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Hydrolytic Polymerization of Chromium(III). 1. Two Dimeric Species

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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 toward the latter only at high acidities, with roughly equal concentrations at 2 M 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.

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 Bjerrum[3] who determined the degree of hydrolysis by measurement of the hydrogen ion concentration with the use of 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[5-8] have reached the same conclusion about the formation of a binuclear complex. More recently, Laswick and Plane[9] and Finholt[10] have exploited the inertness of the chromium(III) hydrolyzed polymers to isolate the individual species with use of 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 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.

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 Figure 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 Figure 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 2 M $HClO_4$. Elsewhere[14] the same equilibrium quotient is evaluated from kinetic

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[1] See, for example, L. G. Sillén, *Q. Rev. Chem. Soc.*, **14**, 147 (1959).
[2] H. Taube, *Chem. Rev.*, **50**, 69 (1952).
[3] N. Bjerrum, Ph.D. Dissertation, Copenhagen, 1908.
[4] L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes", The Chemical Society, London, 1964.
[5] E. Stiasny and D. Balanyi, *Collegium (Darmstadt)*, 86 (1927).
[6] R. Schaal and J. Faucherre, *Bull. Soc. Chim. Fr.*, **14**, 927 (1947).
[7] P. Souchay, *Bull. Soc. Chim. Fr.*, **15**, 143 (1948).
[8] H. T. Hall and H. Eyring, *J. Am. Chem. Soc.*, **72**, 782 (1950).
[9] J. A. Laswick and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3564 (1959).
[10] J. E. Finholt, Ph.D. Thesis, Lawrence Radiation Laboratory Report UCRL-8879, University of California, Berkeley, April 16, 1960.
[11] M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959).
[12] M. Ardon and A. Linenberg, *J. Phys. Chem.*, **65**, 1443 (1961).
[13] R. W. Kolaczkowski and R. A. Plane, *Inorg. Chem.*, **3**, 322 (1964).

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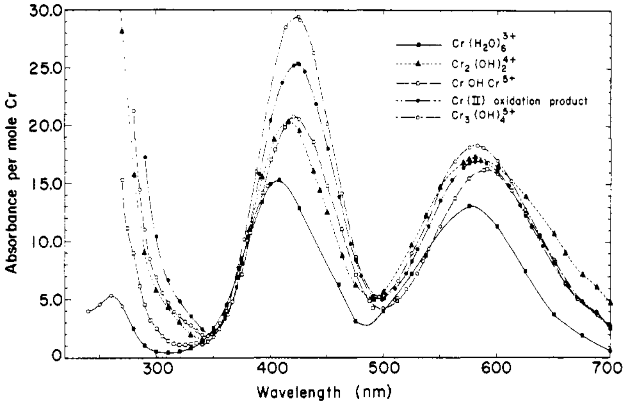
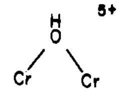


Figure 1. Absorption spectra of chromium(III) species. The ordinate is the molar absorbance divided by the number of chromium atoms per species.

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 °C 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 the absorbance is best fitted by a first-power hydrogen ion dependence, and it is concluded that the intermediate is



with each chromium presumably having five water molecules coordinated to it in addition to the hydroxide group.

So that the nomenclature can be simplified, the doubly bridged dimer (octaaquodi-μ-hydroxo-dichromium(III) ion) and the singly bridged dimer (decaaquo-μ-hydroxo-dichromium(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 Figure 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 displacement 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.

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

μ, M	$10^3[H^+]$, M	$[Cr^{3+}]_0$, M	$10^2 \times [Cr(H_2O)_6^{3+}]$, M	$10^3 \times [Cr_2(OH)_2^{4+}]$, M	10^5Q_{22}, 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

The equilibrium studied[15] was calculated on the basis of

$$2Cr^{3+} + 2H_2O \overset{Q_{22}}{\rightleftharpoons} Cr_2(OH)_2^{4+} + 2H^+$$

where

$$Q_{22} = [Cr_2(OH)_2^{4+}][H^+]^2/[Cr^{3+}]^2$$

and brackets indicate concentrations in moles per liter of solution. The monomer and DBD concentrations were obtained by ion-exchange separation of 1 aliquot of the equilibrated solution. Correction was made for the formation of $CrOH^{2+}$ under each set of conditions with use of 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 fourfold 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 severalfold variation. The value of ΔH for the reaction, determined from a plot of log Q_{22} vs. $1/T$, is 12.7 ± 1.5 kcal and ΔS_{298} is 20 ± 5 eu.

