*97*).

The data in Table XXXV show that common features for these ammonia and amine complexes are very fast isomerization between the cis and trans isomers of the diaqua species and the fact that the trans diaqua isomers are generally more stable than the cis isomers. In the ammine system the activation parameters for k_2 and k_{-2} are consistent with an isomerization process at cobalt(III), but it is at present not clear how this occurs. It need not be a simple cis–trans isomerization occurring at one of the Co(III) centers, but might involve the participation of both metal centers. The isomerization reaction may proceed via intramolecular proton transfer between a water ligand and one of the two hydroxo bridges with simultaneous bridge cleavage and formation

TABLE XXXV

Bridge Cleavage of $L_3Co(OH)_3CoL_3^{3+}$ Species at 20°C in 1.0 *M* (Li,H)ClO$_4$

L_3	k_1/K_a (M^{-1} sec^{-1})	k_{-1} (sec^{-1})	K_1/K_a (M^{-1})	k_2 (sec^{-1})	k_{-2} (sec^{-1})	K_2	K_1K_2/K_a[a] (M^{-1})	Reference
$(NH_3)_3$	2.65	0.94	2.8	0.09	0.0027	33	93	*187*
dien	11.4	10.7	1.07	0.119	0.00043	277	296	*186*
tach	260	12.5	21	0.14	~0.04	~3.5	~74	*186*
tacn	—	—	—	—[b]	0.0024[c]	—	9	*185*

[a] $K_1K_2/K_a \ll 1$ for L_3 = metacn and $(py)_3$ (*97*, *188*).

[b] $k_2K_1/K_a = 0.0225(7)\ M^{-1}\ \text{sec}^{-1}$, $\Delta H^{\ddagger} - \Delta H^0 = 63(2)$ kJ mol^{-1}. $\Delta S^{\ddagger} - \Delta S^0 = -63(5)$ J mol^{-1} K^{-1}.

[c] $\Delta H^{\ddagger} = 100(8)$ kJ mol^{-1}, $\Delta S^{\ddagger} = 50(25)$ J mol^{-1} K^{-1}.

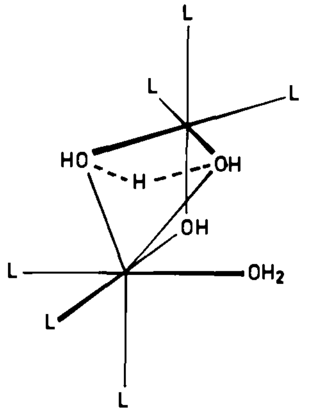


FIG. 17. A possible transition state structure for the "bridge-shift" mechanism for cis–trans equilibria of $XL_3M(OH)_2ML_3Y^{n+}$ species shown for $X = Y = H_2O$.

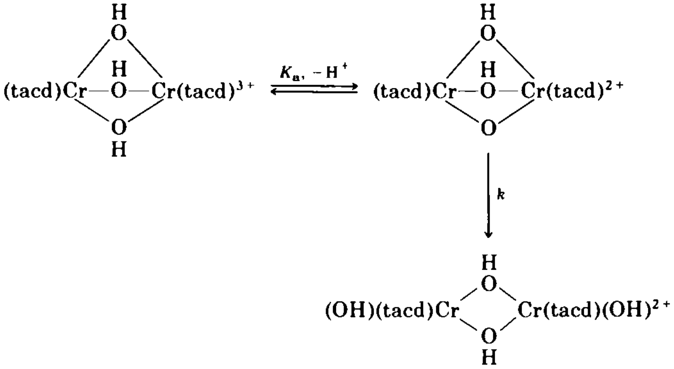
of the new hydroxo bridge. The transition state structure of this intramolecular "bridge shift" mechanism is shown in Fig. 17. This bridge shift mechanism has first been discussed in relation to isomerization reactions of several polynuclear chromium(III) complexes (*118*) (see also Table X).

