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Some Reactions of the Octahalodirhenate(III) Ions. VI. Oxidation by Halogens to Give Nonahalodirhenate Species[1]

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Treatment of the $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$ ions with Cl_2 and Br_2, respectively, in methylene chloride or acetonitrile leads to the $Re_2Cl_9^-$ and $Re_2Br_9^-$ ions, binuclear Re(IV) complexes, which have been isolated as their tetra-*n*-butylammonium salts. These are stable as solids but in solution can be readily reduced, under some conditions by the solvent or by way of disproportionation, to the $Re_2X_9^{2-}$ ions, both of which have also been isolated as tetra-*n*-butylammonium salts. The latter may be reoxidized to the $Re_2X_9^-$ ions. The $Re_2X_9^-$ ions can also be reduced back to the $Re_2X_8^{2-}$ ions and, in fact, can revert at least partially to these species spontaneously in methanol.

Introduction

Following the initial reports[3-5] which gave the correct characterization of the $Re_2X_8^{2-}$ (X = Cl, Br) species, a series of papers has described ligand-substitution reactions[6-9] and electrolytic reduction reactions[10] of $Re_2X_8^{2-}$ species. In view of the recently reported[11] rhenium(IV) chloride, which appeared from its chemistry to contain dinuclear species and which gave rise under certain conditions to $Re_2Cl_9^{2-}$, an investigation of the oxidation products which might be obtained by the action of halogens (Cl_2, Br_2) on the $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$ ions seemed worthwhile. Such an investigation, the chief result of which is the discovery of the new Re(IV) species, $Re_2Cl_9^-$ and $Re_2Br_9^-$, as well as the new Re(III)–Re(IV) (or Re(3.5)) dinuclear complex, $Re_2Br_9^{2-}$, analogous to the previously reported $Re_2Cl_9^{2-}$, is described in detail in this paper. Single-crystal X-ray studies of suitable salts of all four of the new dinuclear anions $Re_2X_9^{n-}$ (X = Cl, Br; n = 1, 2) have been undertaken. This paper will therefore focus on the chemical aspects of the work and discussions of structure will be deferred until the crystallographic investigations have been completed.

Experimental Section

General Remarks.—The starting material, $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$, was prepared as previously described.[6] Chloroform was allowed to stand at least 0.5 hr over anhydrous calcium chloride before use. Metal spatulas and other metallic objects were avoided throughout the preparations and work-up, especially when handling solutions. Analyses were performed by S. M. Nagy, Massachusetts Institute of Technology, and Galbraith Microanalytical Laboratories, Knoxville, Tenn. Analytical data for all new compounds are recorded in Table I. Routine infrared spectra were recorded on a Perkin-Elmer 237B; those reported here were recorded on a Perkin-Elmer 337 (4000–400 cm^{-1}) and a Perkin-Elmer 621 (400–200 cm^{-1}). Ultraviolet and visible spectra (Table II) were obtained with a Beckman DU spectrophotometer. Conductances were measured at about 25° with a commercial Wheatstone bridge circuit and are reported in Table III.

No satisfactory valence determination can be carried out according to Noddack's chromate method, owing to the insolubility of tetrabutylammonium perrhenate.

$[(n\text{-}C_4H_9)_4N]Re_2Cl_9$.—(a) Crude $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ (6.1 g) was dissolved in methylene chloride (200 ml) and chlorine was bubbled through until the solution became green (approximately 5 hr). The solution was then concentrated to small volume at the water pump, without any external heating; excess chloroform was added and the dark green crystals (3.6 g) were filtered and washed with chloroform.

The chlorination of $Re_2Cl_8^{2-}$ can also be carried out in acetonitrile, giving the same product.

When the chlorination was carried out in CH_2Cl_2 but stopped prematurely and the solvent was evaporated, only green and blue crystals of the $Re_2Cl_9^-$ and the $Re_2Cl_8^{2-}$ salts, respectively, were isolated. No other compounds (*e.g.*, salts of $ReCl_6^{2-}$ or $Re_2Cl_9^{2-}$) were detected.

