plexes believed to contain a Re–Re bond. The spectrum was dominated by an intense broad band centered ~17,400 cm^{-1} which would probably obscure any band due to the $\delta \rightarrow \sigma_n$ transition. This higher energy band may arise from a charge-transfer transition of the type bipy(π)→Re.

Under sufficiently acid conditions the bipyridinium salt $(bipyH)_2Re_2Cl_8$ could be isolated.

On refluxing $Re_2Cl_8^{2-}$ with tris(2-cyanoethyl)phosphine in absolute ethanol, the red complex $ReCl_3(CEP)_2 \cdot C_2H_5OH$ could be prepared. The free ligand C≡N stretching frequency (2240 cm^{-1}) was unaffected by complex formation, consistent with the ligand being only phosphorus bonded. The diffuse reflectance spectrum of the complex indicated that the Re–Re bond had been broken, so that octahedral rhenium(III) with coordinated ethanol or a chlorine-bridged dimer with a molecule of ethanol in the lattice (or weakly hydrogen-bonded to the uncoordinated nitrile groups) seem the most likely structural formulations.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS 02139

The Stability and Reactivity of a New Form of Rhenium(IV) Chloride: Studies on Its Disproportionation in Solution[1]

BY F. ALBERT COTTON, WILLIAM R. ROBINSON, AND RICHARD A. WALTON

Received August 13, 1966

Acidified methanol or acetone solutions of black crystalline rhenium(IV) chloride react with halide ion and other donors to form complexes containing the $Re_2X_8^{2-}$ ion or species derived from this dimer, for example, $Re_2(O_2CCH_3)_4Cl_2$, $Re_2(O_2CCH_3)_2Cl_4 \cdot 2H_2O$, and $[ReCl_3P(C_6H_5)_3]_n$. The new complex $[ReCl_3As(C_6H_5)_3]_n$ was also prepared and characterized. In addition, the following oxorhenium(V) complexes were isolated: $ReOCl_3[P(C_6H_5)_3]_2$, $ReOCl_3(bipy)$, $[ReO_2(py)_4]Cl \cdot 2H_2O$, and $Re_2O_3(py)_4Cl_4$. In no instance were rhenium(IV) complexes of the type $ReCl_4L_2$ prepared, and it was only in the complex $[(C_6H_5)_4As]_2Re_2Cl_9$ that rhenium(IV) was believed to be stabilized. This chloro complex is believed to be dinuclear and to contain rhenium in its +3 *and* +4 oxidation states; *i.e.*, a mean formal oxidation state of 3.5. The disproportionation of rhenium(IV) chloride into rhenium(III) and rhenium(V) appears to be quite general in solution. The rhenium(IV) chloride (β form) studied in the present work is believed to be a different form from that already reported in the literature (α). The reaction of rhenium(V) chloride with pyridine has been reinvestigated. Bands due to the Re═O and Re—O—Re stretching vibrations have been assigned in the infrared spectrum of $Re_2O_3(py)_4Cl_4$.

Introduction

The chemistry of rhenium(III) is dominated by the occurrence of metal atom clusters of the types Re_3X_9 and $Re_2X_8^{2-}$, whose stability, reactivity,[2-11] and electronic[12-14] and molecular[15-19] structures have attracted considerable attention in recent years. In 1963 the preparation of rhenium(IV) chloride was reported for the first time,[20] and its magnetic properties have since been interpreted[21] in terms of the trinuclear cluster Re_3Cl_{12}, structurally similar to $Re_3Cl_{12}^{3-}$.[16] However, other than a brief examination of its solubility properties and thermal instability,[20] this substance was not studied further. Brown and Colton[20] also mentioned that they were unable to obtain an X-ray diffraction pattern of this substance, although they reported that "rhenium tetrachloride appears to be crystalline."

We have recently acquired a sample of pure *crystalline* rhenium(IV) chloride and in the present paper report several aspects of its chemical reactivity and stability. Evidence is presented that the sample of rhenium(IV) chloride investigated in the present work is a different form (β) from that prepared by Brown and Colton.[20] The latter form will subsequently be designated α.

Experimental Section

Black crystalline rhenium(IV) chloride was obtained from the S. W. Shattuck Co., Denver, Colo. It was supplied as a sample of "rhenium(III) chloride," and in a subsequent communication

---

(1) This work was supported by the U. S. Atomic Energy Commission under Contract AT(30-1)-1965 and the National Science Foundation under grant No. GP-4329.

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

(3) F. Taha and G. Wilkinson, *ibid.*, 5406 (1963).

(4) N. P. Johnson, C. J. L. Lock, and G. Wilkinson, *ibid.*, 1054 (1964).

