[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

The Structures and Properties of the Rhodo and Erythro Complex Compounds of Chromium[1]

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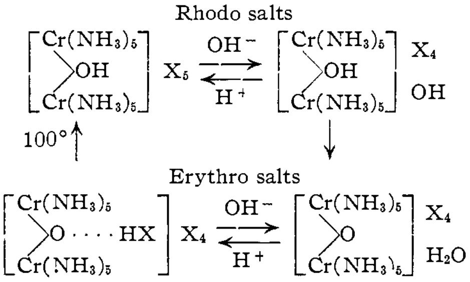
A reinvestigation has been made of the analytical data and degradation reactions of the rhodo and erythro binuclear chromium(III) ammine complexes. This work, combined with acidity constant and magnetic susceptibility measurements, has led to a reformulation of the structures. Unlike the other binuclear ions which were studied, the basic rhodo ion has magnetic properties quite unlike the mononuclear chromium complexes. It has a limiting high temperature magnetic susceptibility at 100° corresponding to approximately one unpaired electron on each chromic ion; at lower temperatures an approach to complete pairing of all electrons within the binuclear unit is achieved. The magnetic susceptibility of the basic rhodo ion is explicable if the three non-bonding electrons are confined to two orbitals. This restriction is most easily understood if it is assumed that, in addition to the six octahedral bonds, each chromic ion forms π-bonds with the bridging oxygen atom. In addition to its unusual magnetic properties, the basic rhodo ion possesses a hydrolytic reactivity very much greater than structurally similar mononuclear compounds. However, this extreme reactivity pertains only to the first stage of the hydrolysis; subsequent replacement of ammonia by water proceeds at a normal rate.

The rhodo and erythro complex compounds of chromium(III) were first reported by Jorgensen in 1882; on the basis of his analytical data the two series of compounds were presumed to be isomeric.[2] Werner,[3] in a later attempt to explain this isomerism, proposed the structures



Rhodo salts

$$\left[\begin{array}{l}\mathrm{Cr(NH_3)_5}\\ \quad\mathrm{>OH}\\ \mathrm{Cr(NH_3)_5}\end{array}\right]\mathrm{X_5}\ \underset{\mathrm{H^+}}{\overset{\mathrm{OH^-}}{\rightleftarrows}}\ \left[\begin{array}{l}\mathrm{Cr(NH_3)_5}\\ \quad\mathrm{>OH}\\ \mathrm{Cr(NH_3)_5}\end{array}\right]\begin{array}{l}\mathrm{X_4}\\ \mathrm{OH}\end{array}$$

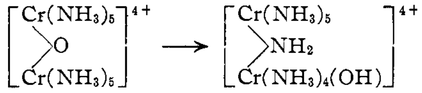
$$100^\circ\uparrow \qquad\qquad \downarrow$$

Erythro salts

$$\left[\begin{array}{l}\mathrm{Cr(NH_3)_5}\\ \quad\mathrm{>O\cdots HX}\\ \mathrm{Cr(NH_3)_5}\end{array}\right]\mathrm{X_4}\ \underset{\mathrm{H^+}}{\overset{\mathrm{OH^-}}{\rightleftarrows}}\ \left[\begin{array}{l}\mathrm{Cr(NH_3)_5}\\ \quad\mathrm{>O}\\ \mathrm{Cr(NH_3)_5}\end{array}\right]\begin{array}{l}\mathrm{X_4}\\ \mathrm{H_2O}\end{array}$$

Although the distinctions in type of bonding implied by the formulas are no longer meaningful, the diagram serves the useful purpose of summarizing the results of Jorgensen's rather extensive observations. The acid–base reactions indicated by the horizontal arrows are rapidly reversible, but if the blue solutions of the basic rhodo ion are allowed to stand at room temperature for a few minutes a color change to carmine serves as visual evidence that the transformation to the erythro series has been completed. The solid phase transformation back to the rhodo series was reported by Jorgensen to be quantitative after 24 hours heating at 100°, but, as we shall show below, other products are also formed under these conditions.