(b) The violet compound, $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_9$, the preparation of which is described later, was dissolved in methylene chloride and chlorine gas was bubbled through. The color changed to green at once. The solvent was removed using a water pump and the residue was extracted several times with chloroform. The green solid residue was identified as $[(n\text{-}C_4H_9)_4N]Re_2Cl_9$ by its melting point, by its mixture melting point (with a sample prepared by procedure a), and by its infrared spectrum.

The compound is soluble and can be recovered from acetone, methylene chloride, acetonitrile, and refluxing sulfur dioxide; it is only sparingly soluble in chloroform and is insoluble in ether, benzene, ethanol, methanol, and concentrated hydrochloric acid.

A solution of this compound in methylene chloride becomes violet on standing for a few hours. A solution in acetonitrile becomes colorless in 4 days. An acetone solution, kept under nitrogen, becomes brown in less than 2 days.

While the compound is not affected by water or 6 *N* hydrochloric acid, it is attacked by 7 *N* ammonia. If acetone is added to a suspension of the compound in 6 *N* hydrochloric acid until it begins to dissolve, decomposition begins at or about the same time.

On mixing a solution of the compound in acetonitrile with a solution of silver nitrate in the same solvent at 25°, there is no reaction; on mixing the solutions at 75°, a cream-colored precipitate is formed and the solution becomes colorless at once.

There was no observable reaction on passing ethylene or car-

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[2] On leave from the Istituto di Chimica Generale of the University of Milan on a NATO fellowship administered by the Consiglio Nazionale delle Ricerche of Italy.

[3] F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, **4**, 326 (1965).

[4] F. A. Cotton and C. B. Harris, *ibid.*, **4**, 330 (1965).

[5] F. A. Cotton, *ibid.*, **4**, 334 (1965).

[6] F. A. Cotton, N. F. Curtis, and W. R. Robinson, *ibid.*, **4**, 1696 (1965).

[7] F. A. Cotton, C. Oldham, and W. R. Robinson, *ibid.*, **5**, 1798 (1966).

[8] F. A. Cotton, C. Oldham, and R. A. Walton, *ibid.*, **6**, 214 (1967).

[9] F. A. Cotton, W. R. Robinson, R. A. Walton, and R. Whyman, *ibid.*, **6**, 929 (1967).

[10] F. A. Cotton, W. R. Robinson, and R. A. Walton, *ibid.*, **6**, 1257 (1967).

[11] F. A. Cotton, W. R. Robinson, and R. A. Walton, *ibid.*, **6**, 223 (1967).

TABLE I

ANALYTICAL DATA AND DECOMPOSITION POINTS

Compound	Color	Dec pt, °C	Analyses, %: C Calcd	C Found	H Calcd	H Found	N Calcd	N Found	Halogen Calcd	Halogen Found
$[(n\text{-}C_4H_9)_4N][[Re_2Cl_9]$	Dark green	169	20.57	20.2	3.88	4.01	1.50	1.51	34.16	34.1
$[(n\text{-}C_4H_9)_4N][Re_2Br_9]$	Dark red	171	14.40	14.4	2.72	2.93	1.05	1.03	53.91	54.0
$[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_9]$	Violet	140[a]	32.67	32.2	6.17	6.09	2.38	2.32	27.12	27.2
$[(n\text{-}C_4H_9)_4N]_2[Re_2Br_9]$	Rusty brown	122	24.37	23.8	4.60	4.42	1.78	1.70	45.62	45.4

[a] Color changes to green prior to melting.

