CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS

Compounds Containing Dirhenium(III) Octahalide Anions[1]

BY F. A. COTTON, N. F. CURTIS, B. F. G. JOHNSON, AND W. R. ROBINSON

Received September 22, 1964

The preparation of compounds containing the binuclear ions $[Re_2Cl_8]^{2-}$ and $[Re_2Br_8]^{2-}$ is described. They can be obtained by reduction of ReO_4^- in aqueous HCl or HBr with H_3PO_2 or by reduction of ReO_4^- or $[ReX_6]^{2-}$ in a bomb with hydrogen under high pressure. The latter method has previously been published by Tronev and co-workers, but they formulated the ions as $[ReX_4]^{2-}$ or $[Re_2X_8]^{4-}$, that is as compounds of Re(II). Various lines of physical and chemical data are reported to show that the $[Re_2X_8]^{2-}$ formula is the correct one. Especially cogent evidence is provided by the facts that, (1) the $[Re_2X_8]^{2-}$ ion reacts smoothly with carboxylic acids to produce the dinuclear $[Re(RCO_2)_2Cl]_2$ compounds of Taha and Wilkinson, and (2) $[Re(C_2H_5CO_2)_2Cl]_2$ reacts smoothly with a mixture of aqueous HCl and propionic acid to give the $[Re_2Cl_8]^{2-}$ ion which can be precipitated with tetraphenylarsonium chloride.

Introduction

Recent studies have shown that rhenium(III) has an extensive chemistry in which some unique structural features are found. Thus, there is an extensive series of compounds based upon the Re_3Cl_9 and Re_3Br_9 units which contain Re_3 clusters,[2-9] as well as compounds containing mononuclear complexes.[7,10]

In this paper we report in detail on the preparation of compounds we believe to be correctly formulated as containing $[Re_2Cl_8]^{2-}$ and $[Re_2Br_8]^{2-}$ species.[7] Some of these compounds appear to have been prepared before[11-14] but differently formulated. A comparison of our results with previous ones and a discussion of the basis for assignment of formulas will be given later. These $[Re_2X_8]^{2-}$ ions further and still more strongly exemplify the great homophilicity[7] of rhenium in the formal oxidation state III.

Experimental

Reduction Using H_3PO_2 in Constant-Boiling HCl.—$KReO_4$ (10 g.), NaCl (10 g.), and 10 ml. of 50% aqueous H_3PO_2 were dissolved in 200 ml. of constant boiling hydrochloric acid. The solution was then heated to *ca.* 95°. The color gradually changed to brownish green and then became very dark after several hours. The very dark color remained for several hours while gentle gas evolution occurred. After about 4 hr., gas evolution ceased.

$[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$.—On adding 3 g. of tetra-*n*-butylammonium chloride to the warm solution, one or both of two things may happen in any particular case. Either a light green flocculent precipitate forms, or a deep blue precipitate, or a mixture of both. When other than a pure blue precipitate is obtained, heating is continued until it has been completely converted to the blue precipitate. The transformation appears to be hastened by addition of about 20 ml. of water. The sparingly soluble compound is thus precipitated while the salt of $[ReCl_6]^{2-}$, which is much more soluble in the warm acid, remains in solution. The blue crystalline precipitate is filtered from the warm liquid and washed with cold, constant-boiling hydrochloric acid. Yields varied from 15 to 20% based upon $KReO_4$. On cooling the filtrate, the remaining rhenium was recovered as the tetrabutylammonium as well as the potassium salt of $[ReCl_6]^{2-}$. Occasionally, additional small quantities of the product were obtained upon heating the filtrate for a further period of time.

The tetrabutylammonium compound is readily soluble in methanol, acetone, acetonitrile, and various other solvents, giving blue solutions. Its color varies slightly from one solvent to another. It may be conveniently recrystallized by dissolving it in methanol, or one of the other solvents, preferably containing a few drops of concentrated hydrochloric acid to repress hydrolysis, filtering, and then adding constant-boiling hydrochloric acid or 2-propanol. The solution is then evaporated, removing the methanol or other volatile solvents, whereupon the compound crystallizes.

The magnetic susceptibility, measured at 25° by the Gouy method, is -530×10^{-6} c.g.s. unit per mole of $[(C_4H_9)_4N]_2Re_2Cl_8$.

