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HYDROLYTIC POLYMERIZATION OF CHROMIUM(III).
I. THE TWO DIMERIC SPECIES

Mary Thompson and Robert E. Connick

August 1980

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Hydrolytic Polymerization of Chromium(III).   LBL 11336

I.   The Two Dimeric Species

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ABSTRACT

In addition to the well known doubly bridged chromium(III) dimer,

$[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{4+}$, a second dimer of formula $[(H_2O)_5CrOHCr(H_2O)_5]^{5+}$

has been found. The formula of the latter was established through

equilibrium measurements and freezing point depression. The equilibrium

between Cr^{3+} and the doubly bridged dimer was measured at various ionic

strengths and temperatures. The equilibrium between the doubly bridged

and singly bridged dimers is shifted strongly towards the latter only at

high acidities, with roughly equal concentrations at 2M acid. Electron

spin resonance spectra were taken for both dimers in order to obtain g

values. The latter were used with magnetic susceptibility measurements

to calculate the spin-spin coupling constants between the two chromiums

of these species. Comparison is made with the coupling constants of other

bridged chromium(III) compounds and the results are shown to be in reasonable

agreement. The striking difference in magnetic susceptibility between

the doubly bridged chromium dimer and the iron(III) dimer of empirical

formula $Fe_2(OH)_2^{4+}$ is discussed in terms of possible structures and

electronic interactions.

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The interest in the hydrolysis and concomitant polymerization of metal ions in aqueous solutions has led to numerous studies of such systems.[1] Mixtures of species are usually present at equilibrium and the interpretation becomes uncertain because of the difficulty of assigning both formulas and equilibrium constants unambiguously. In a few cases the species involved are inert,[2] i.e. they interconvert slowly so that there is the possibility of analyzing the system by separation of the individual components in pure form. Then the establishment of the existence of the individual hydrolyzed species becomes surer and the opportunity to probe the structure much greater. Such a situation prevails with chromium(III).

Numerous investigators have shown by a variety of methods that chromium(III) forms hydrolyzed polymers. One of the earliest studies was that of Niels Bjerrum who made this system a part of the subject of his doctoral thesis.[3] He determined the degree of hydrolysis by measurement of the hydrogen ion concentration using a hydrogen electrode. Hydrolysis to give monomeric species was distinguished from that giving polymeric species by the much slower attainment of equilibrium of the latter. From the dependence on chromic ion concentration he established the stoichiometric formula $Cr_2(OH)_2^{4+}$ for the simplest polymer formed in dilute acid solutions and measured the equilibrium constant for its formation from Cr^{3+} at 75 and $100°C.$[3,4] In addition he postulated the existence of $Cr_6(OH)_{12}^{6+}$ and $Cr_{12}(OH)_{30}^{6+}$ and reported much less certain values for their formation constants.

Subsequent to Bjerrum's work, other investigators have reached the same conclusion about the formation of a binuclear complex. Stiasny

and Balanyi[5] postulated the formation of "ol" complexes in basic chromium(III)
chloride solutions used in tanning and cited in particular the complex
$(H_2O)_4Cr \underset{OH}{\overset{OH}{<}} Cr(H_2O)_4{}^{4+}$ as an explanation for the increase in acidity
upon heating or aging of the tanning liquors. To account for the change
in pH as a function of dilution in solutions of chromium(III) nitrate
containing potassium hydroxide, Schaal and Faucherre[6] proposed a
two-fold condensation of the chromium to form the complex Cr_2O^{4+}. In
the course of some cryoscopic work on saturated solutions of potassium
nitrate, Souchay[7] found that the depression of the freezing point by
chromium(III) nitrate solutions, to which potassium hydroxide had been
added in a less than one-to-one mole ratio, could best be explained
by the presence of a chromium species having the formula $Cr_2(OH)_2{}^{4+}$.
Hall and Eyring[8] noted that chromium(III) nitrate solutions become
acidic upon heating and apparently contain more than one chromium
species. They postulated that some of these species could be represented
as oxygen-bridged complexes since there were fewer than six waters bound
to chromium as determined by their measurements.

More recently Laswick and Plane[9] and Finholt[10] have exploited the
inertness of the chromium(III) hydrolyzed polymers to isolate the
individual species, using ion-exchange separation. A solution of chromic
nitrate or perchlorate refluxed at 100°C for several hours was found to
contain, in addition to monomeric chromium(III), the dimer of formula
$Cr_2(OH)_2{}^{4+}$ and at least one more polymer of higher charge, presumably
a trimer. Ardon and Plane[11] showed that the dimer was identical with the
principal oxygen oxidation product of chromous perchlorate solutions, thus
providing a convenient method for its preparation. The dimeric character

has been confirmed by freezing point lowering,[12] and of the two

possible stoichiometric formulas, $Cr_2(OH)_2^{4+}$ and Cr_2O^{4+}, the former has

been shown to be correct through isotopic studies by Kolaczkowski and Plane.[13]

Kinetic studies by Finholt[10] of the decomposition of the dimer in a

6 M $HClO_4$ revealed a hitherto unobserved complication in the system

in that a relatively rapid spectral change occurred followed by a much

slower change to give Cr^{3+}. The present investigation was undertaken

to clarify this phenomenon and to learn more about some of the properties

of the dimer. In two subsequent papers the kinetics of the interconversion

of the polymers and the characterization of the trimer will be given.