(5) F. A. Cotton, S. J. Lippard, and J. T. Mague, *Inorg. Chem.*, **4**, 508 (1965).

(6) F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *ibid.*, **4**, 326 (1965).

(7) F. A. Cotton, N. F. Curtis, and W. R. Robinson, *ibid.*, **4**, 1969 (1965).

(8) B. H. Robinson and J. E. Fergusson, *J. Chem. Soc.*, 5683 (1965).

(9) F. A. Cotton, C. Oldham, and W. R. Robinson, *Inorg. Chem.*, **5**, 1798 (1966).

(10) F. A. Cotton and R. A. Walton, *ibid.*, **5**, 1802 (1966).

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

(12) F. A. Cotton and T. E. Haas, *ibid.*, **3**, 10 (1964).

(13) F. A. Cotton, *ibid.*, **4**, 334 (1965).

(14) J. E. Fergusson, B. R. Penfold, M. Elder, and B. H. Robinson, *J. Chem. Soc.*, 5500 (1965).

(15) W. T. Robinson, J. E. Ferguson, and B. R. Penfold, *Prod. Chem. Soc.*, 116 (1963).

(16) J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *Inorg. Chem.*, **2**, 1166 (1963).

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

(18) F. A. Cotton and J. T. Mague, *ibid.*, **3**, 1402 (1964).

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

(20) D. Brown and R. Colton, *Nature*, **198**, 300 (1963).

(21) R. Colton and R. L. Martin, *ibid.*, **205**, 239 (1965).

with this company we were informed "that it was prepared by the thermal decomposition of rhenium(V) chloride in a nitrogen sweep in the temperature range 350–375°." Temperatures in excess of this gave the expected trimer Re_3Cl_9.

Anal. Calcd for $ReCl_4$: Re, 56.75; Cl, 43.25. Found: Re, 56.62, 56.92; Cl, 43.40, 43.03.

The identity of the substance as rhenium(IV) chloride is also indicated by a preliminary single crystal X-ray examination. Intensity data have now been collected for a complete structure analysis.

Attempts to repeat this preparation have so far been unsuccessful. Dr. F. Bonati has found[22] that only Re_3Cl_9 is obtained under conditions mentioned above and at present work is in hand to ascertain the *exact* conditions under which rhenium(IV) chloride is formed. Further communications with interested workers in this field will be welcome.

Properties.—β-Rhenium(IV) chloride is attacked by moisture with resulting formation of a sticky black mass. It is insoluble in dry acetonitrile, tetrahydrofuran, and nonpolar solvents, but soluble with reaction in methanol, absolute ethanol, acetone, dimethyl sulfoxide, and concentrated hydrochloric acid. It appears to disproportionate into rhenium(V) and rhenium(III) chlorides when heated in a nitrogen atmosphere at 280–300°.[22]

Reactions of Rhenium(IV) Chloride. (1) **Aqueous Hydrochloric Acid in the Presence of $R_4M^+X^-$.** $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$.—To a hot solution of 0.43 g of $ReCl_4$ in 100 ml of 6 *N* HCl was added 0.6 g of tetra-*n*-butylammonium bromide. The solution was digested at 95° for 1 hr and then filtered to recover the blue insoluble product. The material was washed with 6 *N* HCl and recrystallized from 150 ml of hot methanol by addition of 50 ml of concentrated HCl and subsequent evaporation of the methanol on a steam bath; yield 0.19 g.

Anal. Calcd for $C_{32}H_{72}N_2Re_2Cl_8$: C, 33.60; H, 6.35; N, 2.46. Found: C, 33.92; H, 6.65; N, 2.13.

The following salts were prepared from $ReCl_4$ in a similar manner.

$[(n\text{-}C_4H_9)_4N]_2Re_2Br_8$.—From 0.74 g of $ReCl_4$; yield 0.15 g.

Anal. Calcd for $C_{32}H_{72}N_2Re_2Br_8$: C, 25.67; H, 4.81; N, 1.87. Found: C, 23.90; H, 4.89; N, 1.39.

This complex was soluble in acetonitrile and a 1.23×10^{-1} *M* solution in this solvent had $\Lambda_M = 342$ ohm^{-1} cm^2, close to that expected for a 2:1 electrolyte in this solvent.[6]

$[C_5H_5NH]_2Re_2Cl_8$.—From 0.50 g of $ReCl_4$; yield 0.20 g.

Anal. Calcd for $C_{10}H_{12}N_2Re_2Cl_8$: C, 14.66; H, 1.73. Found: C, 14.68; H, 1.68.

