Table III. Relative Energies (kcal/mol) of B_4X_4 Structures

$T_d - D_{4h}$	STO-3G	STO-3G*	MP2/ STO-3G	KBL[b]
B_4H_4	37.9			38.8[c]
B_4F_4	9.8			10.0[d]
Me_4B_4[a]	38.3			
B_4Cl_4	−18.2	−19.0	35.0	

[a] Methyl groups prevent exact symmetry of D_{4h}. [b] Reference 4. [c] STO-3G basis. [d] Double ζ.

dition to this effect, the zero-point energies of the D_{2d} intermediate and the crossing point geometry will also reduce the calculated barrier because at the crossing point one mode becomes imaginary and does not contribute.

Although B_4F_4 and Me_4B_4 are too large to be studied at the same level of theory as that used here for B_4H_4 (~40 h on a VAX 11/780 computer), we find that STO-3G calculations predict T_d ground states for both B_4F_4 and Me_4B_4. The calculations were made using the boron coordinates optimized in B_4H_4 and bond lengths for carbon (1.57 Å) and fluorine (1.293 Å) taken from STO-3G-optimized[15] bond lengths in BH_2CH_3 and BH_2F. The calculated relative energies for B_4H_4 and B_4F_4 compare well with minimal basis set calculations of KBL (Table III). The T_d structure of Me_4B_4 is predicted to be 38.3 kcal/mol more stable than the structure which has coplanar B and C atoms. This last structure has D_{2d} symmetry rather than D_{4h} symmetry because of the hydrogen atoms. Distortions of the methyl groups similar to those seen experimentally[16] for the *tert*-butyl groups in t-Bu_4C_4 are expected to be small or negligible. However, CI corrections should favor the T_d structure.

Our STO-3G energies for B_4Cl_4 indicate[17] that the planar structure is more stable, in contradiction to experiment. However, this basis set is known to be inadequate[18] for third-period elements. Polarization (STO-3G*) does not affect the predicted relative stabilities of the structures (Table III). Correlation correction at the MP2/STO-3G level, however, is sufficient to reverse these stabilities. The T_d structure is now predicted to be 35.0 kcal/mol more stable than the D_{4h} structure. It is known[19] that B_4Cl_4 is nonfluctional over a 200 °C temperature range.

The recent experimental synthesis of t-Bu_4B_4[1] and B_9I_9[20] have shown that back-bonding from halogen to the boron cage does not rationalize the violation of the often useful framework electron count-structural correlation (Wade's rules).[21] This effect is almost absent in t-Bu_4B_4 and weak for B_9I_9.

Conclusion

The rearrangement of T_d–D_{4h}–T_d is predicted to occur with an orbital crossing but *not* as the rate-limiting step. A D_{2d} intermediate is formed with an approximate 8 kcal/mol barrier to the T_d structure. The D_{4d} structure is a transition state 34 kcal/mol higher than the D_{2d} minimum to an equivalent D_{2d} minimum which then rearranges to its equivalent T_d structure. The angle formed with BH and the center of symmetry is 180° for both the D_{4h} and T_d structures but departs significantly in the reduced symmetry of D_{2d}. The effect of relaxing this earlier constraint has made a major change in prediction.

Although the calculations do not predict the energetics of other competing reactions, B_4H_4 (if made) should be tetrahedral and not fluctional. Back-bonding in B_4F_4 favors the planar structure, and the best estimate by KBL predicts the two forms of B_4F_4 to be about isoenergetic. On the other hand, B_4Cl_4 is calculated as most stable in the tetrahedral geometry if electron correlation corrections are included.

Acknowledgment. We wish to thank the National Science Foundation (Grant CHE77-19899) for financial support, and we acknowledge NSF Grant PCM77-11398 for the computational laboratory. We also wish to thank J. A. Pople for making the GAUSSIAN-80 program available to us.

Registry No. B_4H_4, 27174-99-8.

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Hydrolytic Polymerization of Chromium(III). 2. A Trimeric Species

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Received February 4, 1981

With use of an ion-exchange displacement elution, a green species was separated from mixtures of Cr(III) polymers and its absorption spectrum determined. The hydroxides per chromium atom were found to be $^4/_3$, and the charge per chromium atom was shown to be consistent with this value. The degree of polymerization from freezing point depression was close to 3. Measurements are reported for the equilibrium quotient for the formation of the trimer from the monomer. The ESR spectrum and magnetic susceptibility were determined, and the results are discussed in terms of possible structures.