TABLE II

ELECTRONIC SPECTRA OF THE $Re_2X_9^{n-}$ IONS[a]

Ion	Maxima: mμ	Maxima: $cm^{-1} \times 10^{-3}$	Molar extinction coeff[b]
$Re_2Cl_9^-$	623	16.0	480
	545	18.3	380
	360	27.8	14,000
	321	31.2	22,500
$Re_2Br_9^-$	725	13.8	560
	396	25.2	18,000
$Re_2Cl_9^{2-}$	736	13.6	1,380
	537	18.6	1,250
	357	28.0	530 sh
	322	31.0	9,500
	276	36.1	18,200
	262	38.1	
$Re_2Br_9^{2-}$	718	13.9	1,200
	469	21.3	7,000
	418	23.9	10,800
	388	25.8	11,000
	276	36.2	17,400

[a] Measured using $(n\text{-}C_4H_9)_4N^+$ salts in CH_2Cl_2 solution, from 210 to 1000 mμ. [b] sh = shoulder.

TABLE III

ELECTROLYTIC CONDUCTANCES[a] IN ACETONITRILE

Compound	Molarity × 10^4	Molar conductance, $ohm^{-1}\ cm^2\ mole^{-1}$
$[(n\text{-}C_4H_9)_4N][Re_2Cl_9]$	4.56	147
$[(n\text{-}C_4H_9)_4N][Re_2Br_9]$	6.36	149
$[(n\text{-}C_4H_9)_4N]Br$	6.26	146
$[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_9]$	3.85	334
$[(n\text{-}C_4H_9)_4N]_2[Re_2Br_9]$	3.96	333
$[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$	2.2[b]	298[b]

[a] The measurements were made at 25° immediately upon dissolving the sample. [b] Taken from ref 3.

bon monoxide into solutions of the compound in methylene chloride or acetone.

The compound can be chromatographed on alumina in CH_2Cl_2, but addition of acetone to speed the elution brings about a marked enhancement in the violet band due to the $Re_2Cl_9^{2-}$ salt which is present in only a small quantity in the beginning.

$[(C_6H_5)_4As]Re_2Cl_9$.—The chlorination of a suspension of tetraphenylarsonium octachlorodirhenate(III) (0.4 g) in methylene chloride (100 ml) was carried out over a period of 2 days. The green solution so obtained was concentrated by removal of solvent under reduced pressure at room temperature. White crystals were first obtained. They were filtered and identified as $(C_6H_5)_4AsCl$. On further evaporation the dirhenium complex halide was not obtained in a pure state owing to the relative instability of the solution and to the similar solubility of the tetraphenylarsonium chloride. Examination of the product under a microscope showed that the green crystals were mixed with appreciable amounts of white crystals (presumably $(C_6H_5)_4AsCl$).

$[(n\text{-}C_4H_9)_4N]Re_2Br_9$.—Crude $[(n\text{-}C_4H_9)_4N]Re_2Br_8$ (3.3 g) was dissolved in methylene chloride (100 ml) and bromine (0.5 ml) in the same solvent (25 ml) was added. The color changed slowly. After about 1 hr the dark red solution was evaporated to small volume and the dark red crystals which were deposited (1.8 g) were separated by filtration. They were purified by redissolving them in methylene chloride and adding an excess of chloroform. When only the stoichiometric amount of bromine was used initially, some unreacted starting material was present in the product.

This compound is more soluble than its chloro analog, though its solubility properties are generally similar. It is also more stable: After 5 days an acetonitrile solution was unaltered in appearance and its electrolytic conductance was unchanged.

Conversion of $Re_2X_9^-$ to $Re_2X_8^{2-}$.—(a) $[(n\text{-}C_4H_9)_4N]Re_2Cl_9$ (360 mg) was suspended in methanol (25 ml), and the suspension was heated on a steam bath in a distilling flask. After 10 min nearly all of the solvent had distilled and the solution was violet; the distillate was fed back and moderate heating was continued for an additional 25 min, while the distillate was collected and the solution became green. The distillate was neutral, did not contain chloride ions, and did not give a precipitate with 2,4-dinitrophenylhydrazine. The residue (390 mg) after distillation was pumped dry (0.1 torr, 30 min) and was crystallized by dissolving it in methanol and concentrating this solution to 4.0 ml. The product (80 mg) was obtained as blue prisms, mp 259°. It gave an undepressed mixture melting point and a superimposable infrared spectrum with an authentic sample. On further concentrating the methanol solution, a very small quantity of pale green prisms separated; they were not investigated.