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

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(14) From the third paper of this series.

(15) Results on the trimer are reported in the second paper of this series.

(16) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955).

(17) Sister Gertrude Thompson, C.S.J., Ph.D. Thesis, Lawrence Radiation Laboratory Report UCRL-11410, University of California, Berkeley, June 1964.

The increase in entropy of 20 eu 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/mol and $\Delta S = 28 \pm 5$ eu ($\mu = 1$, 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/mol and $\Delta S = 14.1$ eu ($\mu = 0$, 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/mol and $\Delta S = 25$ eu ($\mu = 0$, 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

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

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 0 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 counterion, 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 °C an equilibrium mixture would contain ca. 80% SBD. Their sample of DBD was prepared in low acid. With a reported rate of cooling of 0.2°/min and a total temperature drop of some 80 °C from room temperature to the freezing point of the eutectic mixture, 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, it was necessary to add a fresh solution of DBD 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 30 min. The solution then contained a mixture of SBD and DBD. The results of these measurements are shown in Table II.

Table II. Freezing Point Lowering of Eutectic of Aqueous Perchloric Acid by SBD and DBD

moles of Cr(III) added/1000 g of 40.7% $HClO_4$	ΔT, deg	$mK_f/\Delta T^c$
	DBD	
0.00711	0.0165	1.91
0.01136	0.0278	1.81
0.01309	0.0284	2.04
0.01421	0.0298	2.11
0.0305	0.0659	2.05
0.0685	0.153	1.98
	SBD and DBD[b]	
0.01136[a]	0.0278	1.81
0.01421[a]	0.0298	2.11
0.0685[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% SBD. [c] m is moles of Cr(III)/kilogram of 40.7% perchloric acid.

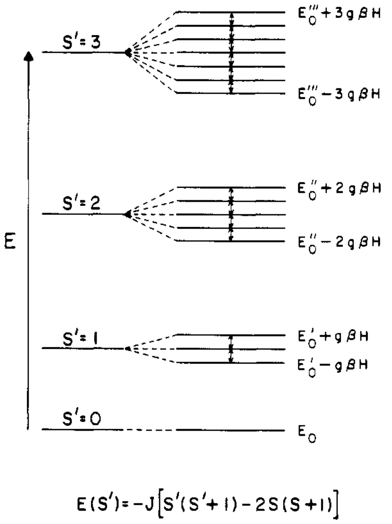

Figure 2. Energy level scheme for Cr(III) dimer.

The experimental freezing point constant, K_f, for the perchloric acid hydrate and ice eutectic is reported to be 4.43 ± 0.31°.[12] Since $mK_f/\Delta T = n$, 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.

In the case of species containing two or more chromium atoms, the Hamiltonian for the monomer[19] should have added to it a term arising from the coupling of the spins of the electrons on adjacent chromium atoms;[20] i.e., for the dimers

$$H' = gH_zS'_z - 2J\mathbf{S}_1\mathbf{S}_2$$

where g, β, and H_z have their usual meaning, J is the exchange coupling constant, $\mathbf{S}_1$ and $\mathbf{S}_2$ are the spin vectors of the two chromium atoms, and S'_z is the z component of S' the total

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[18] R. A. Milburn, *J. Chem. Soc.*, **79**, 537 (1957).

[19] G. Pake, "Paramagnetic Resonance", W. A. Benjamin; New York, 1963.

[20] K. Kambe, *J. Phys. Soc. Jpn.*, **5**, 48 (1950).