Laswick and Plane[2] reported the isolation of a green polymeric species from refluxed solutions of chromium(III) perchlorate by ion-exchange techniques, using a 0.2 M solution of $La(ClO_4)_3$ as eluant. Their investigation showed the green species to be a more highly polymerized form than a second species, later identified as a dimer,[3-5] also isolated from the same refluxed solutions. Their conclusion was based upon the observed elution behavior: the green species is more tightly held than the dimeric species and is far more sensitive to eluant

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concentration. A spectrum of the green polynuclear species was also reported.

Sannikov, Krylov, and Vinogradov[6] have reported spectrophotometric evidence for the doubly bridged dimer, two tetramers ($Cr_4(OH)_4^{8+}$ and $Cr_4(OH)_6^{4+}$), but no trimer. Since the identification depended on curve resolution of the spectra of equilibrium mixtures—a hazardous undertaking considering the similarity in spectra of Cr(III) species (see Figure 1 of paper 1)—the conclusions are open to question. The equilibrium amounts of doubly bridged dimer reported are more than 1 order of magnitude higher than estimated from the results of paper 1.

In the present work the green species was isolated in solution as the perchlorate salt except for the presence of a small amount of perchloric acid. Such pure samples were then used to establish the number of hydroxide (or oxide) ions per chromium by two methods. The degree of polymerization was determined from the freezing point depression of the perchloric acid eutectic and confirmed with equilibrium measurements for the formation from the monomer. The pure solutions were used to measure the following properties of the trimer: absorption spectrum, magnetic susceptibility, and electron spin resonance.

Experimental Section

Chromium(III) solutions containing the green species as well as other polymers and the monomer were prepared either by refluxing $Cr(NO_3)_3$ solutions or by dissolving metallic chromium in perchloric acid to give a high concentration of chromous ion, which was then oxidized to Cr(III) by bubbling oxygen through the solution.[7] The latter method gave a better yield of the green species and higher polymers.

Isolation of the green polynuclear species was carried out[8,9] by a displacement development from the ion-exchange column using thorium(IV) perchlorate as the displacing agent. Two different types of resin proved successful in this type of separation: a colloidal form of Dowex 50W-X12 (no longer available) and Dowex 50W-X2 or X4, 200–400 mesh, both in the hydrogen ion form. Use of this method allowed the separation and collection of pure, concentrated samples of individual chromium(III) species uncontaminated by any cationic species other than hydrogen ion—a distinct advantage over simple elution separation.

Isolated, pure fractions of the green species were used to determine the number of hydroxide groups per chromium atom by the following method. After the solution was analyzed for concentration of free hydrogen ion and for chromium, it was made alkaline by adding a known amount of sodium hydroxide and oxidized by heating with an excess of 30% hydrogen peroxide. The alkali content was then determined by a potentiometric titration with standardized HCl solution to an endpoint of about pH 4.2. The number of hydroxide groups per chromium atom can be calculated from the expression

$$OH^-/Cr = \frac{4C + H_1 + H_2 - B}{C}$$

where C is the number of gram-atoms of chromium, B the equivalents of base added, H_1 the equivalents of acid used in the titration, and H_2 the equivalents of free hydrogen ion present initially. The net reaction for the oxidation of the polymer and subsequent acidification is given by

$$(2/x)Cr_x(OH)_y^{3x-y} + 3H_2O_2 + (8 - 2y/x)OH^- = Cr_2O_7^{2-} + 7H_2O$$

Freezing point lowering experiments were made with fresh samples of the green species prepared from refluxed chromium(III) perchlorate solutions using Dowex 50W-X2. The procedure for measurement is described in paper 1.

The equilibrium measurements were made as described for the dimer in paper 1, and in fact, the same solutions were usually analyzed for both dimer and trimer. The trimer was the last species eluted. Some additional chromium(III) species were not eluted from the column by the $Ca(ClO_4)_2$ solution and are presumed to be higher polymers.