(b) $[(n\text{-}C_4H_9)_4N]Re_2Cl_9$ (530 mg) was dissolved in acetone (25 ml) under nitrogen and a coil of iron wire (1.5 g) was added. The green solution became violet and then brownish. After about 2 hr the coil was removed and the solution was concentrated under vacuum at room temperature, yielding first blue crystals, dec pt 195–201°. After crystallization from methanol containing 1% hydrochloric acid, blue crystals, dec pt 241°, were obtained. On further concentration of the acetone solution, a black, iron-containing powder was isolated, and then, when approaching dryness, a greenish, nearly solid, iron-free residue (220 mg) appeared. This solid was washed free of a white component with chloroform and was recrystallized from methanol–2-propanol in the presence of a few drops of hydrochloric acid, yielding blue crystals, dec pt 257–259°. Upon complete evaporation of the solvent a greenish oily residue was left.

(c) To form $[(n\text{-}C_4H_9)_4]_2Re_2Br_8$ from $[(n\text{-}C_4H_9)_4N]Re_2Cl_9$, the latter (480 mg) and a 1:1 mixture of 48% hydrobromic acid and methanol (100 ml) were placed in a covered beaker and left on a steam bath for 90 min. The yellow solution was then allowed to evaporate on the steam bath and filtered when the volume had been reduced to about 60 ml. The olive prisms were washed with 1:1 48% hydrobromic acid, then methanol, and finally ether. They were identified as $[(n\text{-}C_4H_9)_4N]_2Re_2Br_8$ by their decomposition point, undepressed mixture decomposition point, and comparison of their infrared spectrum with that of an authentic sample obtained from $Re_2Cl_8^{2-}$ and hydrobromic acid in methanol.

$[(n\text{-}C_4H_9)_4N]_2Re_2Cl_9$.—(a) A coil of copper wire (4.712 g) was placed in a green acetone solution (10 ml) of crude $[(n\text{-}C_4H_9)_4N]Re_2Cl_9$ (450 mg) under nitrogen. After 7 min the coil was removed from the violet solution and the latter was evaporated to dryness under reduced pressure at room temperature. The oily violet residue solidified on shaking with ethyl acetate (6 ml) and the filtered, copper-free solid (240 mg) was purified by dissolving it in methyl ethyl ketone (2 ml) and adding ethyl acetate (4 ml). The weight loss of the coil was 27 mg (calcd, 25 mg). The compound is soluble in and can be recovered from acetonitrile, acetone, and methylene chloride; it is insoluble in water and 6 *N* hydrochloric acid. Addition of acetone to the aqueous suspension until dissolution commences causes nearly immediate formation of a brown precipitate; decomposition is slower when acetone is added to the 6 *N* hydrochloric acid suspension, the solution becomes nearly colorless after 2 days, and blue crystals are deposited.

(b) $[(n\text{-}C_4H_9)_4N]Re_2Cl_9$ (1.42 g) was dissolved in acetone (50 ml) under nitrogen, and mercury (1 ml) was added. The color changed slowly, going through blue to violet. After 10 hr the filtered solution was evaporated to dryness under vacuum. The violet, oily residue was treated with about 5 ml of ethyl acetate and the violet solid (550 mg) was filtered and washed with a few drops of ethyl acetate. Upon concentration of the ethyl acetate solution to about 2.5 ml an additional quantity of violet compound, dec pt 139°, was isolated by filtration. After evaporation to dryness a brownish violet oily solid was left, which reacted with methanol and acetonitrile.

(c) The use of mossy tin instead of a copper coil also gave the violet compound, which was isolated as in (a).