Trihydroxo-bridged complexes with $L_3 = (py)_3$, dpt, and metacn have also been reported and are unusually stable with respect to bridge cleavage (*95, 97, 188*). The pyridine complex does not react measurably in $HClO_4$ solutions of concentration up to 6 *M*; in 11 *M* $HClO_4$ it reacts very rapidly and reversibly forming $(H_2O)(py)_3Co(OH)_2Co(py)_3$-$(H_2O)^{4+}$ (*188*). The metacn complex does not undergo bridge cleavage in acidic (2 *M* $HClO_4$) or basic (2 *M* NaOH) solutions. This difference in behavior relative to the analogous tacn complex has been rationalized in terms of steric hindrance in both isomers of (H_2O)(metacn)-$Co(OH)_2Co$(metacn)$(H_2O)^{4+}$ (repulsion between two methyl groups or a methyl group and a water ligand). The Cr(II) reduction of the metacn complex was found to follow a rate law of the form $k_{obs} = a[Cr(II)]$ (*97*).

B. CHROMIUM(III)

Only a few trihydroxo-bridged chromium(III) species are known. The (tacd)$Cr(OH)_3Cr$(tacd)$^{3+}$ and the (metacn)$Cr(OH)_3Cr$(metacn)$^{3+}$ ions are unusually kinetically and thermodynamically stable in acidic solution, i.e., they do not undergo hydroxo-bridge cleavage in 1 *M*

$HClO_4$ (*97, 98*). In strong basic solution the metacn complex deprotonates, giving a di-μ-hydroxo–μ-oxo complex, which rather surprisingly has been reported not to undergo bridge cleavage even in 1 *M* NaOH. The tacd complex hydrolyzes in basic solution, giving a dihydroxo-bridged species by the mechanism shown in Eq. (63).



(63)

At 25°C and $I = 0.4$ *M* [$(Li,H)ClO_4$] the parameters in Eq. (63) are $K_a = 10^{-12.9}$ *M* and $k = 1.02$ sec^{-1} ($\Delta H^{\ddagger} = 71(4)$ kJ mol^{-1} and $\Delta S^{\ddagger} = -3(12)$ J mol^{-1} K^{-1}) (*98*). The difference in reactivity between the tacd and metacn complexes has been rationalized on the basis of steric hindrance, as discussed above for the metacn cobalt(III) complex.

C. Rhodium(III)

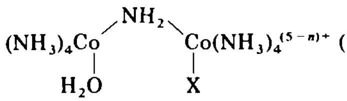
Several trihydroxo-bridged rhodium(III) complexes are known, but their hydrolysis reactions have been studied only briefly. The tacn complex undergoes a rapid two-stage reaction in acidic solution to give *trans*-$(H_2O)(tacn)Rh(OH)_2Rh(tacn)(H_2O)^{4+}$ (*76*), whereas the metacn complex is stable in acid solution (*97*).

XII. Bridge Cleavage of Mixed Bridge Complexes

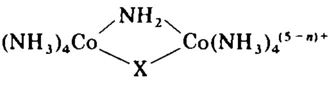
A. Hydroxo Bridge Cleavage of Amido-Bridged Dicobalt(III) Complexes

1. *The μ-Amido–μ-Hydroxo Complex*

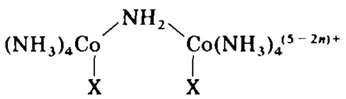
The hetero-bridged complex $(NH_3)_4Co(NH_2)(OH)Co(NH_3)_4{}^{4+}$ in acidic solution undergoes hydroxo bridge cleavage much faster than amido bridge cleavage. The bridge-cleavage reactions in acidic solution in the presence of neutral and anionic nucleophiles, X^{n-}, have been studied intensively by Sykes and co-workers (*372–375*). These reactions have led to the preparation of a series of new amido-bridged complexes of the types **IX, X,** and **XI**. The reactions with Cl^-, Br^-, SO_4^{2-}, SeO_4^{2-},



IX

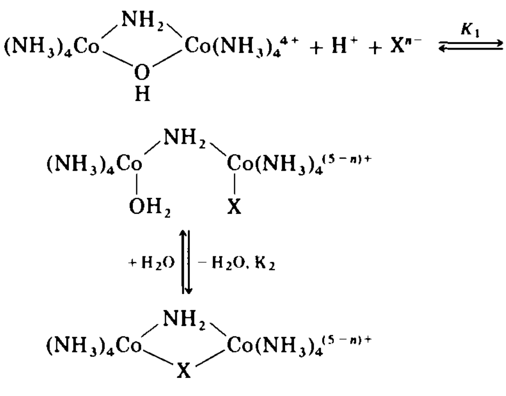


X



XI

$H_2PO_4^-$, and CH_3COOH in acidic solution give complexes of type **X**. As shown in Eq. (64), the conversions are reversible and involve intermediate formation of the corresponding singly bridged complexes **IX** (*376–386*).