Magnetic susceptibility and ESR measurements were made as described in paper 1. Pure solutions of trimer were prepared from a refluxed solution of 1.0 M chromium(III) perchlorate of pH ~3.5 with Dowex 50W-X4, 200–400 mesh, and displacement by 0.25 M thorium perchlorate.

Table I. Hydroxide Ions per Chromium Atom for the Green Species

samp source	Cr, mg-atom	init free H^+, mequiv	added OH^-, mequiv	H^+ used in titration, mequiv	OH^-/Cr atom
hydrolyzed $Cr(ClO_4)_3$	0.487	0.157	2.00	0.567	1.38 ± 0.05
hydrolyzed $Cr(NO_3)_3$	0.144	0.070	1.008	0.550	1.31 ± 0.05

Results and Discussion

Absorption Spectrum. The visible and ultraviolet absorption spectrum of the green species is shown in Figure 1 of paper 1 as that of $Cr_3(OH)_4^{5+}$. The general appearance is the same as reported by Laswick and Plane,[2] but the absorbance per mole of chromium(III) is uniformly lower in the present results by about 7%. The striking similarity of the spectra of all chromium species of Figure 1 of paper 1 indicates little change in structure and probably argues for H_2O or bent OH^- bridges as coordinating ligands in all cases.

Hydroxides per Chromium Atom. The experimental results for the determination of the hydroxides per chromium atom of the green polymer, i.e., y/x in the formula $Cr_x(OH)_y^{3x-y}$, are presented in Table I. Columns 2, 3, 4, and 5 correspond to C, H_2, B, and H_1, respectively, of the Experimental Section. The uncertainty is an estimate of the experimental accuracy. The data lead to an average value of 1.35, which is close to $^4/_3$. The result would be consistent with a trimer containing four hydroxide groups or a multiple of this composition.

Charge per Chromium Atom. Two methods were tried. In method 1 the procedure of Cady and Connick[10] was used in which the concentration of chromium in gram-atoms per liter was measured for the green solution as it came off the column in its preparation by displacement elution. The anion concentration of this solution, assumed to be the same as that of the displacement solution of $Th(ClO_4)_4$, was determined by running the displacement solution into a column in the hydrogen ion form and titrating aliquots of the eluted solution for hydrogen ion. The free hydrogen ion concentration in the green species solution was determined by pH measurement. The results can be expressed as

$$\text{charge/chromium atom} = \frac{a - [H^+]}{[Cr]}$$

where a is the total anion charge concentration in the eluted green solution in equivalents per liter, $[H^+]$ is the free hydrogen in concentration, and [Cr] is the chromium concentration in gram-atoms per liter.

In method 2 an aliquot of the pure green solution was added to a column of resin in the hydrogen ion form, and the hydrogen ions displaced were washed out with water and titrated to give the equivalents of charge per liter in the aliquot. The

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Table II. Charge per Chromium Atom of the Green Species

samp	method	tot charge concn, equiv/L	pH	$[H^+]$, M	[Cr], g-atom/L	charge/Cr atom
1	1	1.100	1.72[a]	0.194	0.599	1.51 ± 0.04
2	1	1.100	1.72[a]	0.194	0.591	1.53 ± 0.04
3	1	1.100	1.72[a]	0.194	0.607	1.49 ± 0.04
2	2	1.211	1.72[a]	0.194	0.591	1.72 ± 0.04
3	2	0.1274	1.72	0.0197	0.0617	1.74 ± 0.04

[a] pH is of the sample diluted 1.016 to 10.00 mL. The hydrogen ion concentration was calculated from the pH measurement by dividing by an empirical factor of 0.97 determined for solutions of chromic nitrate of approximately the same total perchlorate ion concentration.[8]

chromium concentration in gram-atoms per liter and the free hydrogen ion concentration were determined as before. The same formula as for method 1 applies. Results are shown in Table II.

Method 1 yields lower results for the charge per Cr atom than method 2. The second method was tried because of evidence[8] that the green species associates some perchlorate ion with it in the resin. In method 2 any such loosely bound ClO_4^- would be washed out by the water, thus yielding the charge per chromium resulting from the chromium and hydroxide ions only in the species. The average value of 1.73 positive charges/chromium is reasonably consistent with the hydroxides per chromium results determined earlier. For the formula $Cr_x(OH)_y^{+3x-y}$ a value of $y/x = {}^4/_3$ yields ${}^5/_3 = 1.67$ for $(3x - y)/x$, the charge per chromium atom. If consideration is restricted to a trimer, the method 2 results are consistent only with a charge per chromium atom of ${}^5/_3$.