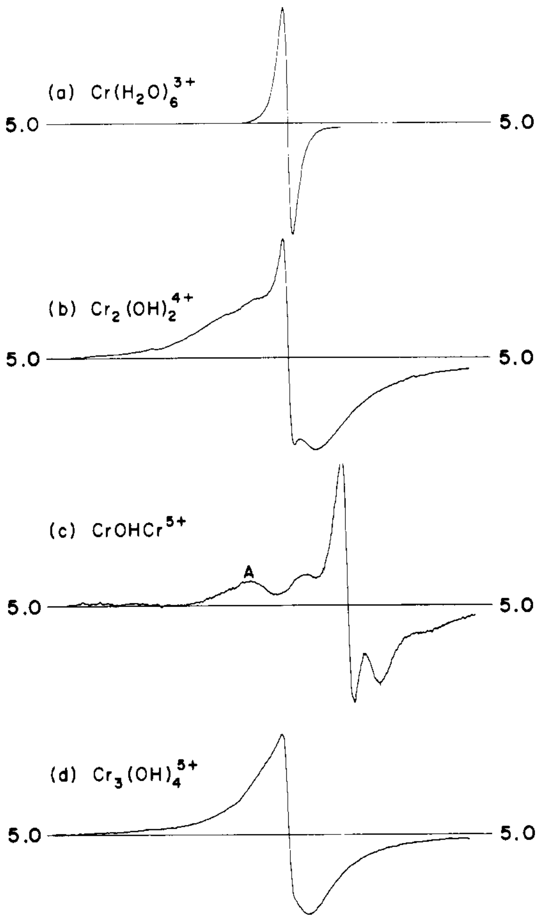

Figure 3. ESR spectra of chromium(III) species. The bump labeled A in the c spectrum is instrumental. The sharp signal in the b–d spectra comes from some $Cr(H_2O)_6{}^{3+}$ in the samples. (The spectrum of the trimer will be discussed in the second paper of this series.)

spin of the species. For a dimer of chromium(III), with $S' = 0–3$ and a multiplicity of $2S' + 1$, the energy level scheme is shown in Figure 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. Figure 3 shows the spectra of the two dimers and the monomer. The presence of some monomer in all samples of polynuclear 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 misleading. In derivative ESR signals such as these, the concentration is proportional to the *square of the width* times the height. The g values determined 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 Figure 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 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, represented by the second term of the Hamiltonian given earlier, which leads to the eigenvalues $-J[S'(S' + 1) - 2S(S + 1)]$, where S is the eigenvalue 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. The variation of the atomic susceptibility, χ_A, with temperature is given by[20,22]

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

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 $(1/\chi_A) \times 10^{-2}$ vs. T for the DBD and SBD is shown in Figure 4. The line drawn through the points is one calculated from the theoretical variation of $1/\chi_A$ vs. 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 such as $Cl_5RuORuCl_5{}^{4-}$,[26] and there is a marked change in the UV–vis spectrum.

A comparison of the magnetic behavior with that of some iron(III) dimers is instructive. The complex having the em-

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(21) C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes", Addison-Wesley, Reading, Massachusetts, 1962.

(22) A. Earnshaw and J. Lewis, *J. Chem. Soc.*, 396 (1961).

(23) C. E. Schaffer and C. K. Jorgensen, *J. Inorg. Nucl. Chem.*, **8**, 143 (1958).

(24) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry", J. Lewis and R. Wilkins, Eds., Interscience, New York, 1960.

(25) W. K. Wilmarth, H. Groff, and S. T. Gustin, *J. Am. Chem. Soc.*, **78**, 2683 (1956).

(26) D. P. Mellor, *Trans. R. Soc. N.Z.*, **77**, 145 (1943).

Table III. Magnetic Susceptibility Data for Various Chromium(III) Dimers

complex[b]	μ_{eff},[c] μ_B	$-J/k$, °C	g	$10^6 N(\alpha)$, cgsu	Θ, °C	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, Ed., Macmillan, New York, 1961, p 520. [b] The following symbols are used: phen = *o*-phenanthroline, gly = glycine, phal = phenylalanine. [c] At 20 °C.