(d) The compound was also formed when iron wire was used as the reducing agent and ethyl acetate as the solvent. However, coating of the iron wire by the violet compound, which was isolated by scraping, prevented complete reduction. Use of acetone in place of ethyl acetate afforded impure $Re_2Cl_8^{2-}$ (see above).

(e) $(n\text{-}C_4H_9)_4NBr$ (3.0 g) was converted to $(n\text{-}C_4H_9)_4NCl$ by dissolving it in concentrated hydrochloric acid and evaporating the solution to dryness; the procedure was repeated and the residue then dissolved in methanol (20 ml). The solution was added to a methanol suspension (20 ml) of $[(n\text{-}C_4H_9)_4N]Re_2Cl_9$ (340 mg). After boiling for 12 min on the steam bath the violet solution was concentrated to half-volume (0.1 torr, 25°) and the violet crystals were filtered and washed twice with methanol. They were identified by decomposition point and mixture decomposition point.

(f) The same compound can be obtained by allowing a methanol suspension of $Re_2Cl_9^-$ to stand under nitrogen for 1 day, some unreacted and undissolved starting material being removed by filtration.

$[(n\text{-}C_4H_9)_4N]_2Re_2Br_9$.—$[(n\text{-}C_4H_9)_4N]Re_2Br_9$ (1.2 g) was dissolved in acetone (25 ml) under nitrogen and a coil of iron wire added. After 70 min the coil was removed from the olive-brown solution and the solution was then evaporated to dryness under vacuum. The dark orange-brown residue was dissolved in chloroform, the solution was concentrated under vacuum to about 5 ml, and the rusty brown product (390 mg) was precipitated by addition of diethyl ether. Evaporation of the mother liquor yielded only a dark brown oily residue.

Discussion

It is known[4,12,13] that the $Re_2X_8^{2-}$ ions have a very short Re–Re bond and an eclipsed rotational configuration, and these structural features have been of salient importance in the formulation[5] of the metal-to-metal bonds as quadruple, consisting of a σ, δ, and two π components. The present work was undertaken with the idea that suitable strong oxidizing agents might be able to remove one or both the electrons occupying the δ-bonding orbital, while leaving the σ and π bonds intact, thus affording new dinuclear species containing Re(IV). It was hoped that perhaps the dinuclear form[11] of rhenium(IV) chloride might thus be obtained. This particular hope has not been realized, and the reaction products are in general rather more complicated than such simple reasoning might lead one to expect.

Preparation and Chemical Properties.—It has been found that, upon treatment of the $Re_2X_8^{2-}$ ions (X = Cl, Br) with the corresponding elemental halogen, X_2, in a halogenated solvent or acetonitrile at room temperature, the following reaction occurs, in good yields: $Re_2X_8^{2-} + X_2 \rightarrow Re_2X_9^- + X^-$.

This is a stoichiometric oxidation of Re(III) to Re(IV). No evidence was found for the formation of ReX_6^{2-}, the well-known type of halo complex of Re(IV), which indicates the strength and stability of the metal-to-metal bond in $Re_2X_8^{2-}$ species. The formulas of the dark green (X = Cl) or dark red (X = Br) $Re_2X_9^-$ products were assigned on the basis of elemental analyses (Table I) and their electrolytic conductances (Table III).

It is interesting to note that in experiments carried out under similar conditions $Re_3Cl_{12}^{3-}$ was found not to react with chlorine; even when the temperature was raised to the boiling point of acetonitrile, there was no observable reaction. This indicates the more "unsaturated" character of the Re–Re quadruple bond (due to the relative weakness of its δ component) as compared to the double bonds in the trinuclear species.

The $Re_2X_9^-$ ions have been isolated as their tetra-*n*-butylammonium salts. Other salts have proved more difficult[14] to obtain in a pure condition, as, for example, the tetraphenylarsonium salt of $Re_2Cl_9^-$ mentioned in the Experimental Section.