(64)

The chloro- and bromo-bridged complexes were first prepared by Werner (*7*). Werner originally formulated these complexes as singly bridged complexes (structure **IX**), but the μ-amido–μ-chloro and μ-amido–μ-bromo structures have recently been demonstrated by crystallographic studies (*387, 388*). The equilibrium constant $K_{12} = K_1 \times K_2$ has been determined spectrophotometrically and the formation of structure **X** for $X^{n-} = Br^-$ is less favorable than its formation for the chloro analog (*376, 379*) (Table XXXVI). The equilibrium between

TABLE XXXVI

Hydroxo Bridge-Cleavage Reactions of $(NH_3)_4Co(NH_2)(OH)Co(NH_3)_4^{4+}$ at 25°C[a]

X^{n-}	$10^4 \times k_0$ (M^{-1} sec^{-1})	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ (J mol^{-1} K^{-1})	$10^4 \times k_1$ (M^{-2} sec^{-1})	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ (J mol^{-1} K^{-1})	$K_{12} = K_1K_2$ (M^{-2})	Reference
SeO_4^{2-}	—	—	—	135	76(1)	−26(4)	265(5)	*383*
SO_4^{2-}	—	—	—	215	74(1)	−28(1)	2240(50)	*382*
$H_2PO_4^-$	—	—	—	11.8	82(3)	−27(10)	376(80)	*384*
$HSeO_4^-$	—	—	—	~2	—	—	—	*383*
HSO_4^-	—	—	—	1.45	75(1)	−67(3)	—	*382*
Br^-	1.4	108(8)	45(24)	4.33	72(3)	−68(11)	1.0(3)	*379*
Cl^-	1.2	105(15)	31(53)	9.6	68(2)	−76(8)	10.6(14)	*376*
NO_3^-	—	—	—	4.2[b]	57(3)	−119(8)	—	*385*
NCS^-	0.028	—	—	4.7	73(2)	−62(6)	—	*377, 381*
H_3PO_4	—	—	—	0.854	60(3)	−122(12)	—	*384*
CH_3COOH	0.014	111(10)	13(29)	0.065[c]	60(3)	−144(8)	—	*386*
H_2O	—	—	—	0.81[c,d]	52(5)	−148(15)	—	*389*

[a] Equation (64). Medium 2 *M* (Na,H)ClO_4, unless otherwise stated.

[b] 2 *M* $NaNO_3$.

[c] 2 *M* $LiClO_4$.

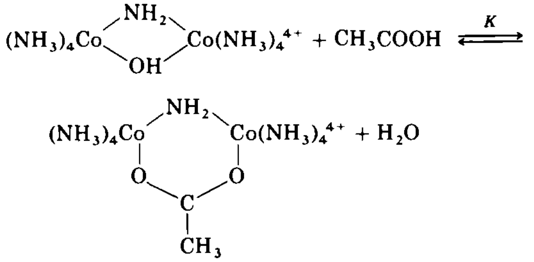
[d] Units of M^{-1} sec^{-1}.

structures **IX** and **X** is fast and lies considerably to the right, as shown by ^{1}H NMR measurements and potentiometric measurements ($K_2 > 20$ for both Cl^- and Br^-) (*378*). At very high [Cl^-] or [Br^-], complexes of type **XI** was formed, although they have not been isolated as crystalline salts (*376, 379*).