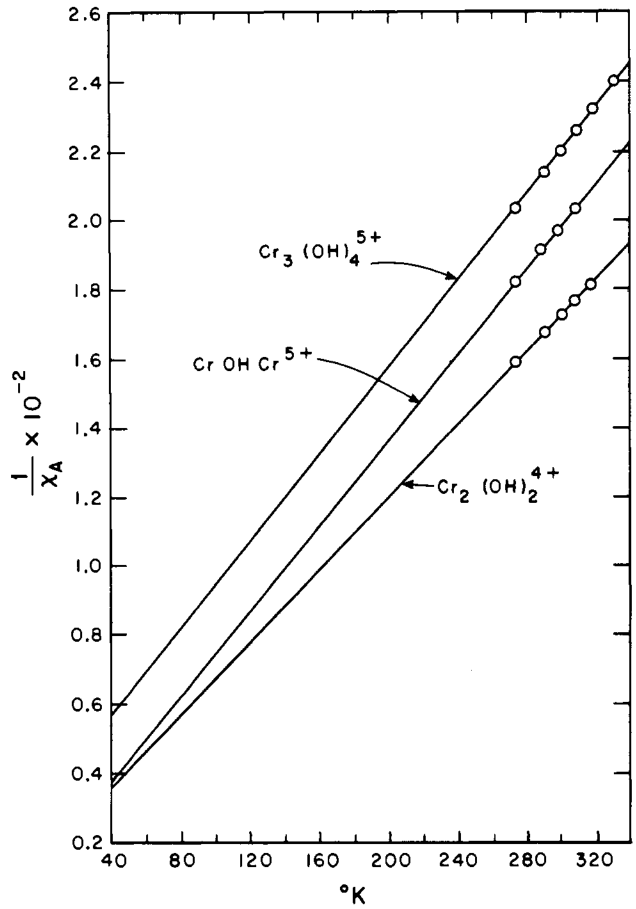

Figure 4. Reciprocal of the magnetic susceptibility plotted vs. the absolute temperature. (The trimer will be discussed in the second paper of this series.)

pirical formula $Fe_2(OH)_2^{4+}$ or Fe_2O^{4+} is well-known, but whether the irons are doubly 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. Mâthé and Bakk-Mâthé,[30] on recalculating Mulay and Selwood's work, report a value of μ_{eff} equal to 3.09 μ_B/iron atom for the dimer at 16 °C, corresponding to about 2.5 unpaired electrons/iron atom. This value of μ_{eff} may be questioned because the formation constant, also deduced from the magnetic data by the 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 semiquantitatively 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 atom 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. 1 unpaired electron/iron atom,[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 nonlinear, 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

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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% 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 5000 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 Section

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 with the use of columns of cation-exchange resin, Dowex AG 50W-X4, 200–400 mesh (Bio-Rad Laboratories, Richmond, CA).

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. So that sufficient amounts of the DBD could be obtained, a modification of the method of Ardon and Plane[11] was used. Chromium(III) 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 min. 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 were separated by displacement development with a 1.2 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 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 measurements.

The SBD was prepared by a 4- to 5-fold evaporation under vacuum of a solution of fresh DBD in 2 M 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 (±0.05), 50.00 (±0.05), and 37.50 (±0.05) °C.

The solutions were contained in 100-cm^3 volumetric flasks placed in a water bath at the appropriate temperature. When the pH of the solution was constant for 24 h, 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 cm^3 of each solution was refluxed for 24 h, transferred to a volumetric flask, diluted to the mark with distilled water, and then allowed to come to equilibrium under the same final conditions in the studies carried out at 50 °C.

So that the dependence of the equilibrium quotient on ionic strength could be tested, 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-cm^3, 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 h 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 Dowex 50W-X4 in the hydrogen ion form. Approximately 10% of the column was loaded with chromium species. Elution was carried out with 0.50–0.65 M 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 concentration determined with use of the molar extinction coefficients for the various species reported in this work. If samples of the green polymer were left overnight 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 Dewar cells similar to those described by McMullen and Corbett.[37] The double-walled cell, to which 10.00 cm^3 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 (no. 32A11) in a small, thin-walled glass well filled with petroleum ether, in thermal contact with the solution.

Electron Spin Resonance. All spectra were taken at room temperature with a conventional X-band (9000 MHz) ESR apparatus. 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. 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 μg. A simple Guoy tube was calibrated with an aqueous solution of nickel chloride (23.88% nickel by analysis). The 4-in. cylindrical pole caps were

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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 G for these measurements, by using 4-in. pole caps at a separation of 1 in. and a current of 6.2 A.

For the second set of measurements, the water-jacketed cavity was used to maintain constant temperature. The Guoy tube, suspended in the cavity, was allowed to come to equilibrium with its surrounding for about 1 h 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 pole gap was increased to 2 in. to accommodate the water jacket, and the field was reduced to 6000 G at the same amperage (6.2 A). The temperature range covered was limited because of the decomposition of the dimers at high temperatures.