In this and the previous determination of the formula, no distinction can be made between oxide ions and twice as many hydroxide ions. Hydroxide ions have been used because the results are simple to express and because the spectrum and considerations of acidity constants make it likely that only hydroxide ions are involved.

While a comparison of the results of methods 1 and 2 gives strong evidence for the association of perchlorate ion with the green polymer in the resin, these results give no information about such a possible association in the aqueous solution.

Attempts[8] to determine the charge per species by the method of Connick and Cady[10] yielded a value of only ca. 3.6 instead of a multiple of 5, presumably because of perchlorate ion association with the green species in the resin, although activity coefficient problems may have been greater than expected.

Degree of Polymerization from Freezing Point Lowering. Since the charge per species determination by ion exchange failed, the degree of polymerization was investigated directly by the lowering of the freezing point of a eutectic mixture of water and perchloric acid on the addition of the green species.[3,11,12] Since the solution of the green species contained only perchlorate anions, a little hydrogen ion, water, and the green species, the freezing point lowering responds only to the added foreign species, i.e., the green polymer. Ardon and Linenberg[3] report the molar freezing point constant for a number of metal perchlorates to be $K_f = 4.43°$ mol^{-1} kg^{-1} eutectic mixture, with an uncertainty of 7%.

The results are given in Table III where it is seen that the value of $mK_f/\Delta T$, which corresponds to the number of chromium atoms per green species, is 3; therefore the polymer is a trimer. From the earlier results it contains four hydroxides and is $Cr_3(OH)_4^{5+}$. From here on we will refer to it as the trimer, rather than the green species.

Table III. Cryoscopy of the Trinuclear Species

mol Cr(III) added/kg eutectic mixture	ΔT, deg	$mK_f/\Delta T$
0.00616	0.0090	3.03
0.0124	0.0184	2.99
0.0284	0.0423	2.97
0.0455	0.0670	3.01

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

Equilibrium Measurements. Values of the equilibrium quotient for the formation of the trimer from the monomer are of importance in assessing its stability and understanding its role in the chemistry of Cr(III). For the calculation of the quotient, the following equilibrium was used:

$$3Cr^{3+} + 4H_2O \overset{Q_{34}}{\rightleftharpoons} Cr_3(OH)_4^{5+} + 4H^+$$

where $Q_{34} = [Cr_3(OH)_4^{5+}][H^+]^4/[Cr^{3+}]^3$. Correction for the formation of $CrOH^{2+}$ according to the equation

$$Cr^{3+} + H_2O \overset{Q_{11}}{\rightleftharpoons} CrOH^{2+} + H^+$$

was made by using values for Q_{11} obtained from Postmus and King's[13] hydrolysis measurements of chromium(III) perchlorate solutions at an ionic strength of 0.034 M and corrected to the desired ionic strength by using ionic strength dependence data for the first hydrolysis of Fe^{3+} in sodium perchlorate solutions at 25 °C.[14]

The experimental results are given in Table IV. At constant ionic strength, there is no systematic variation in Q_{34} as the initial chromium and the hydrogen ion concentrations were varied as much as a factor of 4, although the constancy of Q_{34} leaves much to be desired. This irreproducibility arises in part from the high powers of hydrogen ion and chromic ion concentrations entering into the calculation as well as from the irreproducibility of the analysis for Cr^{3+} and trimer by the ion-exchange separation. An error of 0.04 pH units changes Q_{34} by nearly a factor of 1.5.

The data appear to show an increase in Q_{34} with ionic strength between 0.2 and 2 M. While the Debye–Hückel theory is not applicable for these high ionic strengths, it may be noted that the limiting law gives a dependence of the same sign and probably somewhat greater slope, as is often the case.

From average values of Q_{34} at ionic strength unity in Table IV one estimates ΔH to be approximately 23 kcal and ΔS at 25 °C to be about 75 eu. The entropy increase may result from the following factors: (1) there are eight fewer water molecules ordered in the primary coordination sphere of the three metal ions, (2) the concentration of positive charge of the three chromic ions has been partly compensated for by the dispersal of four positive hydrogen ions, and (3) the +5 charge of the trimer is spread over a large volume and therefore is not nearly as effective as that of a monatomic ion in ordering solvent water.