Preparation of Other Salts.—When other large cations are added to a solution of the tetra-*n*-butylammonium salt in methanol containing about 1 ml. of concentrated aqueous HCl per 100 ml., corresponding salts of $[Re_2Cl_8]^{2-}$ are obtained. Those of $[(C_6H_5)_4As]^+$, $[(C_6H_5)_3(CH_3)As]^+$, $[C_5H_5NH]^+$, and $[C_8H_{11}NH]^+$ (collidinium, 2,4,6-trimethylpyridinium) are representative.

Table I gives the analytical data for the salts of these four cations as well as for the tetrabutylammonium salt.

$[(n\text{-}C_4H_9)_4N]_2Re_2Br_8$.—This compound was prepared by a method very similar to that used for its chloro analog. $KReO_4$ (10 g.), 10 ml. of a 50% aqueous solution of H_3PO_2, and 20 ml. of 48% aqueous HBr were refluxed for 2 hr. and 3 g. of tetra-*n*-butylammonium bromide then was added. The precipitate, which formed before the solution cooled, was separated by filtration and washed with warm dilute HBr until the washings were colorless. The green-brown product was recrystallized from methanol containing a few drops of 48% HBr.

Anal. Calcd. for $C_{32}H_{72}N_2Re_2Br_8$: C, 25.67; H, 4.81; Br, 42.7. Found: C, 25.6; H, 4.85; Br, 43.2.

Alternatively, the bromo compound can be made by heating $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ with 48% aqueous HBr plus an equal volume of methanol for 5 min. The product is isolated and recrystallized as above.

Reduction by Hydrogen under Pressure.—This method is the

---

(1) Supported by the U. S. Atomic Energy Commission.

(2) J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *J. Am. Chem. Soc.*, **85**, 1349 (1963); *Inorg. Chem.*, **2**, 1166 (1963).

(3) W. T. Robinson, J. E. Fergusson, and B. R. Penfold, *Proc. Chem. Soc.*, 116 (1963).

(4) F. A. Cotton and J. T. Mague, *Proc. Chem. Soc.*, 223 (1964); *Inorg. Chem.*, **3**, 1402 (1964).

(5) F. A. Cotton and J. T. Mague, *ibid.*, **3**, 1094 (1964).

(6) J. E. Fergusson, B. R. Penfold, and W. T. Robinson, *Nature*, **201**, 181 (1964).

(7) F. A. Cotton, N. F. Curtis, C. B. Harris, B. F. G. Johnson, S. J. Lippard, J. T. Mague, W. R. Robinson, and J. S. Wood, *Science*, **145**, 1305 (1964).

(8) J. E. Fergusson and W. T. Robinson, *Proc. Chem. Soc.*, 189 (1964).

(9) F. A. Cotton and S. J. Lippard, *J. Am. Chem. Soc.*, **86**, 4497 (1964).

(10) J. C. Chatt and G. A. Rowe, *J. Chem. Soc.*, 4019 (1962).

(11) V. G. Tronev and S. M. Bondin, *Dokl. Akad. Nauk SSSR*, **86**, 87 (1952).

(12) V. G. Tronev and S. M. Bondin, *Khim. Redkikh. Elementov, Akad. Nauk SSSR*, **1**, 40 (1954).

(13) A. S. Kotel'nikov and V. G. Tronev, *Zh. Neorgan. Khim.*, **3**, 1008, (1958); *Russ. J. Inorg. Chem.*, **3**, 268 (1958).

(14) G. K. Babeshkina and V. G. Tronev, *Zh. Neorgan. Khim.*, **7**, 215, (1962); *Russ. J. Inorg. Chem.*, **7**, 108 1962).

TABLE I

ANALYTICAL DATA FOR $[Re_2Cl_8]^{2-}$ SALTS OBTAINED BY H_3PO_2 REDUCTION OF ReO_4^-

		Percentages of elements[a]							
		Cl		N		C		H	
Cation	Color of salt	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
$[(n\text{-}C_4H_9)_4N]^+$	Blue			2.56	2.46	33.7	33.60	6.29	6.35
$[C_5H_5NH]^+$	Dark green	34.9	34.65	3.40	3.42	14.8	14.66	1.65	1.73
$[C_8H_{11}NH]^+$	Dark green	30.9	31.42			21.4	21.29	2.84	2.88
$[(C_6H_5)_4As]^+$	Blue	19.9	19.93			39.8	40.51	2.95	2.84
$[(C_6H_5)_3CH_3As]^+$	Blue-green	21.9	22.32			34.9	35.08	2.79	2.78

[a] Most figures are the averages of at least two determinations, by Galbraith Analytical Laboratories, Knoxville, Tenn., and S. M. Nagy, M.I.T.