In 1937 Jensen[4] reinvestigated this over-all problem. He found, using the X-ray powder pattern technique, that the solid rhodo and erythro acid bromides were isomorphous. Recognizing that Werner's formulation, based on the distinction between primary and secondary valence, was quite inadequate, he suggested that the alkaline conversion to the erythro series involved the following molecular rearrangement

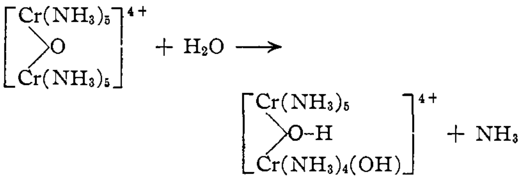


$$\left[\begin{array}{l}\mathrm{Cr(NH_3)_5}\\ \quad\mathrm{>O}\\ \mathrm{Cr(NH_3)_5}\end{array}\right]^{4+}\longrightarrow\left[\begin{array}{l}\mathrm{Cr(NH_3)_5}\\ \quad\mathrm{>NH_2}\\ \mathrm{Cr(NH_3)_4(OH)}\end{array}\right]^{4+}$$

The original purpose of our research was to verify this choice of structures and to investigate in more detail the nature of these molecular rearrangements. During the course of the work it was discovered that the rhodo and erythro ions are not isomeric. The present paper is largely concerned with a correct reassignment of structures, but some of the unique chemical and physical properties of the binuclear ions will be considered, since they have direct bearing upon the structural problem.

Results and Discussion

The Structure of the Rhodo and Erythro Ions.—The simple preparative methods and the complete agreement as to color changes, relative acidities and chromium and halogen analysis leave little doubt that the compounds we have been studying are identical with those prepared by Jorgensen and later by Jensen. In the case of the rhodo salts our nitrogen analysis also agrees with that reported by Jorgensen, but both Dumas and Kjeldahl techniques showed that the erythro ion contains only nine nitrogen atoms.[5] Examination of the mother liquor after completion of the alkaline rhodo–erythro transformation confirmed the analytical results and established the fact that the reaction is simply an exceptionally rapid hydrolytic replacement of a single ammonia ligand.



$$\left[\begin{array}{l}\mathrm{Cr(NH_3)_5}\\ \quad\mathrm{>O}\\ \mathrm{Cr(NH_3)_5}\end{array}\right]^{4+}+\mathrm{H_2O}\longrightarrow\left[\begin{array}{l}\mathrm{Cr(NH_3)_5}\\ \quad\mathrm{>O{-}H}\\ \mathrm{Cr(NH_3)_4(OH)}\end{array}\right]^{4+}+\mathrm{NH_3}\qquad(1)$$

In addition to the conflicting analytical data, two of the reactions which have been reported would have been inconsistent with our formula for the erythro ion. First, there was the statement that

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[1] This investigation was supported by a grant from the United States Office of Naval Research under Task Order IV, Contract No. N6onr-238. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] S. M. Jorgensen, *J. prakt. Chem.*, **25**, 321, 398 (1882).

[3] A. Werner, "Neuere Anschauungen der Anorganischen Chemie," 3rd ed., Friedr. Vieweg and Sohn, Braunschweig, Germany, 1913, pp. 288–289.

[4] K. A. Jensen, *Z. anorg. Chem.*, **232**, 257 (1937).

[5] A careful review of the earlier papers reveals only two instances in which Jorgensen reported a nitrogen analysis for an erythro compound; in one of these cases the nitrogen analysis was appreciably low. Jensen analyzed for chromium and bromine only, and since replacement of an ammonia molecule by water can be detected only by nitrogen analysis, his work has no bearing on this point.

the acidic erythro bromide could be converted quantitatively to the acidic erythro bromide by vacuum heating.[2] Secondly, it was claimed that only bromopentamminechromic bromide was formed in the cleavage of the erythro ion with concentrated hydrobromic acid.[2] Repetition of the experiments did produce the substances which had previously been isolated, but the yields were far from quantitative and other products were also found. When the complete stoichiometries are considered, there is no longer any difficulty in reconciling these reactions with formulas given above.

Next, it should be noted that while our formulation of structures assumes that the rhodo ion contains an oxygen bridge, the nitrogen bridge proposed by Jensen has not been logically excluded. Our preference for the oxygen-bridged structure is based, at least in part, upon the marked difference in acidity constants of the rhodo and erythro acid. If the reasonable assumption is made that a bridging oxygen atom cannot be introduced during the rhodo–erythro transformation, then the marked increase in pK from 2.8 to 7.8 must be associated with the introduction of the aquo group.[6] Conversely, the rhodo acid is much too weakly acidic to contain an aquo liquid, and the oxygen atom here must therefore be present as the only other structural alternative, a bridging hydroxyl group.