$[(C_5H_5NH]_2Re_2Br_8$.—From 0.50 g of $ReCl_4$; yield 0.36 g.

Anal. Calcd for $C_{10}H_{12}N_2Re_2Br_8$: C, 10.25; H, 1.03. Found: C, 10.78; H, 1.41.

The infrared spectra of the above salts showed only bands characteristic of the cations. No bands attributable to the Re=O group were observed.

In the reaction of $ReCl_4$ with tetraphenylarsonium chloride in hydrochloric acid, the product isolated depended upon the experimental conditions used.

(a).—$ReCl_4$ (0.75 g) was dissolved in 50 ml of HCl and 150 ml of methanol on a steam bath, and 1.5 g of $[(C_6H_5)_4As]Cl$ in 25 ml of methanol was added. The solvent was evaporated to half volume and cooled, and the blue-green insoluble salt $[(C_6H_5)_4As]_2Re_2Cl_8$ was separated by filtration, washed with HCl, methanol, ethanol, and ether, and dried under vacuum; yield 0.75 g.

Anal. Calcd for $C_{48}H_{40}As_2Re_2Cl_8$: C, 40.51; H, 2.84. Found: C, 41.30; H, 3.03.

(b).—The reaction at 25–30° of 0.37 g of $ReCl_4$ dissolved in 70 ml of methanol containing 0.4 ml of 12 *N* HCl with 0.55 g of $[(C_6H_5)_4As]Cl$ gave a violet, insoluble product. The reaction mixture was stirred for 30 min and filtered, and the insoluble complex was washed three times with 20-ml portions of methanol and ether; yield 0.43 g.

Anal. Calcd for $C_{48}H_{40}As_2Re_2Cl_9$ (*i.e.*, $[(C_6H_5)_4As]_2Re_2Cl_9$): C, 39.54; H, 2.76; As, 10.28; Cl, 21.9. Found: C, 39.45; H, 2.79; As, 9.66; Cl, 21.14. ($[(C_6H_5)_4As]_2Re_2Cl_8$ requires 19.93% Cl.)

The infrared spectra from 650 to 4000 cm^{-1} of $[(C_6H_5)_4As]_2Re_2Cl_8$ and $[(C_6H_5)_4As]_2Re_2Cl_9$ were essentially identical.

The reactions of this violet complex are shown below.

(i) It decomposed to the insoluble blue salt $[(C_6H_5)_4As]_2Re_2Cl_8$ on shaking with acetone or acetonitrile at room temperature.

Anal. Found: C, 40.32; H, 2.92.

(ii) A 0.25-g sample was heated with 30 ml of concentrated HCl for 14 hr at 95°. The blue precipitate of the corresponding $Re_2Cl_8^{2-}$ salt was filtered off and washed with methanol and ether; yield 0.15 g.

Anal. Found: C, 41.21; H, 3.29.

(iii) A 0.9-g sample was refluxed under nitrogen for 1 hr with 30 ml of acetic acid containing 5 ml of acetic anhydride. The orange precipitate was filtered off, washed with methanol and ether, and dried *in vacuo* at room temperature; yield 0.32 g.

Anal. Calcd for $C_8H_{12}O_8Re_2Cl_2$ (*i.e.*, $Re_2(O_2CCH_3)_4Cl_2$):[3,9] C, 14.14; H, 1.78. Found: C, 14.69; H, 1.56.

The infrared spectrum of this complex was identical with that of an authentic sample.[3]

(iv) A 0.1-g sample was warmed on a steam bath for 10 min with 10 ml of methanol containing 0.5 ml of hydriodic acid. A black microcrystalline solid separated and was filtered off and washed with methanol and ether.

Anal. Found: C, 31.59; H, 2.22; Cl, 5.72; I, 34.12. Complete halogen exchange could not be effected, in keeping with our observations on the reaction of $[(n\text{-}C_4H_9)_4N]Re_2Cl_8$ with methanol–hydriodic acid.[23]

(c).—A procedure similar to (a) but using methanol–hydriodic acid as solvent gave a purple crystalline product containing both chlorine and iodine.

Anal. Found: C, 38.55; H, 2.51; As, 10.25; Cl, 17.25; I, 8.18.

(2) **Acetic Acid.** $Re_2(O_2CCH_3)_4Cl_2$.—$ReCl_4$ (0.5 g) was refluxed under nitrogen with 30 ml of acetic acid for 12 hr. The orange complex was filtered off and washed with ethanol and ether; yield 0.2 g.

Anal. Calcd for $C_8H_{12}O_8Re_2Cl_2$: C, 14.14; H, 1.78; Cl, 10.43. Found: C, 13.93; H, 2.13; Cl, 10.60.