The $[(n\text{-}C_4H_9)_4N][Re_2X_9]$ compounds are stable in the solid state but subject to decomposition in solution or on contact with certain solvents, even under nitrogen. $[(n\text{-}C_4H_9)_4N][Re_2Cl_9]$ is very sparingly soluble in cold methanol. The suspension is altered in the absence or presence of HCl, on short heating or long standing, to give the violet $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_9]$. On further heating, the known $Re_2X_8^{2-}$ species are formed. Since neither formaldehyde nor formic acid was detected in the reaction media and yields were always less than 50% a disproportionation reaction seems likely, although the other product or products were not identified.

This transformation of $Re_2Cl_9^-$ in methanol explains the recently reported[11] isolation of $Re_2Cl_9^{2-}$ and $Re_2Cl_8^{2-}$ species, in moderate yields, ≤40%, from the reactions of rhenium(IV) chloride with halide ions instead of the $Re_2Cl_9^-$ ion which might have been expected. It would appear that the isolation of $Re_2Cl_8^{2-}$ as the final product from these different sources, as well as by the reduction of the perrhenate(VII) ion using H_2 or H_3PO_2 in aqueous HCl, and the strongly reducing character of the $Re_2Cl_8^{3-}$ and $Re_2Cl_8^{4-}$ ions all attest to the remarkable stability of the $Re_2Cl_8^{2-}$ ion.

The $Re_2Cl_9^{2-}$ ion was first encountered[11] as a reaction product of rhenium(IV) chloride. Attempts in this study to treat rhenium(IV) chloride with $(C_6H_5)_4AsCl$ in methylene chloride and with $[(n\text{-}C_4H_9)_4N]Cl$

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[12] V. G. Kuznetsov and P. A. Koz'min, *Zh. Strukt. Khim.*, **4**, 55 (1963).

[13] P. A. Koz'min, V. G. Kuznetsov, and Z. V. Popova, *ibid.*, **6**, 651 (1965).

[14] P. F. Stokely, unpublished work.

in a methylene chloride–benzene mixture, at room temperature, did not afford $Re_2Cl_9^-$ but, instead, violet solutions presumably containing $Re_2Cl_9^{2-}$, though in the first case a transient green color was observed. Thus direct conversion of $(ReCl_4)_x$ to $Re_2Cl_9^-$ by addition of Cl^- has not yet been achieved.

The $Re_2Cl_9^{2-}$ and $Re_2Br_9^{2-}$ ions as their $[(n\text{-}C_4H_9)_4N]^+$ salts can be prepared easily by reduction of the $Re_2X_9^-$ ions. There is no indication, however, that these $Re_2X_9^{2-}$ ions might be isolable during the rather long halogenation of the $Re_2X_8^{2-}$ species. On the contrary, it was found that $Re_2X_9^{2-}$ is oxidized at once by chlorine in methylene chloride solution to $Re_2Cl_9^-$. The $Re_2Cl_9^{2-}$ ion is more stable in solution than the $Re_2Cl_9^-$ ion; its acetone and acetonitrile solutions show no evidence of decomposition over several days.

The reduction of the $Re_2Cl_9^-$ anion can be carried out in many ways: the reductants tin, copper, and even mercury, in a polar solvent, such as acetone, afford violet solutions from which violet $Re_2Cl_9^{2-}$ can be isolated. Iron affords the violet compound only if the reduction is carried out in ethyl acetate, where the compound is sparingly soluble and further reaction is prevented. When acetone is the solvent, the reduction with iron affords impure $Re_2Cl_8^{2-}$, though the violet compound is formed as an intermediate, as evidenced by the intermediate violet color of the solution. In all of these cases the reduction is practically complete in a few hours, often in minutes, so that the isolated products are surely not due to the slower, spontaneous decomposition of $Re_2Cl_9^-$ in solution. Further, the weight losses of the copper or iron wires used for the reductions afford additional evidence on this point and also against a purely catalytic effect of the metal surface on the decomposition of $Re_2Cl_9^-$. Owing to the effect of mercury on the solution of $Re_2Cl_9^-$, no polarographic reduction was carried out on this or on related compounds.