Electronic and Geometrical Configuration of the Basic Rhodo Ion.—In its chemical and physical properties the acidic rhodo ion resembles the structurally related mononuclear ions, but the basic rhodo ion, by contrast, is quite unlike other tripositive chromium complexes. Magnetic susceptibility measurements have recently provided information which clarifies our understanding of this striking difference in behavior. The detailed magnetic, optical and chemical studies of a number of binuclear chromium and cobalt complexes will be reported in another paper,[7] but the magnetic data for the rhodo ions are included here, because of their relevance to the consideration of acidity constants which follows below.

The magnetic susceptibility of the acidic rhodo nitrate follows the Weiss law with a magnetic moment corresponding to three unpaired electrons (μ eff. = 4.01) and a Δ of 90. Both the μ eff. and the Δ value approximate the quantities which characterize all of the binuclear chromium complexes which we have studied except the basic rhodo salts. For the basic rhodo salts, the susceptibility is very much smaller and it increases with increasing temperature. Without describing the analysis of the data in detail, it can be said in summary that at high temperatures the susceptibility would correspond to one unpaired electron on each chromic ion. The decrease in susceptibility at lower temperatures, a complication which has less direct bearing on the present discussion, is to be ascribed to the interaction and resultant pairing of the two remaining electrons within the binuclear unit.

Perhaps the best evidence bearing on the geometric structure of the basic rhodo ion is furnished by studies of the ruthenium complex $K_4[Cl_5RuORuCl_5]\cdot H_2O$. As a general rule the susceptibility of a tetrapositive ruthenium ion corresponds to two unpaired electrons, but this binuclear compound is diamagnetic,[8] a result which logically follows if it is assumed that the four non-bonding electrons are confined to two d-orbitals. Fortunately the crystal structure of the ruthenium complex also has been determined.[9] The Ru–O–Ru unit was found to be linear with a Ru–O distance considerably shorter than the sum of the single bond radii. On theoretical grounds Dunitz and Orgel have recently concluded that both the magnetic and structural data are understandable in terms of the concept that π-bonds are formed between the ruthenium and oxygen atoms.[10] While their approach is primarily from the molecular orbital viewpoint, they describe the bonding situation in valence bond terms as "resonance between a number of structures the extremes of which are $(Cl_5Ru^{IV}\text{–}\overset{2-}{O}\text{–}Ru^{IV}Cl_5)$ and $(Cl_5Ru^{II}{=}\overset{2+}{O}{=}Ru^{II}Cl_5)$."

In view of the similarity in magnetic behavior of the rhodo and ruthenium complex, it is plausible to assume that there is also considerable double bonding between the chromic ions and the bridging oxygen atom. The presence of a single unpaired electron on each chromic ion is to be expected if the three non-binding electrons are confined to two 3d orbitals, the remaining 3d orbital on each chromic ion being required for the π-bonding.[11] Probably the Cr–O–Cr arrangement is also linear, in part because of steric repulsion between the two halves of the molecule, and in part because linearity provides the most favorable geometry for π-bonding.[12]

The X-ray powder pattern evidence also supports the linear Cr–O–Cr arrangement. The acidic rhodo and erythro salts are isomorphous, indicating that the replacement of an ammonia liquid by water does not lead to a change in crystal structure. However, when the substitution also involves replacing a bridging oxygen atom by the hydroxyl group, as in the comparison of the two basic salts, the appearance of two different crystal structures strongly suggests that the two complex cations have different geometries.

The Acidity Constants of Mono- and Binuclear Complex Ions.—Before the complexities associated with the basic rhodo ion were uncovered it was

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(6) It seems unlikely that a molecular rearrangement involving the bridge positions will occur at the transition state. In addition, any mechanism involving reversible cleavage to mononuclear ions is not consistent with the known chemistry of mononuclear ions.

(7) Unpublished experiments by W. K. Wilmarth, S. S. Dharmatti, Taylor Joyner, and Carl Moeller.

(8) D. P. Mellor, *J. Roy. Soc. N.S.W.*, **77**, 145 (1943).

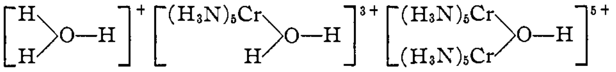
(9) A. McL. Mathieson, D. P. Mellor and N. C. Stephenson, *Acta Cryst.*, **5**, 185 (1952).