TABLE II

ANALYTICAL DATA FOR $[Re_2Cl_8]^{2-}$ COMPOUNDS PREPARED BY HYDROGEN REDUCTION

		Percentages of elements[a]							
		Re		Cl		N		H	
Compound	Color	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
$(NH_4)_2[Re_2Cl_8]\cdot 2H_2O$	Very dark green	50.5	51.14	39.1	38.98	3.97	3.84	1.62	1.65
$(NH_4)_2[Re_2Cl_8]$	Dark green	53.9	53.80	41.1	41.00	4.30	4.04	1.30	1.16
$K_2[Re_2Cl_8]\cdot 2H_2O$	Very dark green	48.5	48.33	36.9	36.84				
$K_2[Re_2Cl_8]$	Dark green	50.4	50.70	38.5	38.64				

[a] Results were provided by Galbraith Analytical Laboratories, Knoxville, Tenn., and S. M. Nagy, M.I.T.

one previously used by Russian workers[11-14] to obtain compounds which they formulated somewhat differently. Since the previous reports[11-14] are not very explicit as to experimental procedure, we give a detailed outline of a specific reaction. Analytical figures are given in Table II.

Potassium Octachlorodirhenate(III) Dihydrate.—Potassium perrhenate (0.5 g.) and concentrated hydrochloric acid (20 ml.), contained in a glass liner inside a steel bomb, were heated (T_{max} 290°) with hydrogen under pressure ($P_{initial}$ 50 atm.) for 1.5 hr. The product consisted of bright green-yellow crystals of K_2ReCl_6 and a deep blue solution. The green-yellow K_2ReCl_6 was filtered off and the deep blue filtrate taken to dryness under vacuum over P_2O_5 and NaOH pellets. The blue residue was then extracted into acetone and the blue solution evaporated slowly *in vacuo*. Dark green crystals were obtained; yield 38%.

Ammonium Octachlorodirhenate(III) Dihydrate was prepared similarly.

Anhydrous K and NH_4 Compounds.—These were obtained by heating the dihydrates for 0.5 hr. at 130°.

Other Compounds.—Compounds with the five cations mentioned in Table I were obtained by adding salts of such cations to the blue acetone solutions, since the resulting compounds are less soluble than the potassium and ammonium ones. The collidinium and pyridinium compounds can also be obtained by using the corresponding salts of $ReCl_6^{2-}$ as starting materials. All of these other compounds so obtained appeared identical in all respects with those with the same cations obtained by the H_3PO_2 reduction method, and we have no reason to doubt that they are in fact identical.

Determination of Valence State.—The basic chromate oxidation (to ReO_4^-) method recommended by the Noddacks,[15] and also used by the Russian workers, was employed. In a test run, 0.2019 g. of K_2ReCl_6 (0.4230 mmole) was treated with excess of a basic solution of CrO_4^{2-}, and 32.71 mg. (0.215 mmole) of Cr_2O_3 was isolated. Thus the original oxidation state is calculated to be $7 - (6 \times 0.215/0.423) = 3.95$, in satisfactory agreement with 4.00.

Triphenylmethylarsonium octachlorodirhenium(III), $[(C_6H_5)_3CH_3As]_2Re_2Cl_8$, (0.2362 g., 0.364 g.-atom of Re) was treated with excess of a basic solution of CrO_4^{2-} for an extended period of time (1 hr.) due to the insolubility of the compound; 37.93 mg. (0.250 mmole) of Cr_2O_3 was isolated. The oxidation state is therefore $7 - (6 \times 0.250/0.364) = 2.88$, which is within 4% of 3.00.