The main paths of interconversion among the $Re_2X_8^{2-}$, $Re_2X_9^{2-}$, and $Re_2X_9^-$ species are summarized in Figure 1.

Physical Data and Structural Considerations.—It is not possible to make any meaningful inferences of the structures of the $Re_2X_9^-$ and $Re_2X_9^{2-}$ ions indirectly from the available physical data. On the contrary, the discussion and interpretation of physical data and also a full understanding of the chemical processes described above must await the completion of X-ray structural studies. At this time, therefore, the discussion will be very brief.

The electronic absorption spectra of the $Re_2X_9^-$ and $Re_2X_9^{2-}$ ions are summarized in Table II. They are, in general, more complex than those of the $Re_2X_8^{2-}$ ions.

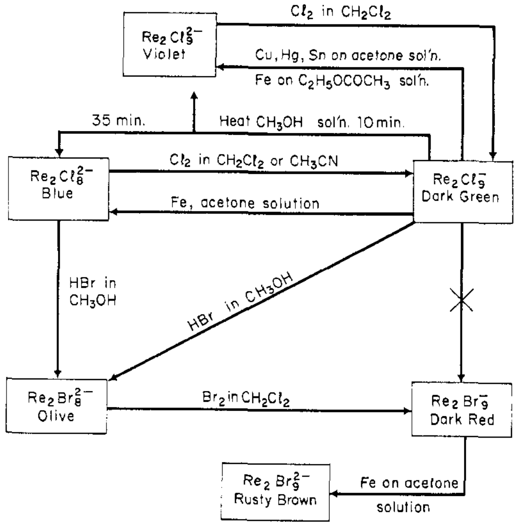

Figure 1.—A flow sheet summarizing the interconversions of the various $Re_2X_8^{2-}$, $Re_2X_9^-$, and $Re_2X_9^{2-}$ species.

The effective magnetic moments of the $Re_2X_9^{2-}$ ions have been measured at 25° and are 1.5 and 1.7 BM/formula unit for the $Re_2Cl_9^{2-}$ and $Re_2Br_9^{2-}$ ions, respectively.

The far-infrared spectrum of $[(n\text{-}C_4H_9)_4N]Re_2Cl_9$ has a strong band with shoulders centered at 353 cm^{-1} and another sharper strong band at 250 cm^{-1}, while the spectrum of the $Re_2Cl_9^{2-}$ ion is distinctly different, having only one strong absorption at 321 cm^{-1}. It thus seems quite possible that the $Re_2Cl_9^-$ and $Re_2Cl_9^{2-}$ ions may have qualitatively different structures.

It has already been suggested,[11] as no more than a speculation, that the $Re_2Cl_9^{2-}$ ion might have a structure derived from that of $Re_2Cl_8^{2-}$ by attachment of an additional Cl atom along the fourfold axis, with or without rotation from the eclipsed to a staggered rotational configuration.

On the other hand, it has since been found[15] that the previously[11] described form of rhenium(IV) chloride, which readily gives rise to $Re_2Cl_8^{2-}$ and to $Re_2Cl_9^{2-}$, has a bioctahedron structure like that of $W_2Cl_9^{3-}$. The Re_2Cl_9 units are strung together by sharing of terminal Cl atoms. In view of this, the structure of $Re_2Cl_9^-$ (and perhaps even that of $Re_2Cl_9^{2-}$) might well be expected to be similar. However, the difference in the far-infrared spectra of the two ions could be an indication that while the $Re_2Cl_9^-$ ion, consisting entirely of Re(IV), is built like the rhenium(IV) chloride, the $Re_2Cl_9^{2-}$ ion may indeed have the previously suggested structure.

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(15) M. J. Bennett, F. A. Cotton, and P. F. Stokely, *J. Am. Chem. Soc.*, in press.