(10) J. D. Dunitz and L. E. Orgel, *J. Chem. Soc.*, 2594 (1953). The authors are indebted to Professor Orgel for his interest in the present work and his suggestion that the pairing of electrons in the basic rhodo ion is most readily understood when considered from the molecular orbital viewpoint.

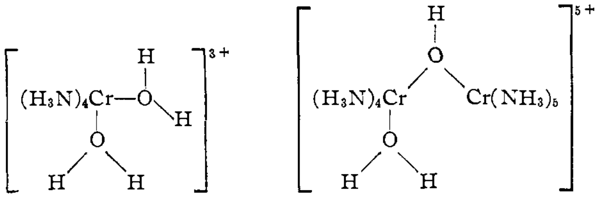
(11) Actually two of the 3d orbitals on each chromic ion project in a direction favorable for π-bonding, and it must be assumed that through resonance both participate in the π-bonding.

(12) This conclusion is strengthened by the observation that when the Cr–O–Cr configuration cannot become linear, as in the ion tetrakis-(ethylenediamine)-μ-oxo-μ-hydroxodichromium(III,III), the susceptibility corresponds to three unpaired electrons per chromic ion. However, it might be noted that L. N. Mulay and P. W. Selwood, THIS JOURNAL, **77**, 2693 (1955), have recently concluded that the ion $[Fe_2(OH)_2]^{4+}$ is diamagnetic.

hoped that the acidity constants of the following series of ions would provide a fairly direct measure of the acid weakening inductive effects occurring in progressive substitution of the protons in hydronium ion by $[Cr(NH_3)_5]^{3+}$ groups.[13] However, it is evident from the discussion above that ionization of the rhodo ion is accompanied by marked changes in electronic structure of the chromic ions, probable rehybridization of the σ-bonds of the bridging oxygen atom, release of steric strain and the formation of new π-bonds in the basic ion. The energy change summing over all of these perturbations must be favorable, since the hypothetical basic rhodo ion with properties analogous to those of the acidic rhodo ion is not observed. Consequently, as the trend in the above pK values might also suggest, the acidity constant of the rhodo ion only sets a lower limit to the acid weakening inductive effect associated with the second stage of the substitution.



On the basis of the above series of ions, it might have been supposed that acid weakening would result from the structural replacement of a proton by the $[Cr(NH_3)_5]^{3+}$ group at any point in a complex ion. Yet, in the following comparison, where the point of substitution is several atoms removed from the acidic site, an acid strengthening is observed.



Actually, there is some uncertainty here since the *cis–trans* configuration of either ion is known. However, even if the comparison should prove to be valid the reversal in inductive effects would not be inexplicable, since the inductive action of the proton may be especially favored when the point of substitution is the acid group itself, as it is in the first series of ions.

Hydrolytic Behavior of the Basic Rhodo Ions.—There are several unique features associated with the hydrolysis of the basic rhodo ion (equation 1). Perhaps most striking is the rapidity with which the reaction occurs; it is essentially complete within a few minutes at room temperature and within 15 minutes at 0°. Unlike the hydrolysis reactions of most complex ammines, the first stage of the hydrolysis is quite cleancut, at least in solutions of moderate alkalinity. For example, at 0° and a pH of 10 the product of the reaction, the erythro ion, is not appreciably hydrolyzed in a period of six hours. Lastly, it might be noted that in all solutions alkaline enough to neutralize the rhodo ion the rate of reaction (1) appears to be independent of pH, even in solution as concentrated as 6.0 N NaOH.

All of these observations become understandable if it is assumed that it is the chromium–oxygen π-bonding which provides the driving force for the hydrolysis of the basic rhodo ion. The π-bonding with its displacement of electrons from oxygen toward chromium produces an accumulation of negative charge upon the chromic ion. Presumably this weakens the chromium–ammonia bond, although the experimental results indicate only that the bond becomes more labile. In view of the lack of dependence of rate upon alkalinity, it would seem likely that the actual displacement of the ammonia ligand occurs through an S_N1 mechanism, with the formation of an intermediate containing a chromic ion with a coördination number of five. However, other mechanisms would also be consistent with the observed lack of dependence upon pH.

Experimental

Acidic Rhodo Compounds.—An acid solution of the chromic bromide was obtained by reduction of aqueous dichromate with concentrated hydrobromic acid and removal of the bromine by steam distillation. The chromic ion was reduced to the chromium(II) state with metallic zinc and, using essentially Jorgensen's procedure, the basic rhodo bromide was formed by aerative oxidation in a strongly buffered ammoniacal solution.[2] The precipitate of the blue basic rhodo bromide was immediately converted to its red conjugate acid by treatment with concentrated hydrobromic acid. The crude acid bromide was recrystallized four times by addition of concentrated hydrobromic acid to its aqueous solution. A yield of 30% of purified product was obtained.