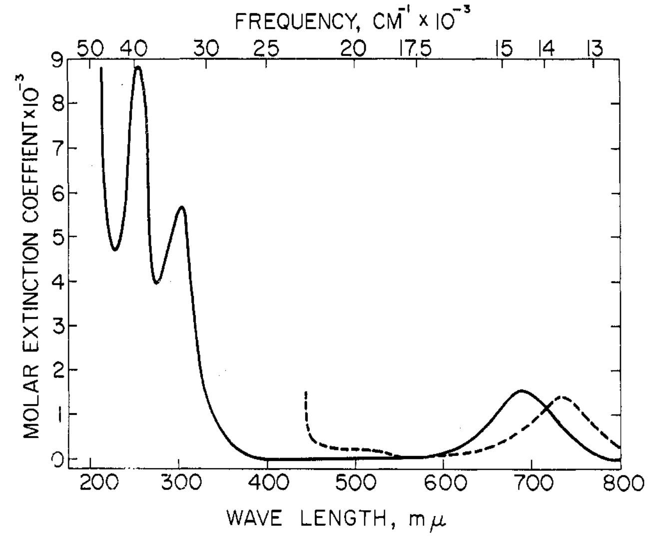

Figure 1.—Solid curve: the absorption spectrum of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$, 14 mg. per 100 ml. of methanol (containing 1 ml. of concentrated aqueous HCl per 100 ml.). Dashed curve: a portion of the spectrum of $[(n\text{-}C_4H_9)_4N]_2[Re_2Br_8]$ in acetone.

Magnetic Susceptibility.—The measurement was made on a powdered sample by the Gouy method.

Absorption Spectra.—These were recorded on a Cary Model 14 recording spectrophotometer. Typical spectra are given in Figure 1.

Electrolytic Conductances.—These were measured using a commercial Wheatstone bridge circuit. Results are collected in Table III.

Conversion of $[Re_2Cl_8]^{2-}$ to $Re_2(RCO_2)_4Cl_2$.—Tetra-*n*-butylammonium octachlorodirhenium(III) (0.5 g.) was refluxed for 10 min. in glacial acetic acid (50 ml.) containing about 1 ml. of acetic anhydride. The blue solid dissolved, at least partially, to give a blue solution. After about 20 min., the solution was purple and the solid was orange. The orange solid was filtered, washed with acetone, and dried under vacuum at 80°; yield 0.25 g., 85%.

---

(15) I. Noddack and W. Noddack, *Z. anorg. allgem. Chem.*, **215**, 182 (1933).

Anal. Calcd. for $C_8H_{12}Cl_2O_8Re_2$: C, 14.1; H, 1.8. Found: C, 14.2; H, 2.1.

Tetrabutylammonium octachlorodirhenium(III) (0.3 g.) was refluxed for about 1 hr. in a mixture of propionic acid (15 ml.) and propionic anhydride (5 ml.). The starting material dissolved completely or nearly completely to give a deep blue solution which gradually became red-purple while very small orange crystals precipitated. The product was washed with 6 *M* aqueous HCl, then acetone, and dried at 120°; yield 0.15 g., 80%.

Table III

Electrolytic Conductance Data for the $[Re_2Cl_8]^{2-}$ Compounds, and Others for Comparison, in Acetonitrile

Compound	Molarity	Temp., °C.	Molar conductivity, Λ_M, ohm^{-1} mole^{-1}
$(NH_4)_2[Re_2Cl_8]\cdot 2H_2O$	3.8×10^{-4}	27	290
$(NH_4)_2[Re_2Cl_8]$	4.9×10^{-4}	26	296
$K_2[Re_2Cl_8]\cdot 2H_2O$	3.7×10^{-4}	27	294
$K_2[Re_2Cl_8]$	4.4×10^{-4}	26	300
$[(C_6H_5)_3CH_3As]_2[Re_2Cl_8]$	5.0×10^{-4}	25	300
$[(n\text{-}C_4H_9)_4N][Re_2Cl_8]$	2.2×10^{-4}	26	298
$[(C_6H_5)_3CH_3As][FeCl_4]$	$\sim 10^{-3}$	25	150
$[(C_6H_5)_4As]_2[NiCl_4]$	$\sim 10^{-3}$	25	302
$[(CH_3)_4N]_2[CoCl_4]$	$\sim 10^{-3}$	25	294

Anal. Calcd. for $C_{12}H_{20}Cl_2O_8Re_2$: C, 19.6; H, 2.72. Found: C, 19.2; H, 2.68.