Reaction of the μ-amido–μ-hydroxo complex with excess sulfate gives a quantitative yield of μ-amido–μ-sulfato complex, which can be isolated as salts with various anions (*382*). Similarly, salts of the μ-amido–μ-selenato species have been isolated (*383*). The reaction with phosphate yields a μ-amido–μ-phosphate complex, which has been isolated both in its monoprotonated and unprotonated forms (as the nitrate and bromide salts, respectively), and support for the phosphato-bridged structures was provided by spectral (IR/UV) studies (*384*). For $X^{n-} = SO_4^{2-}$, SeO_4^{2-}, or PO_4^{3-}, the intermediate structure **IX** has not been detected, and presumably never attains a high concentration. For $X^{n-} = SO_4^{2-}$ and SeO_4^{2-}, values for K_{12} have been determined spectrophotometrically (Table XXXVI), and kinetic studies (see below) support these values. For $X^{n-} = H_2PO_4^-$, the value for K_{12} given in Table XXXVI has been deduced from kinetic parameters.

Reaction with NO_3^- yields an aqua nitrato complex (structure **IX**), and $K_1 = 0.022\ M^{-2}$ (25°C, 2 M $NaNO_3$) has been determined spectrophotometrically. At very high nitric acid concentration, evidence for another nitrato complex has been obtained and a μ-amido–μ-nitrato complex is considered more likely than, e.g., a dinitrato complex (*385*).

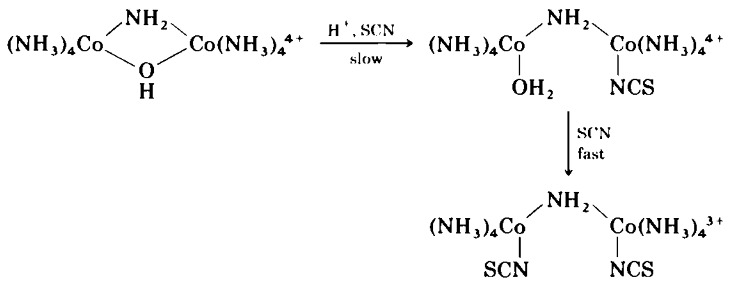
Reaction with carboxylic acids leads to formation of μ-amido–μ-carboxylato complexes, and complexes with structure **X** have been isolated for $X^{n-} = CH_3COO^-$ and $HCOO^-$. For equilibrium Eq. (65), a value of $K = 53\ M^{-1}$ (50°C, 2 M $LiClO_4$) has been determined from kinetic data (*386*).



(65)

The kinetics of equilibrium Eq. (64) have been studied in detail for each of the nucleophiles mentioned above, i.e., for $X^{n-} = Cl^-$, Br^-, SO_4^{2-}, SeO_4^{2-}, $H_2PO_4^-$, NO_3^-, and CH_3COOH. For solutions containing initially $(NH_3)_4Co(NH_2)(OH)Co(NH_3)_4^{4+}$ and a large excess of the nucleophile X^{n-} a rate law of the form $k_{obs} = k_0[X^{n-}] + k_1[X^{n-}][H^+]$ [forward reaction in Eq. (64)] was observed. Only for $X^{n-} = Cl^-$, Br^-, SCN^-, or CH_3COOH does the uncatalyzed (k_0) path contribute significantly. Values for the rate constants for the uncatalyzed (k_0) and the acid-catalyzed (k_1) bridge-cleavage reactions are listed in Table XXXVI and are discussed later. Kinetic data for the reverse reaction, cleavage of $(NH_3)_4Co(OH)(X)Co(NH_3)_4^{(5-n)+}$, have also been reported, but will not be discussed further.

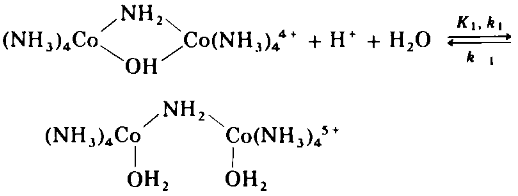
The reaction with thiocyanate yields a μ-amido-bis(tetraammine-thiocyanatocobalt(III) complex (*377*). The kinetic data are consistent with a dominant reaction path such as in Eq. (66) (*377, 381*). There is



(66)