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Normal-Coordinate Analyses for the Vibrations of Tetraphenyl- and Tetramethyldithioimidodiphosphinate and the Adamantane-like Cage Structure $Cu^{I}_4S_6$

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Normal-coordinate analyses have been performed for 1:1 metal–ligand models of bis(tetraphenyldithioimidodiphosphinato)manganese(II) and bis(tetramethyldithioimidodiphosphinato)cobalt(II) and for the $Cu^{I}_4S_6$ core of the tris(tetraphenyldithioimidodiphosphinato)tetracopper(I) cation in C_2 and T_d point symmetries, respectively. Results of the calculations support the assignment of ν_{as}(PNP) and ν_s(PNP) to bands near 1210 and 820 cm^{-1}, ν(PC) to bands between 680 and 750 cm^{-1}, ν_{as}(PS) and ν_s(PS) to bands between 500 and 600 cm^{-1}, and ν_{as}(MS) and ν_s(MS) to bands between 240 and 320 cm^{-1}. Bonding stretching force constants show that Co–S bonds in the tetramethyl compound are stronger than Mn–S bonds in the tetraphenyl compound, and this is compensated by a lower K(P–S) value in the Co(II) complex. The lack of infrared and Raman intensity in ν_s(PNP) is explained in terms of opposing σ and π contributions to the dipole moment and polarizability changes during the symmetric PNP stretching vibration. Only in resonance Raman spectra where other contributions to the band intensity are operative was ν_s(PNP) observed. Analysis of the $Cu^{I}_4S_6$ cluster vibrations showed that only weak Cu⋯Cu bonding interactions were present. ν(Cu(I)–S) modes were located between 280 and 170 cm^{-1} in the infrared and Raman spectra. The K(Cu–S) value was about the same magnitude as K(Mn–S) for the bis chelate.

Introduction

Dithioimidodiphosphinates, $SPR_2NR_2PS^-$, where R = phenyl (L) or methyl (L′), coordinate to divalent first-row transition-metal ions to form bis complexes[1] that contain a tetrahedral $M^{II}S_4$ core geometry. The preference for tetrahedral[2,1b] over square-planar geometry, even for the nickel complex, was thought at first to reflect a low ligand field strength with this bidentate sulfur ligand. Yet analyses of ligand field spectra[1a,b] of Mn(II), Fe(II), Co(II), and Ni(II) complexes showed that L^- presented a field of intermediate strength. To clarify the metal–sulfur and chelate ring bonding picture in these chelates, we undertook an infrared–Raman spectral study[1d] and herein present the results of normal-coordinate calculations on several metal dithioimidodiphosphinates.

Measurement of Raman intensities has been useful in studies of molecular structure and bonding, particularly in the estimation of bond orders. In the theory of Raman intensities the mean molecular polarizability, $\bar{\alpha}$, is directly related[3] to the observed intensity of a totally symmetric Raman band. Approximate methods have been devised[4] to express terms in the molecular polarizability derivative as a superposition of principal polarizability components of individual bonds. Bond polarizabilities, $\bar{\alpha}_u$, are related to molecular polarizabilities by the equation

$$\frac{\partial\bar{\alpha}}{\partial Q_i} = \sum_u l_{ui}\frac{\partial\bar{\alpha}_u}{\partial R_u}$$

where l_{ui} is the **L** matrix (eigenvectors for the normal vibrations Q_i) element between internal coordinates R_u and Q_i. The sum is taken over bonds, u. We suggest that further division of bond polarizabilities into two components, σ and π, may be justified in cases where the two contributions occur in opposing directions, i.e., are of opposite sign. One of the apparent anomalies in the vibrational spectra of imidodiphosphinates[1d,5] was the absence of any intensity in the symmetric $P\cdots N\cdots P$ stretching band in either infrared or Raman spectra. Only in resonance Raman spectra was it observed. The reasons for a very small change in polarizability as well as in dipole moment with respect to this normal coordinate are explored in terms of σ and π bonding in the imidodiphosphinate group.

Short Cu⋯Cu distances within several copper cluster compounds have been cited as evidence for some metal–metal bonding.[6] Raman intensities of metal cluster[7] related vibrational bands are expected to depend on the extent of metal–metal interaction. Since Cu⋯Cu distances in the

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