These reactions have also been carried out under anaerobic conditions. A few hundred milligrams of a $[Re_2Cl_8]^{2-}$ compound was placed in a tube and covered with several ml. of the acid to which a small amount of the anhydride was added. The tube was then attached to a vacuum line and pumped, frozen in liquid nitrogen, and thawed, this sequence of operations being repeated three times. The tube was then sealed off under vacuum and heated for 0.5–2.0 hr. at 60–80°. The blue solid began to dissolve when the heating commenced. Finally, there was only a pale blue color in the liquid and there was an orange solid. Further heating failed to diminish the blue color.

Conversion of $[Re(C_2H_5CO_2)_2Cl]_2$ to $[(C_6H_5)_4As]_2[Re_2Cl_8]$.—$[Re(C_2H_5CO_2)_2Cl]_2$ (0.2 g.) was treated with a refluxing mixture of 10 ml. of concentrated aqueous HCl and 10 ml. of propionic acid for 60 min. A considerable fraction of the orange solid dissolved to give a deep blue solution. A 50% excess (0.3 g.) of $(C_6H_5)_4AsCl$ was then added and the mixture refluxed for another 60 min. After cooling, the solution was filtered and 0.1 g. of $[(C_6H_5)_4As]_2[Re_2Cl_8]$ was isolated. The product was identified by analysis [*Anal.* Calcd. for $C_{48}H_{40}As_2Cl_8Re_2$: C, 40.51; H, 2.83. Found: C, 40.5; H, 3.04] and comparison of its X-ray powder diffraction pattern with that of an authentic sample of the compound, prepared as described earlier.

Discussion

The formulation of all the compounds reported here as compounds of $[Re_2X]_8^{2-}$ rather than of ReX_4^- or of $[Re_3X_{12}]^{3-}$ may be most conclusively justified by recourse to X-ray diffraction data, as indicated in the following paper.[16] We shall attempt to show here that other physical data are consistent with the presence of these dimeric anions and that these other data provide additional evidence that the anions are in fact precisely $[Re_2X_8]^{2-}$ and not species which either have a different charge or contain hydrogen. The presence or absence of hydrogen atoms cannot of course be decided solely from X-ray work.

Comparison with Prior Work.—Tronev and several co-workers have previously[11–14] studied blue and green compounds obtained by reduction of aqueous hydrochloric acid solutions of ReO_4^- with molecular hydrogen in a bomb at temperatures of the order of 300° and autogenous pressures of about 100 atm. Aside from their claim[12] to have obtained the rhenium(III) complexes, K_3ReCl_6 and $(NH_4)_3ReCl_6$, which we have already shown to be in error,[17] they have reported several compounds which they formulate as complexes of Re(II).

First, they reported[11,12] $(NH_4)_2ReCl_4$ and K_2ReCl_4, some reactions of which they described, but, so far as we can ascertain, no such compounds were formed when we attempted to duplicate their work. Curiously, these compounds are not mentioned again in their later and more detailed papers, all direct products of the reduction being assigned formulas of the type $M^IHReCl_4\cdot H_2O$.

According to Kotel'nikov and Tronev,[13] the major product aside from K_2ReCl_6 (K_3ReCl_6 is also not mentioned in this paper or in any others in the series except ref. 12) obtained on evaporating the dark blue liquor after filtering off K_2ReCl_6 is a compound to which they assign the formula $KHReCl_4\cdot H_2O$. This substance, which they repeatedly describe as "dark" without stating any particular color, was reported to lose weight at 130° corresponding closely to the expected amount for loss of one molecule of water. Both the hydrate and the anhydrous compound were reported to have Re and Cl analyses in good agreement with the proposed formulas. It was also stated that quantitative reduction of alkaline chromate to Cr_2O_3 demonstrated a valence of II for the rhenium. As far as we can tell, these compounds are identical with those we have isolated by a similar bomb reduction and which we formulate as the rhenium(III) compounds, $K_2[Re_2Cl_8]\cdot 2H_2O$ and $K_2[Re_2Cl_8]$, respectively. It is also claimed[13] that by bomb reduction of NH_4ReO_4 in place of $KReO_4$ the compound "$NH_4HReCl_4\cdot H_2O$" is obtained and that, again, the molecule of water can be readily removed giving "NH_4HReCl_4." So far as we can tell, we have also reproduced these compounds, which we formulate as $(NH_4)_2[Re_2Cl_8]\cdot 2H_2O$ and $(NH_4)_2[Re_2Cl_8]$, respectively.