The nitrate and chloride salts were prepared by precipitation with the appropriate concentrated acid from solutions of the crude rhodo bromide.

Anal. Calcd. for $[(H_3N)_5Cr(OH)Cr(NH_3)_5]Br_5 \cdot H_2O$: N, 19.76; Br, 56.3. Found: N, 19.91; Br, 55.4. Calcd. for $[(H_3N)_5Br(OH)Cr(NH_3)_5](NO_3)_5$: Cr, 17.29; NH_3, 28.32. Found: Cr, 17.31; NH_3 (Kjeldahl), 28.35.

Acidic Erythro Compounds.—The acid erythro bromide was best prepared by treating a concentrated solution of rhodo chloride with a slight excess of ammonium hydroxide. After standing for one-half hour at room temperature the solution was cooled and the acid erythro bromide precipitated by adding concentrated hydrobromic acid. After four recrystallizations a 90% yield of purified product was obtained.

The erythro nitrate was precipitated from a concentrated aqueous solution of the erythro bromide with concentrated nitric acid. The crude product was purified by four reprecipitations.

Anal. Calcd. for $[(H_3N)_5Cr(OH)Cr(NH_3)_4(OH_2)]Br_5 \cdot H_2O$: N, 17.77; Br, 56.2. Found: N, 17.44; Br, 55.2. Calcd. for $[(H_3N)_5Cr(OH)Cr(NH_3)_4(OH_2)](NO_3)_5 \cdot H_2O$: Cr, 16.79; NH_3, 24.67. Found: Cr, 16.72; NH_3 (Kjeldahl), 24.42.

Supporting evidence for the formula assigned to the erythro ion was obtained by carrying out the rhodo–erythro transformation in alkaline solution, precipitating the erythro ion and analyzing for the ammonia remaining in the mother liquor. In order to exactly duplicate Jorgensen's conditions, the solution was made alkaline with ammonium hydroxide; the ammonia found in the mother liquor after completing the experiment was therefore the sum of that present initially and that produced during the reaction.

In a typical experiment 10 ml. of 0.0673 N ammonium hydroxide (0.673 mmole) was added to a solution containing 0.2870 g. (0.589 mmole) of acid rhodo chloride. Fifteen minutes later, after the color change indicated conversion was complete, 20 ml. of 6.0 N H_2SO_4 and 8 ml. of ethyl alcohol were added to precipitate the erythro sulfate. The re-

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[13] As usual the term inductive effect, by definition, is here meant to include the total effect of the group, whether it be transmitted through polarization of chemical bonds, directly through space, or indirectly through the solvent. Our point of view is approximately that of Branch and Calvin in their text, "The Theory of Organic Chemistry," and it is their value for the pK of hydronium ion which is listed above.

sulting mother liquor was colorless, and the weight of the erythro sulfate corresponded to quantitative precipitation. Kjeldahl analysis of the mother liquor was then carried out.

Anal. Calcd. for release of one mole of NH_3 per mole of complex: 1.26 mmoles of NH_3. Found: 1.26 mmoles of NH_3.

Aquopentamminechromic Nitrate.—Chloropentamminechromic chloride was dissolved in hot, dilute acid solution and maintained at 100° for a few minutes. After cooling to 0° the aquopentamminechromic nitrate was precipitated by addition of concentrated nitric acid.

Anal. Calcd. for $[Cr(NH_3)_5(H_2O)](NO_3)_3$: Cr, 15.04; NH_3, 24.96. Found: Cr, 15.03; NH_3, 24.89.

Dehydration Studies.—The water of crystallization of the complex compounds was calculated by measuring the reversible weight loss produced by vacuum heating. The results generally confirm the less detailed work of Jorgensen.

The acidic rhodo bromide lost one water of crystallization after heating for one hour at 100°; calcd. 2.54%; found 2.72%. Longer heating at 100° gave no further loss of weight, but ten hours at 153° resulted in a 5.8% decrease in weight. The weight loss at 100° was rapidly regained upon exposure to laboratory air, but the product formed at 153° more than regained its original weight indicating the thermal formation of a new substance.