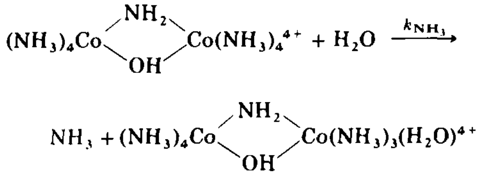
no evidence for buildup of the intermediate aqua thiocyanato complex or of a μ-thiocyanato complex, as would correspond to the results for the analogous reactions with Cl^- or Br^-. At $[H^+] \leq 0.4$ *M*, the rate law is of the form $k_{obs} = k_0[NCS^-] + k_1[H^+][NCS^-]$. This corresponds to the dependence mentioned above, and k_0 and k_1 have been interpreted likewise (Table XXXVI). At $[H^+] > 0.4$ *M*, k_{obs} becomes nonlinear in $[H^+]$.

The conversion of the μ-amido–μ-hydroxo complex to the diaqua μ-amido complex in Eq. (67) has been difficult to study because the spectra of the two species are similar and because the equilibrium constant, K_1, is too small to be measured in, e.g., 2 *M* $(Na,H)ClO_4$ (*389–391*).



(67)

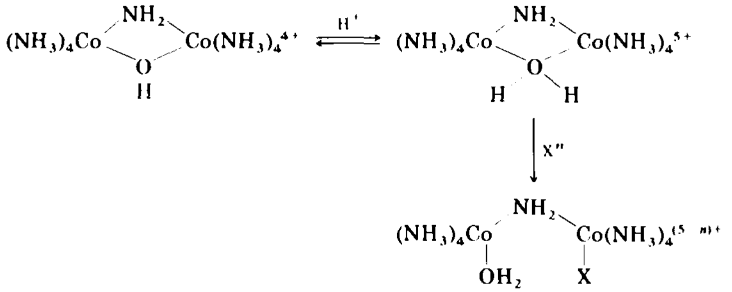
There is, however, spectroscopic evidence for the formation of the diaqua complex in approximately 6 *M* $HClO_4$, and a value of $K_1 = 0.05(2)$ M^{-1} (1.5°C) has been obtained from spectrophotometric measurements in 0–6 *M* $HClO_4$ (*391*). A further complication is the fact that ammonia hydrolysis [Eq. (68)] takes place at a rate which



$$(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(NH_3)_4^{4+} + H_2O \xrightarrow{k_{NH_3}} NH_3 + (NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(NH_3)_3(H_2O)^{4+} \qquad (68)$$

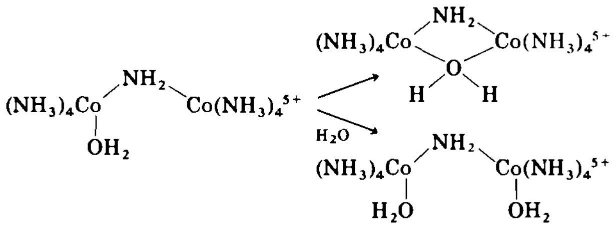
is comparable to that of acid-catalyzed hydroxo bridge cleavage. Both rate constants, k_1 and k_{NH_3}, have been determined from kinetic studies (*389*) of the vanadium(II) and chromium(II) reductions of the μ-amido μ-hydroxo complexes in acidic solution, which gave $k_{NH_3} = 0.46 \times 10^{-4}$ sec^{-1} (25°C, 2 *M* $LiClO_4$) and k_1 as listed in Table XXXVI. Evidence for the formation of an aqua perchlorato as well as a μ-perchlorato complex at very high concentrations of perchloric acid (8–12 *M*) has been presented (*390*), and further characterization would be of interest.

The rate constants k_1 for acid-catalyzed cleavage of the μ-amido–μ-hydroxo complex given in Table XXXVI fall into three distinct groups, depending on the charge of the ligand X^{n-}. Rate constants (M^{-2} sec^{-1}) for doubly charged anions are about 10^{-2}, for singly charged anions from 10^{-4} to 10^{-3}, and for uncharged nucleophiles from 10^{-5} to 10^{-4}. The various nucleophiles are believed to react via a common mechanism, Eq. (69), involving protonation of the hydroxo bridge followed by rate-determining bridge cleavage and formation of structure **IX** (*372*). An S_N2 mechanism can be excluded since $k_{NCS}/k_{Cl} \sim 0.5$, which is much smaller than the value of about 50 found for S_N2 reactions of Cr^{3+}, V^{3+},