Kotel'nikov and Tronev[13] also report various other compounds which they formulate as Re(II) complexes, but we have not yet attempted to prepare them and thus cannot and do not attempt to judge the correctness of the formulas they suggest in these other cases.

Evidence for the Formula $[Re_2Cl_8]^{2-}$.—Clearly, analytical figures for these compounds cannot satisfactorily distinguish between the formulas $M^I_2[Re_2Cl_8]\cdot nH_2O$ and $M^IHReCl_4\cdot(n/2)H_2O$ (or the corresponding dimer) where $n = 2$ or 0. The only piece of evidence presented by the Russian workers which would appear to offer direct support for their formulation as opposed to ours was the determination of oxidation state by reaction with alkaline CrO_4^{2-}. This method in our

---

(16) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **4**, 330 (1965).

(17) F. A. Cotton and B. F. G. Johnson, *ibid.*, **3**, 780 (1964).

hands, however, leads to the conclusion that we are dealing with Re(III).

The electrolytic conductances in acetonitrile, Table III, provide further evidence against the presence of protonic hydrogen. To begin with, it may be observed that these conductances do not in themselves discriminate between the monomeric, $[ReCl_4]^-$, and dimeric, $[Re_2Cl_8]^{2-}$, formulas. However, since, from X-ray work, dimeric formulas are known to be correct, the presence of protonic hydrogen would be difficult to reconcile with the observed conductances. For the hydrates, it would seem virtually certain that were the protons present they would attach themselves to the water molecules to give H_3O^+ ions, thus making the compounds 4:2 electrolytes. This, however, is scarcely possible since the molar conductances are practically the same as those for authentic 2:1 electrolytes. It might also be assumed that in the crystalline hydrates there would be H_3O^+ ions, but, as shown in the next paper,[16] the oxygen atoms are so close to the potassium ions in $K_2[Re_2Cl_8]\cdot 2H_2O$ that they must be part of H_2O molecules coordinated to K^+, whereas H_3O^+ ions would not approach K^+ ions very closely. Furthermore, if protons were present in the anhydrous compounds, it is difficult to imagine to what atoms they would be bound.

The possibility that the $[Re_2X_8]^{2-}$ ions might be $[Re_2X_8H_2]^{2-}$ ions, containing coordinated hydride ions, which was *not* suggested by Tronev, *et al.*, should also be examined. This is not ruled out by analytical data, by conductance data, by the X-ray structural work, or by the valence state determination since Re(IV) + H^- (assuming H^- would react quantitatively with CrO_4^{2-} to give H_2) would give the same result as Re(III). Besides several lines of physical evidence which make this appear unlikely, there is chemical evidence which disproves it quite conclusively. None of the infrared spectra of the compounds shows absorption attributable to an Re–H stretching mode, although metal–H stretches seem generally to give sharp, relatively strong absorption bands.[18] Much less conclusive is the fact that a search of the proton nuclear resonance spectra of several of the compounds revealed no absorption in the region of high shielding which is characteristic of hydrogen bound to transition metals.[18,19]

Chemical evidence which we believe conclusively favors the $[Re_2X_8]^{2-}$ formulas is provided by the forward and reverse reactions of the $[Re_2Cl_8]^{2-}$ salts with acetic and propionic acids to produce the $[Re(RCO_2)_2Cl]_2$ compounds which have recently been described and shown to be dimers by Taha and Wilkinson.[20] As shown in the Experimental section, when the reactions are carried out in sealed tubes from which all air has been removed by alternate freezing and pumping, the conversion of the blue solid to the yellow solid product is complete except for a light blue coloration in the liquid. Since these reaction conditions are neither oxidizing nor reducing in character, it would be very difficult to understand the reactions unless the rhenium is in the same oxidation state, namely the III state, in both the reactants and the products. In that case, however, the transformation is very simply explained by the reaction

$$[Cl_4Re{-}ReCl_4]^{2-} + 4RCO_2H = ClRe(RCO_2)_4ReCl(s) + 4HCl + 2Cl^- \qquad (1)$$

The light blue color of the liquid is presumably due to the equilibrium not lying entirely to the right so that a small amount of blue $[Re_2Cl_8]^{2-}$ remains in solution.