The Singly Bridged Dimer. Extension of Finholt's observations to

other acidities revealed that the decomposition of the doubly bridged

dimer occurs in two successive steps. The obvious candidate for the

intermediate is the singly bridged dimer and this proved to be the case.

The following observations were used to establish its formula.

The fraction of the doubly bridged dimer converted to the intermediate

depends on the acidity. The spectral change appears to approach a limiting

value around 11 M perchloric acid. Over the whole range studied the second

step of the decomposition was sufficiently slow compared to the first step

that the doubly bridged dimer and the intermediate were nearly at

equilibrium before appreciable decomposition to Cr^{3+} took place. The

changes in molar absorbance between the doubly bridged dimer and the

intermediate were small at most wavelengths, as is the case for all of the

Cr(III) species studied (see Fig. 1). The spectrum shown for the singly

bridged dimer may contain a small component of the doubly bridged dimer

if the equilibrium was not completely shifted toward the former species

in concentrated perchloric acid. The color change is from blue for doubly bridged dimer to green for the intermediate. (The spectra of all of the species studied in this work are shown in Fig. 1 for purposes of comparison.)

The molar absorbances at 270 nm for the equilibrium mixture of the doubly bridged dimer and the intermediate were determined as a function of the perchloric acid concentration at 25° and 45°C. These values were obtained by extrapolating back to zero time the slowly varying absorbance in the second step of the reaction. In principle one could fit such data to an equilibrium constant and a molar extinction coefficient for the intermediate. A good fit over the range was not obtained, as might have been anticipated because of the strongly changing medium which could affect both activity coefficients and molar extinction coefficients. Roughly equal concentrations of the two dimers were present in 2M $HClO_4$. Elsewhere[14] the same equilibrium quotient is evaluated from kinetic data at an ionic strength of 2.0 M. Those values are probably within experimental error of the values one obtains from the equilibrium data although a "best fit" for the latter would lead to a somewhat greater stability for the intermediate singly bridged dimer than the kinetic data indicate.

At 5.76 M $HClO_4$ and 25° the total chromium concentration was varied from 6.5×10^{-3} to 6.5×10^{-2} M without significant change in apparent molar absorbance of the equilibrium mixture of doubly bridged dimer and intermediate, thus establishing that both species contain the same number of chromium atoms and that the intermediate is therefore a dimer. Confirmation of this conclusion by cryoscopic measurements is given later.

The acidity dependence of ϵ_f in Fig. 2 is best fitted by a first power
hydrogen ion dependence, and it is concluded that the intermediate is

$$
\begin{array}{cc}
 & H \qquad 5+ \\
 & O \\
Cr^{\diagup} & {}^{\diagdown}Cr
\end{array}
$$
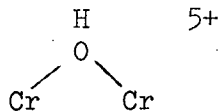
with each chromium presumably having 5 waters coordinated to it in addition
to the hydroxide group.

To simplify the nomenclature the doubly bridged dimer (octaaquo-μ-
dihydroxodichromium(III) ion) and the singly bridged dimer (decaaquo-μ-
hydroxodichromium(III) ion) will now be designated DBD and SBD, respectively.

Equilibrium Between the Monomer and Doubly Bridged Dimer. Although
Bjerrum[3] had obtained values of the equilibrium constant for the formation
of the dimer at two elevated temperatures, the results were not precise
and were beclouded by corrections for higher polymers whose formulas are
almost certainly in error. The feasibility of analysis by separation of
the individual species now makes more accurate measurements possible.

The absorbancies of the three species isolated from Cr(III) solution
do not differ widely from one another at any point in their spectra (see
Fig. 1), and therefore spectral analysis of equilibrated solutions without
separation is not highly accurate. In addition other polymers might
be present in sufficient amount to invalidate such a spectral analysis;
such species have been detected on ion-exchange columns.

The technique of ion-exchange separation by a combination of displace-
ment development and elution development with a single eluant proved
successful in the analysis of the chromium species. Calcium perchlorate

can be used to displace the monomer from the resin and elute the polymeric forms at different rates. The equilibrium hydrogen ion concentration can be determined readily by pH measurements with a glass electrode.