$$(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(NH_3)_4^{4+} \overset{H^+}{\rightleftharpoons} (NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH_2)Co(NH_3)_4^{5+} \xrightarrow{X^{n-}} (NH_3)_4(H_2O)Co(\mu\text{-}NH_2)Co(NH_3)_4X^{(5-n)+} \qquad (69)$$

and Mo^{3+}. The data are therefore more consistent with an S_N1 mechanism, and a mechanism of the "nonlimiting" type was preferred and it was discussed how such a mechanism could rationalize the kinetic data in terms of ion-pair and ion-triplet formation, in spite of the fact that the required less-than-first-order dependence on $[X^{n-}]$ is not observed. A "limiting" S_N1 mechanism was shown to require that a five-coordinated cobalt(III) center captures coordinated water by an intramolecular reaction [Eq. (70a)] much faster than it captures bulk water Eq. (70b)], and this was considered unlikely (*372*). In the light of



(70a)

(70b)

more recent studies, however, it could be argued that proximity effects would favor Eq. (70a) considerably. As discussed in Section IX,D, the $(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(H_2O)^{5+}$ ion forms the presumed μ-aqua–μ-hydroxo intermediate at a rate which is comparable to the rate of water exchange in *cis*-$Rh(NH_3)_4(H_2O)_2^{3+}$ (Table XXXIII). Therefore, a "limiting" S_N1 mechanism should not be entirely discounted on the basis of the present data.

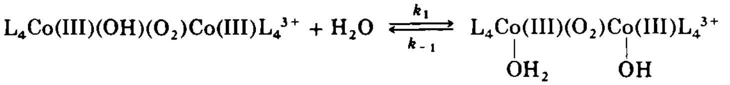
2. The μ-Amido–Di-μ-hydroxo Complex

Acid cleavage of the hetero-bridged complex $(NH_3)_3Co(NH_2)(OH)_2Co(NH_3)_3^{3+}$ yields $(H_2O)(NH_3)_3Co(NH_2)(OH)Co(NH_3)_3(H_2O)^{4+}$, which has been tentatively assigned a trans configuration on the basis of the expected similarity in behavior to the trihydroxo-bridged complexes discussed in Section XI (*259, 371*). The equilibrium constant $K = [(H_2O)Co(NH_2)(OH)Co(H_2O)^{4+}]/[Co(NH_2)(OH)_2Co^{3+}][H^+]$ has been determined spectrophotometrically as $K = 62(3)\ M^{-1}$ (1 M $LiClO_4$, 25°C), which is close to the value 65.2 M^{-1} found for $(NH_3)_3Co(OH)_3Co(NH_3)_3^{3+}$. The kinetics of the equilibration between the amido-bridged complexes showed only one stage, the rate expression being $k_{obs} = k_a + k_b[H^+]$. In 1 M $LiClO_4$ and at 25°C, the kinetic parameters are $k_a = 1.96 \times 10^{-2}\ sec^{-1}$ and $k_b = 1.01\ M^{-1}\ sec^{-1}$ (*371*).

B. OTHER COMPLEXES

In most other hetero-bridged systems studied the hydroxo bridge is kinetically more stable than the X^{n-} bridge. Base hydrolysis of $(en)_2Cr(OH)(X)Cr(en)_2{}^{(4-n)+}$ has been reported to give essentially X^{n-} bridge cleavage for $X^{n-} = SO_4{}^{2-}$, $RCH(NH_2)COO^-$, and CF_3COO^-. A similar result has been reported for the acid hydrolysis for $X^{n-} = CF_3COO^-$ (*105, 107, 262–263*). The complex $(tacn)Cr(OH)_2(CO_3)$-$Cr(tacn)^{2+}$ and its rhodium(III) analog undergo carbonato bridge cleavage in acidic solution, and the kinetics of these reactions have been reported (*100*).