The reactions carried out on a preparative scale were not done with exclusion of air; the more intense, purple colors of the final solutions and the less than quantitative recovery of products evidently shows that there has been some oxidation to produce the purple carboxylate derivatives of Re(IV) and Re(V), also reported by Taha and Wilkinson.

The final and singularly conclusive piece of chemical evidence for the formula $[Re_2Cl_8]^{2-}$ comes from the direct observation that reaction 1 is readily reversible. When $[Re(C_2H_5CO_2)_2Cl]_2$ is treated with excess aqueous HCl and the cation $(C_6H_5)_4As^+$ added, it is converted to $[(C_6H_5)_4As]_2[Re_2Cl_8]$. This reaction was carried out in the presence of air. It seems inconceivable that either reduction of Re(III) to Re(II) or production of hydride ions could occur under these conditions.

It will be shown in a later paper that the eclipsed configuration of the $[Re_2Cl_8]^{2-}$ ion has a ready explanation if this is in fact the proper formula for it, whereas there would appear to be no explanation if it is $[Re_2Cl_8H_2]^{2-}$.

Preparation of the $[Re_2X_8]^{2-}$ Species.—There are three methods of preparation now known. Two of these consist in reduction of ReO_4^- in acid solution by either molecular hydrogen or by hypophosphorous acid. The third, which we have not yet attempted to optimize as a preparative procedure *per se*, is by conversion of the $[Re(R_2CO_2)_2X]_2$ compounds. At present we consider our hypophosphorous acid reduction method to be the most convenient. The reduction by molecular hydrogen requires the use of high pressure equipment which, unless constructed of special alloys, is subject to corrosion by the acid vapors and gives yields of only 35–40%. The reduction by hypophosphorous acid can be easily carried out on a large scale using only ordinary laboratory glassware, which compensates for the low yields, ~20%. Since the only available method[20] for making the $[Re(RCO_2)_2X]_2$ compounds for use as starting materials to synthesize $[Re_2X_8]^{2-}$ compounds requires the relatively expensive rhenium(III) chloride (or necessitates making this compound, which is not a simple operation) and produces yields of only ~10%, this route is at present quite unsuitable as a preparative procedure.

The reason for the low yields of $[Re_2X_8]^{2-}$ ions by reduction of ReO_4^- is not known. The by-product seems, in each method, to be largely or entirely $[ReX_6]^{2-}$. These ions are evidently not reduced at all,

---

(18) J. C. Chatt, *Proc. Chem. Soc.*, 318 (1962).

(19) Both Re^{185} and Re^{187} have nuclear spins of $^5/_2$; since J_{Re-H} would presumably be large,[18] the n.m.r. absorption would be spread over a considerable range, thus making it more difficult to detect.

(20) F. Taha and G. Wilkinson, *J. Chem. Soc.*, 5406 (1963).

or only slowly, to $[Re_2X_8]^{2-}$. It is also puzzling that no other reducing agents have been found which lead to any isolable quantity of $[Re_2X_8]^{2-}$ salts, although $NaBH_4$ and hydrazine have been tried under a variety of conditions. The mechanism by which the binuclear ions are formed from the mononuclear starting material is at present entirely obscure.

Characteristic Properties of the $[Re_2X_8]^{2-}$ Ions.—The magnetic susceptibility of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ was found to be -530×10^{-6} c.g.s. unit at 25°. From Pascal's constants[21] for the cations and the chlorine atoms, and taking -40×10^{-6} for a rhenium atom, we estimate the diamagnetic susceptibility to be about -600×10^{-6}. Thus, while there may be a small, probably temperature-independent paramagnetism, the $[Re_2Cl_8]^{2-}$ ion is essentially diamagnetic. It has no unpaired electrons and thus consists entirely of closed shells of electrons. A treatment of its electronic structure must account for this fact.

Other properties of the $[Re_2X_8]^{2-}$ compounds have been mentioned and discussed above. It remains only to report their electronic spectra.