Magnetic Susceptibility and ESR Measurements. The magnetic susceptibility gives information on the intensity of magnetic interaction between neighboring chromium atoms in the polymer and therefore potentially contains structural and bonding information. Results for the trimer are shown in Table V along with the effective magnetic moment in Bohr magnetons. Values of χ_A were calculated from experimental data as described in paper 1.

Although the magnetic properties of several dimeric complexes of chromium(III), bridged by either oxide or hydroxide groups, have been investigated,[15-17] only one trimeric species

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Table IV. Equilibrium Quotient for the Formation of $Cr_3(OH)_4^{5+}$

μ, M	$10^3 \times$ [H^+], M	$10^2 \times$ $[Cr^{3+}]_0$,[b] M	$10^2 \times$ [$Cr(H_2O)_6^{3+}$], M	$10^3 \times$ [$Cr_3(OH)_4^{5+}$], M	$10^8 Q_{34}$
			67.5 °C		
0.201	4.5	2.94	1.32	1.94[a]	35[a]
1.00	5.7	2.50	1.32	1.93	89
1.00	6.5	10.0	2.97	7.7	53 } av 76
1.00	6.6	2.50	1.48	1.85	108
1.00	25.0	10.4	8.4	0.82[a]	54[a]
2.00	18.5	20.0	13.1	16.1	84
2.00	20.9	29.5	14.7	27.7	167
			50.0 °C		
0.184	3.78	2.50	1.61	1.06[a]	5.2[a]
0.74	7.4	10.0	6.7	4.30[a]	4.3[a]
1.00	7.6	10.0	6.4	6.6	8.4
1.00	7.7	2.60	2.29	0.173	5.1
1.00	9.1	2.60	2.38	0.192	9.8
1.00	9.9	10.0	5.7	5.5	29 } av 14, omitting next to last expt
1.00	11.5	10.4	8.6	3.32	9.1
1.00	12.0	10.4	9.2	1.21	3.2
1.00	15.1	10.4	8.9	2.76	20
			37.5 °C		
0.185	2.35	2.50	1.59	1.30	0.99
0.74	6.7	10.4	7.3	5.6	2.9
1.00	2.62	2.50	1.44	1.64	2.6
1.00	5.9	10.0	6.6	8.0	3.4 } av 2.9
1.00	5.9	10.0	6.3	5.8	2.8

[a] Some of the green trimer may not have been removed from the column in the analysis and therefore these values may be somewhat low. [b] Total chromium concentration in the equilibrated solution.

Table V. Magnetic Susceptibility

T, °C	$10^6 \chi_A$	μ_{eff}, μ_B
274.0	4920	3.29
290.2	4681	3.30
300.0	4543	3.30
308.7	4425	3.31
318.4	4309	3.31
329.9	4158	3.30

has been extensively studied, $[Cr_3O(CH_3CO_2)_6(H_2O)_3]^+$. It is best described as an equilateral triangle of chromium(III) atoms surrounding an O^{2-} and with O–C–O links between the Cr atoms.[18] The J/k value reported is −10.4° and μ_{eff} at room temperature in solution is 3.37 μ_B.[19] A further example of a chromium(III) complex whose magnetic properties have been examined is $[Cr_4(OH)_6(en)_6]^{6+}$, a planar rhomboid of chromium atoms held together by four bridging hydroxo groups and with two of the opposing chromiums bridged by an additional pair of hydroxides.[20,21] The two values of J/k equal to −10 and −20.5° correspond to coupling in the rhomboid and between the chromiums bridged by the additional pair of hydroxides, respectively.