The acid erythro bromide reversibly lost one water molecule in the vacuum oven at room temperature; calcd. 2.5%; found 2.39%.

The acid rhodo nitrate appeared to be anhydrous. Vacuum heating at 118° was without effect. In six hours at 153° it decomposed irreversibly to a brick red solid of unknown structure.

X-Ray Powder Patterns.—X-Ray powder patterns were obtained using a North American Phillips X-ray diffraction unit with a copper target. The camera radius was 57.3 mm., and the exposure time was 12 hours for dial settings of 35 kv. and 15 ma. The *d*-values were read from an interplanar scale manufactured by N. P. Nies, 1495 Coolidge Avenue, Pasadena 7, California.

The powder pattern data tabulated below refer to the monohydrate in each case.

Acidic bromides				Basic bromides			
Rhodo		Erythro		Rhodo		Erythro	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
3.96	s.	3.97	s.	7.4	m.	10.5	m.
3.58	v.s.	3.57	v.s.	4.25	v.s.	4.90	v.s.
2.78	v.s.	2.76	v.s.	3.61	v.v.s.	4.15	m.
2.53	m.	2.54	m.	3.31	s.	3.70	s.
2.38	m.	2.38	m.	3.00	m.	3.38	m.
				2.76	m.	2.81	v.v.s.
						2.46	m.

The "lines" at a *d*-value 3.96 in the acidic bromides and at 3.70 in the basic erythro bromide are close-lying triplets. In addition to the data listed above, many weak lines are also observed.

Acidity Constants.—Acid-base titration curves were obtained at 10° for approximately 0.01 *M* solutions of the rhodo ion, erythro ion, aquopentamminechromic ion and diaquotetramminechromic ion (obtained from acid cleavage of the erythro ion); nitrate salts were used except for the latter ion where only the bromide salt was available. The Beckman *p*H meter was calibrated at 10° assuming a *p*H of 3.97 for 0.05 *M* potassium acid phthalate.[14] The rapid hydrolysis of the rhodo ion was circumvented by using individual aliquots of the aqueous solution for each point on the titration curve. Evidence that side reactions did not complicate the titration was obtained for all ions by plotting log $(A)^{+(n-1)}/(HA)^{+n}$ *vs.* *p*H; a straight line with the theoretical slope was obtained in each instance.

Cleavage of the Erythro Ion in Hydrobromic Acid.—Acid erythro bromide (0.666 g., 0.95 mmole) was dissolved in 70 ml. of concentrated hydrobromic acid, and the resulting solution maintained at 75° for five minutes. During the period of heating a precipitate gradually formed; upon cooling to room temperature 0.650 g. of solid was obtained by filtration. The solid was dissolved in 250 ml. of water, and the less soluble component, bromopentamminechromic bromide, was precipitated by addition of 12.0 ml. of concentrated hydrobromic acid. Both the yield of 0.372 g. (0.99 mmole) and the failure to obtain more solid by addition of excess concentrated hydrobromic acid indicated that the precipitation was essentially quantitative. After recrystallization the solid was analyzed for ionic bromide by precipitation of silver bromide with excess cold silver nitrate solution. Total bromide was also obtained by carrying out the precipitation over a two-hour period.

Anal. Calcd. for $[Cr(NH_3)_5Br]Br_2$: ionic Br, 42.5; total Br, 60.8. Found: ionic Br, 43.3; total Br, 62.3.

The initial cleavage in concentrated hydrobromic acid was repeated and the solid products again removed by filtration. Experiments indicated that the more soluble component could be separated by rapid extraction with cold water; a solution containing 44.6 mg. in 4.0 ml. of water was obtained in this manner. Titration of this solution with 0.02 *N* base indicated the presence of a dibasic acid with *pK* values of approximately 5.5 and 7.5.

Anal. Calcd. for $[Cr(NH_3)_5(H_2O)_2]Br_3$: mol. wt., 396; Br, 60.6. Found: mol. wt., 370; Br, 58.4.

Thermal Degradation of the Erythro Bromide.—In a duplication of the experiment described by Jorgensen a sample of the acidic erythro bromide monohydrate was heated in a vacuum oven for 24 hours at 100°. The total weight loss of 3.82% was considerably in excess of the 2.53% to be expected for the loss of hydrate water only. In addition, the nitrogen content of a representative sample of the product had decreased to 17.1% from an initial value of 18.2%, indicating a loss of nitrogen in the form of volatile products during the vacuum heating.