The equilibrium studied[15] was calculated on the following basis:

$$2Cr^{3+} + 2H_2O \overset{Q_{22}}{\rightleftharpoons} Cr_2(OH)_2{}^{4+} + 2H^+$$
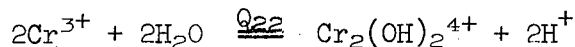
where $$Q_{22} = \frac{[Cr_2(OH)_2{}^{4+}][H^+]^2}{[Cr^{3+}]^2} \quad .$$

and brackets indicate concentrations in moles per liter of solution. The monomer and DBD concentrations were obtained by ion exchange separation of an aliquot of the equilibrated solution. Correction was made for the formation of $CrOH^{2+}$ under each set of conditions using the results of Postmus and King[16] who studied the hydrolysis of Cr^{3+} in solutions of similar composition and ionic strength. Experiments reported elsewhere[17] showed that at an ionic strength of 1.00 M the pH meter gave readings quite close to the actual hydrogen ion concentration. At other ionic strengths there may have been appreciable deviations. Table I gives the values of the equilibrium quotient for the formation of DBD from the monomer obtained in these experiments. At constant ionic strength a four-fold variation in Cr^{3+} concentration produces no systematic effect on Q_{22}. Similarly Q_{22} appears to be independent of hydrogen ion concentration for a several fold variation. The value of ΔH for the reaction, determined from a plot of log Q_{22} versus $1/T$, is 12.7 kcal and $\Delta S_{298}°$ is 20 e.u.

Bjerrum[3] reported ΔH to be 15.4 kcal/mole for the same reaction from his measurements at 75 and 100°C, and one calculates 15 e.u. for

Table I. Equilibrium Quotients for the Formation of $Cr_2(OH)_2^{4+}$

μ M	$[H^+]$ $M \times 10^3$	$[Cr^{3+}]_o$ M	$[Cr(H_2O)_6^{3+}]$ $M \times 10^2$	$[Cr_2(OH)_2^{4+}]$ $M \times 10^3$	$Q_{22} \times 10^5$ M
			67.5°C		
0.201	4.5	0.0294	1.32	1.20	13.9
1.00	5.7	0.0250	1.32	0.93	17.3
1.00	6.5	0.100	2.97	3.93	18.8
1.00	6.6	0.0250	1.48	0.92	18.3
1.00	25.0	0.104	8.4	1.81	16.0
2.00	18.5	0.200	13.1	8.2	16.4
2.00	20.9	0.295	14.7	11.5	23.2
			50.0°C		
0.184	3.78	0.0250	1.61	1.02	5.6
0.74	7.4	0.100	6.7	4.7	5.7
1.00	4.0	0.0260	2.11	0.93	3.3
1.00	7.6	0.100	6.4	4.2	5.9
1.00	7.7	0.0260	2.29	0.52	5.9
1.00	9.1	0.0260	2.38	0.40	5.8
1.00	9.9	0.100	5.7	1.96	5.9
1.00	11.5	0.104	8.6	3.15	5.6
1.00	12.0	0.104	9.2	3.14	5.3
1.00	15.1	0.104	8.9	1.87	5.4
			37.5°C		
0.185	2.35	0.0250	1.59	0.73	1.59
0.74	6.7	0.104	7.3	3.34	2.8
1.00	2.62	0.0250	1.44	0.95	3.1
1.00	5.9	0.100	6.6	3.19	2.5
1.00	5.9	0.100	6.3	3.44	3.0

$\Delta S_{298}°$ for his data. Perhaps Bjerrum's correction for the higher polymers, assumed by him to be $Cr_6(OH)_{12}^{6+}$ and $Cr_{12}(OH)_{30}^{6+}$, can explain the discrepancy in the heats.

The increase in entropy of 20 e.u. may be attributed to the following factors: 1) two water molecules are freed from the first coordinations sphere, if an octahedral environment is assumed for each chromium, 2) in addition to the water, two independently moving particles are converted to three, i.e. the dimer and two hydrogen ions, and 3) the two triply charged monomers are changed to a dimer of charge +4, but with the charges widely distributed, and two singly charged hydrogen ions. All of these changes would be expected to lead to positive entropy increments.

Milburn[18] has reported ΔH and ΔS for the formation of the analogous iron dimer, $Fe_2(OH)_2^{4+}$: $\Delta H = 12.2 \pm 1.0$ kcal/mole and $\Delta S = 28 \pm 5$ e.u. ($\mu = 1$, 25°C). The entropy changes for the two reactions may actually be the same within the experimental accuracy, but in any event the smaller size of the Fe(III) ion might be expected to favor a larger entropy change. Similar trends are observed in the hydrolysis constants (K_1) of the two ions: $\Delta H = 9.4$ kcal/mole and $\Delta S = 14.1$ e.u. ($\mu = 0$, 25°C) for the reaction:

$$Cr^{3+} + H_2O = CrOH^{2+} + H^+$$
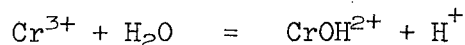
reported by Postmus and King,[16] and Milburn[18] gives $\Delta H = 10.4$ kcal/mole and $\Delta S = 25$ e.u. ($\mu = 0$, 25°C) for the corresponding Fe(III) reaction.