In the complex reported here, the bridging groups were assumed to be hydroxide groups since their presence has been established for both of the dimeric species.[5] Two different arrangements of chromium(III) atoms have been postulated for trimeric species: an equilateral triangle with the chromium atoms at the vertices or a linear array of chromium atoms (see

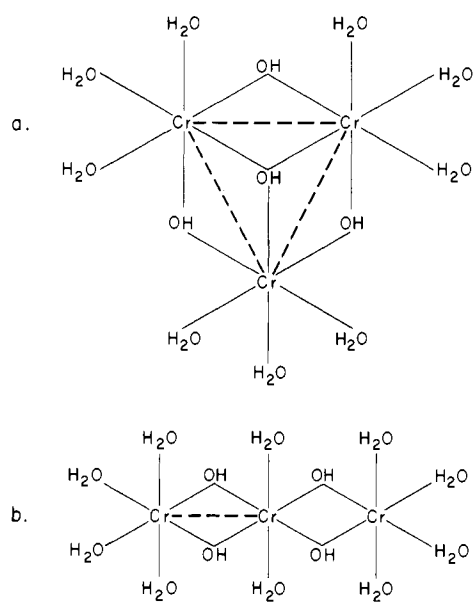

Figure 1. Possible structures of the chromium(III) trimer: (a) the symmetric triangular structure; (b) the linear structure.

Figure 1). For the first structure, the Hamiltonian, if Kambe's general procedure is followed, as all other treatments whose J values are reported do, is given by

$$H_j = -2(J_{12}S_1 \cdot S_2 + J_{23}S_2 \cdot S_3 + J_{31}S_1 \cdot S_3)$$

where J_{ij}'s and the S_i's are equal since the atoms composing the system are equivalent. The energy levels are $-J[S'(S'+1) - 3S(S+1)]$ where S' is the total spin and S the spin of one chromium, i.e., $^3/_2$. The expression for the variation of atomic susceptibility with temperature is then given by eq 1,

$$\chi_A = (g^2N\beta^2/12kT)\{[2 + 40\exp(-3x) + 105\exp(-8x) + 168\exp(-15x) + 165\exp(-24x)]/[2 + 8\exp(-3x) + 9\exp(-8x) + 8\exp(-15x) + 5\exp(-24x)]\} + N(\alpha) \quad (1)$$

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where $x = -J/kT$, g is the spectroscopic splitting factor, and $N(\alpha)$ is the temperature-independent, high-field paramagnetic factor. For the second structure (Figure 1b), if it is assumed that the exchange integral between the central and end chromium atoms is the same for either end of the complex and the exchange integral between the end chromiums is zero, the energy states become

$$-J\{S'(S'+1) - S(S+1) - S^*(S^*+1)\}$$

where $S^* = S_1 + S_3 = 3, 2, 1$, and 0, $S' = S_1 + S_2 + S_3 = {}^9/_2, {}^7/_2, {}^5/_2, {}^3/_2$, and ${}^1/_2$, and the central chromium is numbered 2. The magnetic susceptibility is given by eq 2. Independent

$$\chi_A = (g^2N\beta^2/12kT)\{165\exp(-21x) + 84[\exp(-12x) + \exp(-18x)] + 35[\exp(-5x) + \exp(-11x) + \exp(-15x)] + 10[1 + \exp(-6x) + \exp(-10x) + \exp(-12x)] + \exp(-7x) + \exp(-3x)\}/\{5\exp(-21x) + 4[\exp(-12x) + \exp(-18x)] + 3[\exp(-5x) + \exp(-11x) + \exp(-15x)] + 2[1 + \exp(-6x) + \exp(-10x) + \exp(-12x)] + \exp(-7x) + \exp(-3x)]\} + N(\alpha) \quad (2)$$

measurements of the g value (1.942) of the trimer were carried out by ESR (paper 1, Figure 3d), and thus J and $N(\alpha)$ are the only parameters to be fitted. In the fitting $N(\alpha)$ was assumed to be zero because it is generally small for Cr(III)[15] and has a minor effect on the fitting. The experimental $1/\chi_A$ values, plotted in paper 1, Figure 4 as a function of temperature, lie on a good straight line. The slope of this line, however, is appreciably greater than the theoretical line calculated from either the symmetric triangle model or the linear model by about 19% in both cases. The reason for this discrepancy is not apparent. If the theoretical curves are made to pass through about the middle temperature of the data, values of J/k of −16 and −22° are found for the symmetric triangle and the linear models, respectively. The fit does not help to distinguish between the two structures.[23]

Because of the similarity[24] of the spectrum to that of $Cr(H_2O)_6^{3+}$ (paper 1, Figure 1) and the relatively small value of $-J/k$[25] it is likely that the chromiums are not connected by linear oxide bridges but rather by bent oxide or hydroxide bridges.[15] From the empirical formula, acidity considerations, and symmetry of structures, it is likely that only OH^- groups would be present in the two structures of Figure 1. The value of $-J/k = 22°$ for the linear structure seems rather large compared to values of 6–10° in double-hydroxide-bridged dimers (except for the tetramer[20,21]). It is more difficult to predict a $-J/k$ value for the symmetric triangular structure of Figure 2a of paper 1, but the experimental value of 16° would appear possible.