A portion of the product was dissolved in water and enough concentrated hydrobromic acid added to quantitatively precipitate any acidic rhodo bromide present in the solution. A yield of about 50% of material identified as rhodo bromide was obtained.

In an attempt to characterize the more soluble products a sample of the vacuum heated solid was extracted with 5 ml. of cold water. In this process most of the rhodo bromide remained behind in the solid phase; the small amount which dissolved was precipitated by adding ethyl alcohol to the 5 cc. of solution. After filtration the water and alcohol were removed by vacuum distillation at room temperature and a very soluble purple solid was isolated. Three successive extractions of the purple solid with ethyl alcohol, followed by volatilization of the alcohol, yielded ammonium bromide in amounts corresponding to 0.6 mole of ammonium bromide per mole of the erythro bromide starting material. Analysis of the purple solid remaining after the alcohol extract showed that it contained a ratio of ammonia to chromium of three, but it was not further identified.

Rate of Hydrolysis of the Rhodo and Erythro Ions.—The rate of hydrolysis of the rhodo and erythro ions was studied at 5° and at a *p*H of 10. In these experiments a *p*H meter was used to determine the amount of alkali required initially to bring the *p*H of the solution to 10. As the hydrolysis proceeded the ammonia which was generated was neutralized with acid as often as necessary to maintain the desired *p*H.

Visual observation was used to determine the time required for essentially complete hydrolysis of the rhodo ion. The color of the basic rhodo ion is so intense that 5% of the starting material could have been readily detected. Then further, much slower hydrolysis of the erythro ion was followed by acid titration of the ammonia produced in aliquots of the solution. The results indicated that the rhodo hydrolysis is complete within 15 minutes; after five hours, further hydrolysis produced less than 0.05 equivalent of ammonia per mole of complex. A solution of the erythro ion prepared by solution of solid acid erythro bromide in alkaline solution was equally inert; again less than 0.05 equivalent of ammonia appeared in the solution after 4.0 hours time.

The hydrolysis of the basic rhodo ion was also followed at various alkalinities up to 6.0 *N* alkali. As far as could be determined from visual observations the rate was completely independent of the hydroxide concentration over the entire range 10^{-4} to 6.0 *N* alkali. By contrast the rate of hydrolysis of the basic erythro ion at a *p*H of 11.5 had increased to approximately 25% of the rate of hydrolysis of the rhodo ion.

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[14] M. Dole, "The Glass Electrode," John Wiley and Sons, Inc., New York, N. Y., 1941, pp. 298–299.

Magnetic Susceptibility Measurements.—For the experiments involving solids each compound was carefully packed in the conventional glass tube and measured using the Gouy technique. At temperatures other than room temperature the sample tube was suspended inside an aluminum block surrounded by a glass Dewar. Heating and cooling coils in the aluminum block were actuated by a thermocouple control, and any temperature from −170 to 100° could be maintained automatically by the control system.

LOS ANGELES, CALIFORNIA

[CONTRIBUTION OF CENTRAL EXPERIMENT STATION U. S. BUREAU OF MINES]

Infrared Spectrum and Structure of Chromium Hexacarbonyl, $Cr(CO)_6$

BY S. LEONARD SHUFLER, HEINZ W. STERNBERG AND R. A. FRIEDEL

RECEIVED SEPTEMBER 30, 1955

The infrared spectrum of chromium hexacarbonyl, $Cr(CO)_6$, previously reported[1] in connection with a study of $Fe(CO)_6^{++}$, indicates only one intense C≡O stretching frequency in the vapor phase. This constitutes strong evidence for the equivalence of all C≡O bonds and a regular octahedral structure for chromium hexacarbonyl and other metal hexacarbonyls. These results provide an experimental means for detecting the presence of a metal hexacarbonyl in metal carbonyl reactions.

In the study[1] of $Fe(CO)_6^{++}$, an infrared spectrum of a metal hexacarbonyl was desired. The spectrum of $Cr(CO)_6$ was reported to indicate an octahedral structure.[1] An infrared spectrum of solid $W(CO)_6$, previously reported,[2] was inadequate due to scattering by solid particles. To avoid the uncertainty of a structural assignment from a solid state spectrum, the spectrum of $Cr(CO)_6$ has been determined in the gas phase. One sharp, strong band at 2000 cm.$^{-1}$ was observed (Fig. 1) in the C≡O stretching region, a fact which, according to group theory, supports the structure of a regular octahedron (structure I, Fig. 2). The band at 668 cm.$^{-1}$, near the location of a similar band in cobalt hydrocarbonyl,[3] is either a CO bending or a Cr–C stretching vibration.