The lack of any marked dependence of Q_{22} on ionic strength within the range studied is shown in Table I. If one considers the activity coefficients of the constituents, then

$$K_{22} = Q_{22} \frac{\gamma_{Cr_2(OH)_2^{4+}} \gamma_{H^+}^2}{\gamma_{Cr^{3+}}^2}$$

The values of these activity coefficients in solutions of high ionic

strength, as is the case here, are unknown. It is interesting that ΔZ^2,

the change in the square of the ionic charges, is zero for the reaction

and therefore the Debye-Hückel limiting law yields zero dependence on

ionic strength at low ionic strength. Obviously the Debye-Hückel limiting

law cannot be applied in such concentrated solutions, but at least the

prediction from it is not in disagreement with the observations.

Characterization of the Dimeric Species

Freezing Point Lowering. The determination of the freezing point

depression of a eutectic mixture of perchloric acid hydrate and water

by what they assumed to be the DBD has been carried out by Ardon and

Linenberg.[12] Through the use of this particular solvent the chromium

complex is the only foreign ion in the solution: the counter-ion,

perchlorate, is already present, as is hydrogen ion, and neither will

therefore affect the freezing point appreciably. As Ardon and Linenberg

point out, the actual charge of the complex is not determined but only the

number of foreign ions in solution. Therefore formation of perchlorate

complexes will not affect the freezing point depression, or be detectable.

Since the eutectic mixture is 5.27 M in perchloric acid the question

arises whether Ardon and Linenberg observed the freezing point depression

of DBD or that of a mixture of DBD and SBD. At 25° an equilibrium mixture

would contain ca. 80 percent SBD. Their sample of DBD was prepared in

low acid. With a reported rate of cooling of 0.2° per minute and a

total temperature drop of same 80°C from room temperature to the freezing

point of the eutectic, sufficient time would have elapsed to permit formation of a large percentage of SBD. The formation of monomer from the SBD in the high acid is sufficiently slow that its presence may be neglected in the freezing point measurement.

To verify that the DBD is truly dimeric a fresh solution of DBD was added to a chilled perchloric acid solution of eutectic composition and the solution was cooled to the eutectic freezing point. The solution was allowed to warm to room temperature and then rechilled after a period of thirty minutes. The solution then contained a mixture of SBD and DBD. The results of these measurements are shown in Table II.

The experimental freezing point constant, K_f, for the perchloric acid hydrate and ice eutectic is reported to be $4.43 \pm 0.31°$.[12] Since $\frac{mK_f}{\Delta T} = n$, where n is the number of chromium atoms per complex ion, the last column of Table II shows that the two species, SBD and DBD, contain two chromium atoms.

ESR Spectra. The g values of the chromium(III) species were measured to permit a more reliable interpretation of the variation of χ_A, the atomic susceptibility, with temperature.

Chromium(III) has three $\underline{d}$ electrons and a ground state $^4F_{3/2}$. The spin angular momentum, which cannot be zero, accounts for most of the paramagnetism of the ion. The orbital angular momentum is nearly quenched by the field of the ligands surrounding the ion: the $\underline{d}$ electrons spend most of their time in the outer regions of the ion and experience interactions with the ligand field which are more powerful than their own spin-orbit coupling. The small residual orbital effect is related to the ratio of the spin-orbit coupling constant and the magnitude of the ligand field splitting.

Table II. Freezing Point Lowering of Eutectic of

Aqueous Perchloric Acid by SBD and DBD

Moles Cr(III) added per 1000 g of 40.7% HClO$_4$	ΔT	$\dfrac{mK_f}{\Delta T}$ [c]
D B D		
.00711	.0165°	1.91
.01136	.0278°	1.81
.01309	.0284°	2.04
.01421	.0298°	2.11
.0305	.0659°	2.05
.0685	.153°	1.98
S B D and D B D[b]		
.01136[a]	.0278°	1.81
.01421[a]	.0298°	2.11
.0685[a]	0.153°	1.98

[a] Solutions originally containing DBD were warmed to room temperature and then rechilled.

[b] These solutions should have contained ca. 80 percent SBD.

[c] m is moles Cr(III) per kilogram of 40.7% perchloric acid.

It can be shown[19] that in the presence of an external magnetic field
the term in the Hamiltonian of importance for the ESR of Cr^{3+} transitions
in solution is

$$\mathcal{H}' = g \beta H_z S_z$$

where g is the spectroscopic splitting factor, β the Bohr magneton, H_z
the external field, and S_z the quantum number for the z component of the
electron spin. The hyperfine and quadrupole interactions are omitted
because the resonances of interest here are too broad to allow of their
detection. The small contribution arising from spin-orbit interaction
is included in the g factor.