Acknowledgment. The original research was supported by the U.S. Atomic Energy Commission, and present research is supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract number W-7405-ENG-48.

Registry No. $Cr_3(OH)_4(OH_2)_{10}$, 60938-70-7; $Cr_3(OH)_4(OH_2)_9$, 78939-63-6.

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Kinetic Studies on the Oxidation of Trimeric Aquomolybdenum(IV)†

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Received April 9, 1981

Oxidations of the Mo(IV) aquo trimer, $Mo_3O_4^{4+}$, with $IrCl_6^{2-}$ and $Fe(phen)_3^{3+}$ have been studied under the conditions $[H^+] = 0.6$–2.0 M and $I = 2.0$ M ($LiClO_4$). With Mo^{IV}_3 in large excess, the $IrCl_6^{2-}$ reaction can be expressed as $2Mo^{IV}_3 + 6Ir^{IV} \rightarrow 3Mo^{V}_2 + 6Ir^{III}$, and the initial step $Mo^{IV}_3 + IrCl_6^{2-}$ is rate determining. Second-order rate constants k_{Ir} are dependent on $[H^+]$: $k_{Ir} = k_{-1}[H^+]^{-1}$, where at 25 °C $k_{-1} = 1.36$ s^{-1}, $\Delta H^* = 14.1$ kcal mol^{-1}, and $\Delta S^* = -9.6$ cal K^{-1} mol^{-1}. An alternative stoichiometry $Mo^{IV}_3 + 4Ir^{IV} \rightarrow Mo^{V}_2 + Mo^{VI} + 4Ir^{III}$ cannot be entirely ruled out, and at nearly equivalent amounts of reactants the slower oxidation of Mo^{V}_2 to Mo^{VI} contributes. With $Fe(phen)_3^{3+}$ a different reactivity pattern is observed in that oxidation of Mo^{V}_2 is more rapid than that of Mo^{IV}_3, and the equation $Mo^{IV}_3 + 6Fe(phen)_3^{3+} \rightarrow 3Mo^{VI} + 6Fe(phen)_3^{2+}$ applies. This different behavior is accounted for by the reaction of $Fe(phen)_3^{3+}$ occurring exclusively by an outer-sphere mechanism, whereas $IrCl_6^{2-}$ can react inner sphere. The initial step, $Mo^{IV}_3 + Fe(phen)_3^{3+}$, is again rate determining and at 25 °C k_{-1} for the $[H^+]^{-1}$-dependent path is 0.53 s^{-1}, $I = 2.0$ M. No evidence was obtained for stable trimeric mixed-oxidation-state species as product(s) of the oxidation of Mo^{IV}_3. The complex $Co(C_2O_4)_3^{3-}$ does not oxidize Mo^{IV}_3, whereas (as reported elsewhere) oxidation of aquo Mo^{III} and Mo^{III}_2 through to Mo^{V}_2 is rapid. It is concluded that oxidation of monomeric and/or dimeric Mo(IV) occurs more readily than that of the trimer. No oxidation of Mo^{IV}_3 by the two-electron oxidant $PtCl_6^{2-}$ is observed.

Introduction

The aim in this and related studies is a better understanding of the redox solution chemistry of aquomolybdenum ions. Studies on aquo ions are generally regarded as a point of reference indicating the behavior expected of a paticular oxidation state. In the case of molybdenum the aquo ions are not always simple monomeric species, and the versatility observed is quite striking.[1] Known ions include for Mo(III) the monomer, $Mo(H_2O)_6^{3+}$,[2,3] and the aquo dimer, here written as Mo^{III}_2.[4] Recent work by Murmann and Shelton,[5] following earlier crystallographic studies by Cotton and co-workers with

† No reprints available.

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