Electronic Absorption Spectra.—The electronic absorption spectra in the visible and near-ultraviolet regions for the $[Re_2Cl_8]^{2-}$ and $[Re_2Br_8]^{2-}$ ions have been measured by reflectance on all the compounds prepared and are essentially constant and characteristic. Figure 1 shows the complete spectrum of the $[Re_2Cl_8]^{2-}$ ion from 200 to 800 mμ and Table IV gives numerical data for this spectrum recorded in acidified methanol as well as for spectra recorded in other solvents.

Table IV

Spectral Data for $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$

Solvent	Maxima mμ	Maxima cm.⁻¹	Molar extinction coeff.	Oscillator strength[a]
Methanol[b]	690	14,500	1530	0.023
	305	32,800	5650	0.31
	255	39,200	8840	0.65
Acetonitrile	680	14,700	2340	0.035
	307	32,600	8670	0.48
	250	40,000	9970	0.73
Acetone	680	14,700	2480	0.030

[a] Calculated from the formula $f = 4.6 \times 10^{-9}\epsilon_{max}\Delta\nu$, where ϵ_{max} is the decadic molar extinction coefficient and $\Delta\nu$ is the frequency difference, in cm.⁻¹, between the points where ϵ is ~0. For the higher energy peaks, $\Delta\nu$ is estimated by resolution of the observed envelope into Gaussian peaks. [b] Containing 1 ml. of concentrated aqueous HCl per 100 ml.

It may first be noted that this spectrum is quite different from that of the $[Re_3Cl_{12}]^{3-}$ ion, or those of any compounds containing the Re_3Cl_9 group,[4-6] and is sufficient evidence, in itself, that we are dealing here with a different type of compound.

The spectrum consists of three bands, one at ~14,500 cm.⁻¹ which, from its oscillator strength of ~0.03, is a forbidden band and two others at ~33,000 and ~40,000 cm.⁻¹ which are presumably electric-dipole-allowed transitions since their oscillator strengths are ~0.4 and ~0.7, respectively. Discussion of the assignments of these bands will be given in a later article. The spectrum of the $[Re_2Br_8]^{2-}$ ion is similar to that of the $[Re_2Cl_8]^{2-}$ ion in the red, but absorption rises sharply around 450 mμ. More extensive experimental studies of the spectra are being conducted.

---

[21] See, for example, P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, New York, N. Y., 1956, p. 93.

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts

The Crystal and Molecular Structure of Dipotassium Octachlorodirhenate(III) Dihydrate, $K_2[Re_2Cl_8] \cdot 2H_2O$[1]

By F. A. Cotton and C. B. Harris

Received September 22, 1964

A three-dimensional, single crystal X-ray diffraction study of the structure of $K_2[Re_2Cl_8] \cdot 2H_2O$ is reported. The crystals are triclinic with $a = 6.75$, $b = 7.86$, and $c = 7.61$ Å. and $\alpha = 102.0°$, $\beta = 109°$, and $\gamma = 105°$. There is one formula unit in the cell, and the space group is $P\bar{1}$. The $[Re_2Cl_8]^{2-}$ ion therefore has a center of symmetry; its idealized point symmetry is 4/mmm (D_{4h}). The mean Re–Cl distance is 2.29 Å., the mean Re–Re–Cl angle is 104°, the mean Cl–Re–Cl angle is 87°, and the Re–Re distance is 2.24 Å. The water molecules are coordinated to K^+ ions.

Introduction

The preparation and characterization of compounds containing the octachlorodirhenate(III) and octabromodirhenate(III) ions, $[Re_2Cl_8]^{2-}$ and $[Re_2Br_8]^{2-}$, has been reported.[2] The full characterization of these species requires both chemical and X-ray evidence. The preceding paper[2] describes the chemistry and certain physical properties of various compounds; this paper reports an X-ray diffraction study of the crystal and molecular structure of one such compound, namely, $K_2[Re_2Cl_8] \cdot 2H_2O$, of sufficient accuracy to show unambiguously the structure of the $[Re_2Cl_8]^{2-}$ ion.

Experimental

The crystals of $K_2[Re_2Cl_8] \cdot 2H_2O$ were obtained from a sample of the compound prepared in a manner described elsewhere.[2]

---

[1] Supported by the U. S. Atomic Energy Commission.

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