In the case of species containing two or more chromium atoms Kambe[20]
has proposed that the Hamiltonian should include a term arising from the
coupling of the spins of the electrons on adjacent chromium atoms, i.e.
for the dimers:

$$\mathcal{H}' = g \beta H_z S_z' - 2J \underset{\sim}{S_1} \cdot \underset{\sim}{S_2}$$

where J is the exchange coupling constant, $\underset{\sim}{S_1}$ and $\underset{\sim}{S_2}$ are the spin vectors
of the two chromium atoms and S_z' is the z component of S' the total spin
of the species. For a dimer of chromium(III), with S' = 0, 1, 2, 3 and a
multiplicity of 2S' + 1, the energy level scheme is shown in Fig. 2.[20]
Only because J has a small value compared to kT can ESR spectra be observed
for these species since the energy difference between the singlet orbital
ground state and the next higher level is 2J, where J is the exchange
coupling interaction. Transitions following the selection rules, $\Delta S' = 0$ and $\Delta M_S = \pm 1$ are observed. Fig. 3 shows the spectra of the two dimers

and the monomer. The presence of some monomer in all samples of poly-
nuclear species is not unexpected; it does not exceed a few percent in the
DBD sample. The sharp-peaked spectrum of the monomer, nearly equivalent
in height to that of the polymer in the DBD spectrum is somewhat mislead-
ing. In derivative ESR signals such as these, the concentration is pro-
portional to the square of the width times the height. The g values deter-
mined for the DBD and SBD are 1.976 and 1.916, respectively, in comparison
to 1.980 for the monomer, and the line widths of both signals are 4-6 times
broader than that of the monomer.

The value of the spectroscopic splitting factor, g, should be dependent
on the spin-orbit coupling constant λ and the ligand field splitting, Δ.
For chromium(III) in an octahedral field, g is expected to be given by:[21]

$$g = 2.002 - 8\lambda/3\Delta,$$

with λ reported as 273 cm^{-1} for Cr(III) and Δ of the order of 17,500 cm^{-1}
for all chromium complexes being considered here (see Fig. 1). The small
variation in the g values of the two species and the monomer is consistent
with the small variation in Δ. The g values, however, differ appreciably
from either the spin-only value (2.0023) or the g calculated for Cr(III)
in an octahedral field from the above expression, i.e. 1.962. The
approximations in this formula are not adequate to explain the g values in
detail.

Magnetic Susceptibility Measurements. Earnshaw and Lewis[22] have
investigated the magnetic properties of several binuclear complexes of
chromium(III). These complexes are interesting since interaction between
the metal atoms depends on both the number and nature of the bridging groups.
Kolaczkowski and Plane[13] have shown that the bridging groups in the DBD are

-15-

hydroxide ions rather than an oxide ion, and a single hydroxide group must bridge in the SBD. Schaffer and Jorgensen[23] have demonstrated that there is a good correlation between the bridging group, i.e. hydroxide or oxide, and the magnetic as well as spectral behavior in the case of the Cr(III) amines. The similarity in magnetic properties and spectra of DBD, SBD and the monomer is quite consistent with their findings.

Kambe[20] has shown that the magnetic interaction can be treated as a spin-spin coupling with the following Hamiltonian for the dimer

$$\mathcal{H} = -2J\ \underline{S_1} \cdot \underline{S_2}\ ;$$

leading to the eigen values $-J[S'(S'+1) - 2S(S+1)]$, where S is the eigen value of the spin vector of each atom, (i.e. 3/2 for Cr(III)), and S' the total spin of the species, i.e. 3, 2, 1 or 0. Following Kambe[20] and Earnshaw and Lewis,[22] the variation of the atomic susceptibility, χ_A, with temperature is given by

$$\chi_A = \frac{g^2\ N\ \beta^2}{3\ kT} \left\{ \frac{42 + 15\ \exp\ (6x) + 3\ \exp\ (10x)}{7\ +\ 5\ \exp\ (6x)\ +\ 3\ \exp\ (10x)\ +\ \exp\ (12x)} \right\} + N(\alpha)$$

where $x = -J/kT$ and $N(\alpha)$ is the temperature-independent, high-field paramagnetic term. A finite value of θ in the Curie-Weiss equation, $\chi = C/(T + \theta)$, can be related in many cases to the presence of coupling (J).

Values of χ_A were calculated from the experimental data as described by Figgis and Lewis[24]. A tabulation of the experimental quantities may be found elsewhere[17]. A plot of the observed χ_A in the form $1/\chi_A \times 10^{-2}$ versus T for the DBD and SBD is shown in Fig. 4. The line drawn through the points is one calculated from the theoretical variation of $1/\chi_A$ versus T for the given g value of each complex and selected values of

J and $N(\alpha)$. Table III gives the effective magnetic moment (μ_{eff}) at 20°C and the values of J, g and $N(\alpha)$ used in fitting the data to the theoretical equation. The apparent values of θ are included for comparison. Also given are values from the literature for compounds with analogous bridging structures.

From Table III it is seen that the values of J, g, $N(\alpha)$ and θ-for the DBD correspond closely to those found for similar doubly bridged chromium-(III) compounds. For the SBD, the same parameters correspond well to those found for other hydroxy singly bridged chromium(III) species, except for θ. A single oxide bridging group has been shown to produce a strong coupling in the basic rhodo complexes of chromium(III), $(NH_3)_5CrOCr(NH_3)_5^{4+}$,[22,25] and complexes as $Cl_5RuORuCl_5^{4-}$[26], and there is a marked change in the visible-uv spectrum.