A weak band was found at 1965 cm.$^{-1}$ at about the usual interval for metal carbonyls,[3] 35 cm.$^{-1}$, away from the fundamental on the low-frequency side. This band occurs in the spectra of many metal carbonyls and was originally labeled as a combination band.[3] But it is more likely attributable to a vibration involving C^{13},[4] the carbon isotope which occurs in nature in concentrations of about 1.1%. Intensity measurements on the 1965 cm.$^{-1}$ band for $Cr(CO)_6$ and for the corresponding band in other metal carbonyls (Table III of ref. 3) show that with one exception the intensity of this band is about 1–2% of the intensity of the nearest strong band. For cobalt hydrocarbonyl, the intensity of the band at 2010 cm.$^{-1}$ is over 4% of the intensity of the nearest strong band; Edgell has assigned this band as a fundamental.[4]

According to electron-diffraction data,[5] the most probable structure of the metal hexacarbonyls $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ is that of a regular octahedron of O_h symmetry (structure I). If a distinction could be made between polar and equatorial bonds in metal hexacarbonyls, as assumed by Sheline in the case of $W(CO)_6$,[2] the structure would be a tetragonal bipyramid of D_{4h} symmetry (structure II or III), and two infrared-active C≡O stretchings would be expected. But the geometry of a regular octahedron precludes any differentiation between polar and equatorial bonds. The fact that only one intense infrared band is observed in the 2,000 cm.$^{-1}$ region is definite evidence that all C≡O bonds in $Cr(CO)_6$ are equivalent (structure I).

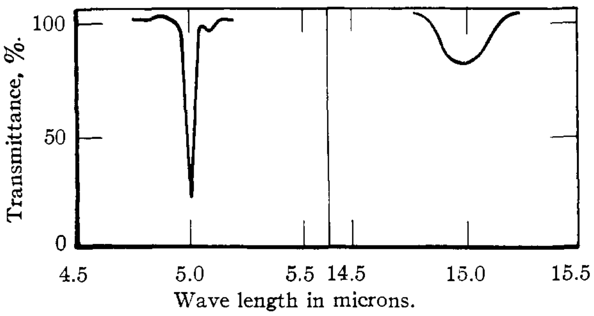

Fig. 1.—Infrared spectrum of $Cr(CO)_6$ vapor.

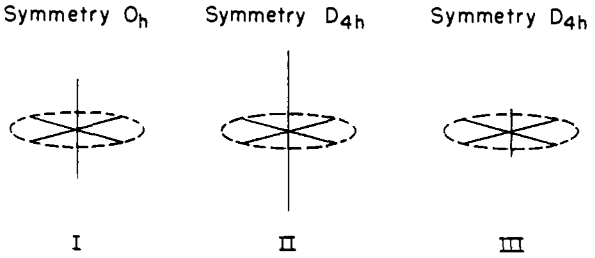

Fig. 2.—Possible structures of metal hexacarbonyls: I = regular octahedron, II and III = bipyramid.

Experimental

A few crystals of $Cr(CO)_6$ were placed in a round-bottom flask provided with a ground joint.[6] A stopcock fitted with a ground joint was attached to the flask, the flask evacuated, the stopcock closed, and the flask immersed in a steam-bath. An evacuated, 10-cm., KBr cell was then connected to the flask, the stopcock opened and the pressure allowed to equilibrate between the flask and the cell. To obtain the relative transmission of the vapor in the 2–15 mu region, an evacuated KBr cell was used as a reference. The instrument was a Perkin-Elmer Model 21, double-beam spectrophotometer.

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[1] H. W. Sternberg, R. A. Friedel, S. L. Shufler and I. Wender, THIS JOURNAL, **77**, 2675 (1955).

[2] R. K. Sheline, *ibid.*, **72**, 5761 (1950).

[3] R. A. Friedel, I. Wender, S. L. Shufler and Heinz W. Sternberg, *ibid.*, **77**, 3951 (1955).

[4] W. F. Edgell, private communication.

[5] L. O. Brockway, R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, **34**, 1350 (1938).

[6] We wish to thank Drs. E. O. Brimm and M. A. Lynch, Jr., of Linde Air Products Co., Tonawanda, N. Y., for supplying a sample of $Cr(CO)_6$.