The kinetics of formation from and decomposition into Co(II) and O_2 of μ-hydroxo–μ-peroxo dicobalt(III) complexes have been studied in detail, and the mechanistic aspects have been discussed in a recent article by Fallab and Mitchell (*119*). Two different mechanisms have been invoked to explain the kinetics of the first bridge cleavage of $L_4Co(OH)(O_2)CoL_4{}^{3+}$ species. One mechanism involves hydroxo bridge cleavage and formation, as shown in Eq. (71). The parameter values



$$L_4Co(III)(OH)(O_2)Co(III)L_4{}^{3+} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} L_4\underset{\substack{|\\ OH_2}}{Co}(III)(O_2)\underset{\substack{|\\ OH}}{Co}(III)L_4{}^{3+} \qquad (71)$$

for $(tren)Co(OH)(O_2)Co(tren)^{3+}$ are $k_1 = 5 \times 10^{-5}$ sec^{-1} and $k_{-1} = 3.25$ sec^{-1} at 25°C (*392*) and similar values have been reported for other amine systems (*119*). However, doubt has been expressed concerning this mechanism, since it involves a comparatively fast substitution at a cobalt(III) center. Accordingly, an alternative reaction mechanism has been proposed, involving reductive peroxo bridge cleavage to give a hydroxo-bridged cobalt(II)–cobalt(III) intermediate containing terminally coordinated superoxide $Co(III)(OH)Co(II)O_2$ (*119*).

Preliminary studies seem to indicate that acid hydrolysis of corresponding rhodium(III) complexes leads to peroxo bridge cleavage rather than hydroxo bridge cleavage (*124*).

XIII. Concluding Remarks

Structural, thermodynamic, and kinetic studies have shown that hydroxo-bridged polynuclear complexes of chromium(III), cobalt(III), rhodium(III), and iridium(III) have many general features in common. Structurally, the four metal ions exhibit an almost identical pattern, and in particular the occurrence of many well-characterized oligomers of chromium(III) and cobalt(III) shows that the same structures are favored for these two ions. The nature of the nonbridging ligands is of great importance in influencing the formation of a specific oligomer (or isomer).

The thermodynamic and kinetic properties exhibit trends similar to those found for the "parent" mononuclear complexes, but properties specific to the polynuclear complexes have considerable influence. Important factors of the latter kind are high charge, proximity effects, and intramolecular hydrogen bond formation. Intramolecular hydrogen bonds can be formed in several ways and between a variety of acceptor and donor groups. A particularly strong effect has been observed in complexes in which the hydrogen bond is between terminally coordinated hydroxide and water ligands, and it is now well established that interaction of this kind may have a strong impact, e.g., on the aqua-ligand acidity, on the stability of different isomers, and on kinetic parameters.

Only a few thermodynamic studies have been made of intermolecular condensation reactions between mononuclear and relatively simple oligomeric species, and kinetic studies of such reactions have first been reported only quite recently. Charge effects seem to play a dominant role, although another important factor may be the formation of intermolecular hydrogen-bonded cation pairs.

A large body of thermodynamic as well as kinetic data for intramolecular bridge-cleavage and -formation reactions has been accumulated during the last two decades. These reactions are usually very fast and reversible, and in this sense are related to the preequilibria observed during the hydrolysis of bidentate ligands.

Bridge-cleavage and -formation reactions proceed via an uncatalyzed (k_0) (spontaneous) and an acid-catalyzed (k_H) path. It is generally accepted that the acid-catalyzed path involves the formation of a labile aqua-bridged intermediate. The aqua-bridged complex is believed to be a very strong acid ($pK \ll 0$), but it has not yet been identified. The uncatalyzed path is the dominant pathway in all the chromium(III) systems studied until now ($k_H/k_0 \lesssim 1\ M$ for the bridge-cleavage reactions) whereas the acid-catalyzed path dominates in the reactions of the three d^6 metals (k_H/k_0 being typically in the region of 10–$10^3\ M$ for the bridge-cleavage reactions). The rate of the first bridge cleavage in mono-, di-, and trihydroxo-bridged complexes, respectively, increases in this order, which may well be a result of increasing strain in the bridge system.