A comparison of the magnetic behavior with that of some iron(III) dimers is instructive. The complex having the empirical formula $Fe_2(OH)_2^{4+}$ or Fe_2O^{4+} is well known, but whether the irons are double bridged by hydroxide groups or singly bridged by an oxide ion has been uncertain. Schugar, Walling, Jones and Gray[27] have concluded it has the double hydroxide bridge on the basis of comparison of its magnetic behavior and infrared spectrum with that of iron compounds whose structures are known.

Mulay and Selwood[28] originally reported the dimer to be diamagnetic, but several investigators[27,29,30] have since offered evidence that it is paramagnetic, although weakly so. Máthé and Bakk-Máthé[30] on recalculating Mulay and Selwood's work, report a value of μ_{eff} equal to 3.09 Bohr magnetons per iron for the dimer at 16°C, corresponding to about two and one-half unpaired electrons per iron. This value of μ_{eff} may be questioned because the formation constant, also deduced from the magnetic data by the

Table III

Magnetic Susceptibility Data for Various Chromium(III) Dimers

Complex[b]	μ_{eff} at 20°C (B.M.)	-J/k (°)	g	N(α) x 10⁶ (c.g.s.)	θ	Ref.
$[(phen)_2Cr(OH)_2Cr(phen)_2]I_4 \cdot 4H_2O$	3.67	10	1.99	58	35°	22
$[(gly)_2Cr(OH)_2Cr(gly)_2]H_2O$	3.80	6	2.01	52	20	22
$[(phal)_2Cr(OH)_2Cr(phal)_2]$	3.84	7	2.03	44	30	22
$[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{4+}$ (DBD)	3.74	7.5	1.96	58	27	this work
	3.76	—	—	—	—	a
$[(NH_3)_5CrOCr(NH_3)_5]Br_4$	1.29	—	—	—	—	22
$[(NH_3)_5CrOHCr(NH_3)_5]Br_5$	3.44	20.25	1.94	62	120	22
$[(NH_3)_5CrOHCr(NH_3)_4(H_2O)]Br_5$	3.52	20.7	1.99	56	130	22
$[(NH_3)_5CrOHCr(NH_3)_4(H_2O)]Cl_5$	3.62	20.7	1.99	56	130	22
$[(NH_3)_5CrOHCr(NH_3)_4(OH)]Br_4$	3.50	14	1.91	56	70	22
$[(H_2O)_5CrOHCr(H_2O)_5]^{5+}$ (SBD)	3.48	16	1.96	52	22	this work
$[Cr(H_2O)_6]^{3+}$	3.87	—	—	—	—	a
	3.89	—	1.980	—	—	this work

[a] L. N. Mulay and M. C. Naylor, Advances in the Chemistry of the Coordination Compounds, S. Kirschner, Editor, the MacMillan Co., New York, 1961, p. 520.

[b] The following symbols are used: phen = o-phenanthroline, gly = glycine, phal = phenylalaine.

authors, is considerably larger than reported elsewhere in the literature.[31] A smaller equilibrium constant would give a smaller magnetic moment for the dimer, as Schugar et al[27] showed semi-quantitatively by a recalculation of Mulay and Selwood's data using Milburn and Vosburg's[32] equilibrium values.

Although the number of unpaired electrons is not known accurately, the magnetism of Fe(III) in the doubly bridged dimer appears to be considerably reduced relative to that of the free ion, Fe^{3+}, with five unpaired electrons. This behavior is unlike that of the DBD of Cr(III) where the magnetism per chromium is still nearly the same as for Cr^{3+}.

That coupling reduces appreciably the magnetic moment of the iron dimer is not surprising since two of the unpaired electrons of each iron have orbitals pointing directly at the bridging oxygens. Thus coupling might be expected to be considerably stronger than is the case with Cr(III) where none of the d orbitals of the unpaired electrons point toward the bridging oxygens. Further, in the case of iron dimers linearly bridged by a single O^{2-}, the coupling is strong enough to reduce the magnetism to ca. one unpaired electron per iron,[22,27] as expected from a molecular orbital treatment involving strong π bonding.[33] As pointed out by Schugar et al[27], it is reasonable that the DBD of Fe(III) have a magnetic moment between that of oxide ion bridged dimers, and the uncoupled ions.

Chromium(III) dimers exhibit a behavior similar to those of Fe(III) when bridged by a single oxide ion, as shown by the decamine dimers of Table III, entries 5 and 6.

The following picture thus emerges: For both Fe(III) and Cr(III) dimers linearly bridged by O^{2-} the strong σ and π bonding through the bridge splits energy levels sufficiently to give partial pairing of d electrons involved in these molecular orbitals, thus reducing appreciably the paramagnetism.

Alternatively, one can say that the strong magnetic coupling through the bonding in the bridge leads to large negative J values.

For non-linear, hydroxide bridged species, Fe(III) can have d electrons participating in σ as well as π bonding molecular orbitals involving the bridge. Chromium(III) on the other hand, will have d electrons involved only in π molecular orbitals to the bridging hydroxide. The resulting coupling of spins turns out to be considerably weaker for Cr(III) than for Fe(III).

The J values for the singly bridged dimer are larger than for the doubly bridged species, perhaps because of a more favorable bonding angle for coupling through the bridge in the former case. This result would seem to argue against direct coupling between the chromiums.

Only in the last dozen years has there been evidence reported for a single hydroxide bridged dimer of hydrated Fe^{3+}.[34] From potentiometric measurements of the activity of Fe^{3+} as a function of pH, the formulas and equilibrium constants of various species in solution were deduced. Since at most, only 12 percent of the iron was believed to be in the form of the SBD, the results must be treated with caution.

A more recent study by Nikol'skii et al[35] reports evidence from Mössbauer spectroscopy for the existence of the SBD of Fe^{3+}. Samples of aqueous solutions were frozen rapidly in order to make the measurements. The value of the equilibrium quotient for formation of the SBD of $\sim 3 \times 10^{-2}$ indicates a much higher stability for the SBD of Fe^{3+} than for Cr^{3+}; the value of the formation constant reported is some 5,000 times greater than that for Cr^{3+}. In comparison, the formation constants for the DBD and for the MOH^{2+} species are only some 150 and 20-fold greater, respectively for Fe(III) than for Cr(III).

EXPERIMENTAL

Reagents

A stock solution of chromic perchlorate was prepared by reducing CrO_3 with 30% hydrogen peroxide in the presence of an excess of perchloric acid and was partially neutralized (ca. pH 3) before refluxing by adding $NaHCO_3$ in small amounts and stirring continuously. The refluxed solutions were separated using columns of cation-exchange resin, Dowex AG 50W-X4, 200-400 mesh (Bio Rad Laboratories, Richmond, California).

Sodium perchlorate solution was prepared by treatment of $NaHCO_3$ with a small excess of perchloric acid and then adjusted to pH 6 with sodium hydroxide.

All perchloric acid solutions were prepared by diluting 70% doubly distilled G. F. Smith perchloric acid.

Calcium perchlorate and thorium perchlorate, obtained from G. F. Smith, were used without further purification. All other reagents were reagent grade.

Preparation of the DBD and SBD Species. To obtain sufficient amounts of the DBD, a modification of the method of Ardon and Plane[11] was used. Chromium(II) perchlorate was prepared by passing chromium stock solution through a Jones Reductor. The resulting solution was oxidized by bubbling vigorously with oxygen for a period of 30 minutes. The oxidation product was next applied to a previously prepared column of Dowex 50W-X8, 200-400 mesh, hydrogen ion form, and the chromium species separated by displacement development with a 1.2 $\underline{N}$ solution of thorium perchlorate. Three bands developed on the column. A small green band, seen only in these solutions

and from its spectrum identified as $CrCl^{2+}$, preceded a violet band. The
violet band of chromium(III) monomer represented ca. 10% of the total
chromium. It was followed by a large, dense blue-green band. After
displacement of these bands, some green-colored chromium(III) species
remained on the column, strongly held by the resin. The DBD thus isolated
was used in the freezing point, ESR, and magnetic susceptibility measure-
ments.

The SBD was prepared by a 4- to 5-fold evaporation under vacuum
of a solution of fresh DBD in 2M perchloric acid, and subsequent addition
of this solution to concentrated perchloric acid. Fine crystals of a
small amount of monomeric chromium(III) were thrown down as soon as the
concentrated solutions were mixed.

Equilibrium Studies. Solutions were prepared by treating the chromic
perchlorate stock solution with additional $NaHCO_3$ while stirring. Two
sets of solutions were used, each with an ionic strength of 1.00, maintained
by the addition of suitable amounts of sodium perchlorate: the first with
a chromium concentration of 0.10 M, the second a chromium concentration
of 0.025 M. Temperatures chosen were 67.50 $(\pm.05)°C$, 50.00 $(\pm.05)°C$, and
37.50 $(\pm.05)°C$.

The solutions were contained in 100 cc volumetric flasks placed in a
water bath at the appropriate temperature. When the pH of the solution
was constant for 24 hours, the solutions were left in the bath for a
period of time equivalent to that during which they had already been
equilibrating and the pH checked again. An additional 100 cc of each
solution was refluxed for 24 hours, transferred to a volumetric flask
and diluted to the mark with distilled water, then allowed to come to

equilibrium under the same final conditions in the studies carried out at 50°C.

To test the dependence of the equilibrium quotient on ionic strength, another series of solutions was prepared varying in ionic strength from 0.184 to 2.00, but maintaining the same chromium concentration for those solutions below 1.00 in ionic strength.

The pH of all solutions was measured at the temperature of equilibration against a Beckman pH 4 buffer standardized at the same temperature. The values used for the pH buffer at each temperature were as follows: 4.03 at 37.5°C, 4.08 at 50.0°C and 4.12 at 67.5°C.[36]

For the pH measurements a small insulated copper block was maintained at constant temperature by water from the temperature reservoir circulating through the block. Three wells in the vessel held 100 cc, tall-form rimless beakers fitted with Lucite tops into which three holes were drilled to fit snugly a thermometer, glass electrode, and salt bridge, respectively. The glass electrode was kept at the temperature of the solution to be measured for at least 24 hours prior to measurement.