Hydroxo bridge cleavage in the presence of anionic nucleophiles, which is a facile method for the synthesis of mixed bridge complexes, has been studied kinetically [particularly for cobalt(III)] and has been discussed in terms of different reactivities of protonated and unprotonated ion doublets and triplets. Bridge cleavage of complexes of the type $M(OH)(X)M^{(5-n)+}$ may occur by hydroxo bridge cleavage ($X^{n-} = NH_2^-$, O_2^{2-}) or by cleavage of the X^{n-} bridge ($X^{n-} = CO_3^{2-}$, SO_4^{2-}, $RCOO^-$, etc.).

Hydroxo-bridged complexes are of relevance to applied chemistry. One well-known example is the importance of hydroxo-bridged chromium(III) aqua oligomers in the chromium(III) tanning process. Mention should also be made of the application of hydroxo-bridged chromium(III) complexes in coating materials for magnetic toners used in electrostatic printing, in coatings for printing papers to improve their water resistance and printability, and in coatings for paper liners used in gypsum board manufacturing (*393–395*). Chromium(III) and cobalt(III) hydroxo-bridged oligomers have been used in silicon residue varnishes to improve the drying and hardening process (*396, 397*).

Finally, it should be noted that this chemistry may have biological relevance. Several metalloenzymes are believed to contain more than one metal ion bound at the active site. One relevant example is the glucose tolerance factor (GTF) which is important for the metabolic degradation of glucose (*398–401*). GTF is a low-molecular-weight protein which contains chromium(III). Its structure is not known, but it has been suggested that the active site contains a dinuclear chromium(III) complex (*401*). The fact that hydroxo-bridged dinuclear chromium(III) complexes exhibit reactions which are often very fast compared with those observed for the "parent" mononuclear species seems to support such a proposal.

XIV. Abbreviations for Ligands and Solvents

A. GENERAL

L_n, One or several ligands which coordinate at *n* sites

X or Y, Uni- or bidentate ligand

B. SPECIFIC

acac, Acetylacetonate
ala, Alaninate

bamp, 2,6-Bis(aminomethyl)pyridine
bipy, 2,2′-Bipyridine
bn, Butanediamine
bispicam, *N*,*N*′-Bis(2-pyridylmethyl)amine
bispicen, *N*,*N*′-Bis(2-pyridylmethyl)-1,2-ethanediamine
bispicpn, *N*,*N*′-Bis(2-pyridylmethyl)-1,2-propanediamine
bispictn, *N*,*N*′-Bis(2-pyridylmethyl)-1,3-propanediamine

chlorodipic, 4-Chloro-2,6-pyridinedicarboxylate
chxn, 1,2-Cyclohexanediamine

dien, Diethylenetriamine
dipic, 2,6-Pyridinedicarboxylate (dipicolinate)
DMF, Dimethyl formamide
DMSO, Dimethyl sulfoxide
dmpz, 3,5-Dimethylpyrazole
dpt, Di(3-aminopropyl)amine (dipropylenetriamine)

edda, *N*,*N*′-Ethylenediaminediacetate
en, Ethylenediamine (1,2-ethanediamine)

gly, Glycinate

hydroxodipic, 4-Hydroxo-2,6-pyridinedicarboxylate

ibn, Isobutylenediamine (2-methyl-1,2-propanediamine)

mal, Malonate
mepic, 1-(2-Pyridyl)ethylamine
metacn, 1,4,7-Trimethyl-1,4,7-triazacyclononane

nta, Nitrilotriacetate

ox, Oxalate

PBu_3, Tributylphosphine
phen, 1,10-Phenanthroline
pic, 2-Picolylamine [1-(2-pyridyl)methylamine]
pn, Propylenediamine (1,2-propanediamine)
pro, Prolinate
py, Pyridine

salen, *N*,*N*′-Ethylenebis(salicylideneiminate)

tacd, 1,5,9-Triazacyclododecane
tach, *cis*,*cis*-1,3,5-Cyclohexanetriamine
tacn, 1,4,7-Triazacyclononane
tame, 1,1,1-Tris(aminomethyl)ethane
tn, Trimethylenediamine (1,3-propanediamine)

tpyea, Tris(2-pyrazol-1-ylethyl)amine
trans-[14]diene, 5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene
tren, 2,2′,2″-Triaminotriethylamine
trien, Triethylenetetramine

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