The equilibrated solutions themselves were quickly quenched by transferring them to small, chilled vessels immersed in an ice-bath. The pH was checked for consistency against a Beckman Research pH meter, calibrated with a chilled 4.00 buffer, all at 0.8°C. Aliquots of the chilled solution were withdrawn by pipet and applied to prepared columns of Dowes 50W-X4 in the hydrogen ion form. Approximately 10% of the column was loaded with chromium species. Elution was carried out with 0.50-0.65M calcium perchlorate. The resin was colorless in the area between the bands of chromium material after a short period of time and as the elution continued,

the separation between the bands increased. Samples were collected in
volumetric flasks of appropriate size and the fractions diluted to the
mark. The spectrum of each fraction was taken and the chromium concentra-
tion determined using the molar extinction coefficients for the various
species reported in this work. If samples of the green polymer were
left over-night on a column in contact with the eluant, a significant
change was observed in the spectrum of the eluted polynuclear species
in the near-uv region.

Freezing Point Depression. Freezing point determinations were carried
out in Dewared cells similar to those described by McMullen and Corbett.[37]
The double-walled cell, to which 10.00 cc of the solution was added, was
cooled by immersion in a bath of ethyl alcohol and dry ice (-78.5°C)
contained in a second Dewar. The solution was stirred by means of a
small Teflon- or glass-coated stirring bar. Temperature was measured by a
Veco thermistor (#32A11) in a small, thin-walled glass well filled with
petroleum ether, in thermal contact with the solution. Resistance measurements
were made using a Leeds and Northrup Wheatstone Bridge (Test Set #5305),
a Honeywell galvanometer (Model 104W1), and a 1.5 volt external battery.
The thermistors used were calibrated with an alcohol thermometer and
checked against a thermocouple to take into account stem-warming.

Electron Spin Resonance. All spectra were taken at room temperature
with a conventional X-band (9000 MHz) ESR apparatus employing various
field modulations. The samples were contained in sealed melting point
capillary tubing, with the exception of the SBD which was contained in a
flat, thin-walled standard cell from Varian. Magnetic field measurements
were made with a proton resonance probe and frequency counter. Line widths

reported refer to the full width at points of maximum slope of the signal and are designated as ΔH. The magnetic field modulation was 100 Hz for the monomer and 500 Hz for the DBD:

Magnetic Susceptibility. Magnetic susceptibility measurements were made with a water-cooled magnet from Spectromagnetic Industries (Model 4-100) and a Mettler balance equipped with a Vernier gauge enabling readings to be made to the nearest 10 micrograms. A simple Guoy tube was calibrated with an aqueous solution of nickel chloride (23.88% nickel by analysis). Four-inch cylindrical pole caps were separated sufficiently to accommodate the tube itself or a hollow Pyrex water thermostated condenser in which the Guoy tube could be freely suspended.

Measurements were first made on each species at room temperature after flushing the solutions with nitrogen. Density was determined by pycnometer. The field was maintained at 8000 gauss for these measurements, using four-inch pole caps at a separation of one inch and a current of 6.2 amperes.

For the second set of measurements, the water-jacketed cavity was used to maintain constant temperature. The Guoy tube suspended in the cavity and was allowed to come to equilibrium with its surrounding for about an hour or until readings with the field off were constant. The temperature of the cavity, assumed to be the same as the temperature of the sample, was determined by hanging a NBS mercury thermometer in the cavity, under the same conditions. The temperature of the input and output water was also measured and found to differ by 1° on the average while the observed temperature of the cavity lay between these two readings. The pole gap was increased to two inches to accomodate the water jacket and

the field was reduced to 6000 gauss at the same amperage (6.2 amperes).
The temperature range covered was limited because of the decomposition
of the dimers at high temperatures.

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Figure 1.   Absorption spectra of chromium(III) species. The ordinate

is the molar absorbance divided by the number of chromiums

per species.

Figure 2.   Energy level scheme for Cr(III) dimer.

Figure 3.   ESR spectra of chromium (III) species. The bump labeled

A in the (c) spectrum is instrumental. The sharp signal

in the (b), (c) and (d) spectra comes from some $Cr(H_2O)_6^{3+}$

in the samples. (The spectrum of the trimer will be

discussed in Paper II of this series.)

Figure 4.   Reciprocal of the magnetic susceptibility plotted versus

the absolute temperature. (The trimer will be discussed

in Paper II of this series.)

Fig. 1

MU-34089

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$$E(S') = -J\left[S'(S'+1) - 2S(S+1)\right]$$

Fig. 2

MU-34085-A

(a) $Cr(H_2O)_6^{3+}$

5.0

5.0

(b) $Cr_2(OH)_2^{4+}$

5.0

5.0

(c) $CrOHCr^{5+}$

A

5.0

5.0

(d) $Cr_3(OH)_4^{5+}$

5.0

5.0

Fig. 3

MU-34086

Fig. 4