$Re_2(O_2CCH_3)_2Cl_4 \cdot 2H_2O$.—$ReCl_4$ (0.3 g) was dissolved with warming in 15 ml of 12 *N* HCl and 10 ml of acetic acid added. The blue solution was allowed to evaporate slowly to dryness at room temprature over a period of 2 weeks. The very dark blue residue was washed sparingly with acetone and ether and dried under vacuum.

Anal. Calcd for $C_4H_{10}O_6Re_2Cl_4$: Cl, 21.22. Found: Cl, 21.48. This complex had an infrared spectrum identical with that of an authentic sample of $Re_2(O_2CCH_3)_2Cl_4 \cdot 2H_2O$.[10]

(3) **2,5-Dithiahexane (DTH).** $(ReCl_3(DTH))_n$.—$ReCl_4$ (0.1 g) was dissolved in methanol–hydrochloric acid solution and excess DTH added. The solution was allowed to stand overnight, during which time the initial dark green solution turned pale orange and a brown solid precipitated. The complex was isolated by filtration, washed with methanol and ether, and dried *in vacuo*.

Anal. Calcd for $C_4H_{10}S_2ReCl_3$: C, 11.59; H, 2.43; S, 15.46. Found: C, 11.78; H, 2.53; S, 15.94.

The infrared spectrum of this complex was identical with that of a sample of $(ReCl_3(DTH))_n$ prepared from $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$.[10]

(4) **Thiourea (tu).** $ReCl_3(tu)_3 \cdot {}^1/_3(CH_3)_2CO$.—$ReCl_4$ (0.18 g) was dissolved in 20 ml of acetone, and 0.20 g of thiourea was added. The orange-red complex precipitated and was filtered off and washed with acetone, dichloromethane, and ether; yield 0.07 g.

Anal. Calcd for $C_3H_{12}N_6S_3ReCl_3 \cdot (C_3H_6O)_{0.33}$: C, 8.97; H,

---

(22) F. Bonati, unpublished observations in these laboratories.

(23) R. A. Walton, unpublished observations.

2.77; N, 15.74; S, 17.69. Found: C, 7.50; H, 2.65; N, 15.01; S, 16.63.

The analytical data indicated that this complex was contaminated with an impurity. However, its infrared and diffuse reflectance spectra and solubility properties were very similar to those of an authentic sample of $ReCl_3(tu)_3 \cdot {}^1/_3(CH_3)_2CO$.[10]

(5) **Triphenylphosphine.** **$[ReCl_3P(C_6H_5)_3]_n$.**—Triphenylphosphine (1 g) was added to 0.65 g of $ReCl_4$ dissolved in 150 ml of methanol containing 5 ml of hydrochloric acid, and the reaction mixture was stirred for 1 hr. The green precipitate that formed was filtered off, washed with acetone and ether, and dried *in vacuo;* yield 0.55 g.

Anal. Calcd for $C_{18}H_{15}PReCl_3$: C, 38.95; H, 2.72. Found: C, 40.91; H, 3.19.

The infrared spectrum of this complex had a band of medium-weak intensity at 975 cm^{-1}, suggesting some contamination with $ReOCl_3[(C_6H_5)_3P]_2$.

$ReOCl_3[(C_6H_5)_3P]_2$.—$ReCl_4$ (0.2 g) was dissolved in 20 ml of reagent grade acetone, and the green solution was allowed to stand for 1 day in contact with the atmosphere. An acetone solution of triphenylphosphine was then added, and the green insoluble complex was filtered off and washed with acetone and ether.

Anal. Calcd for $C_{36}H_{30}OP_2ReCl_3$: C, 52.00; H, 3.61. Found: C, 51.89; H, 4.08.

This complex had a strong band at 975 cm^{-1} in its infrared spectrum, assigned to $\nu(Re{=}O)$.

(6) **Triphenylarsine.** **$[ReCl_3As(C_6H_5)_3]_n$.**—This yellow-green complex was obtained in low yield by mixing acetone solutions of $ReCl_4$ and triphenylarsine at room temperature.

Anal. Calcd for $C_{18}H_{15}AsReCl_3$: C, 36.11; H, 2.53. Found (for separate preparations): C, 37.36, 37.86; H, 2.96, 2.96.

As for its triphenylphosphine analog this complex was contaminated with a trace of $ReOCl_3[As(C_6H_5)_3]_2$. It was insoluble in acetone, ether, dichloromethane, tetrahydrofuran, and acetonitrile.

(7) **2,2′-Bipyridyl.** **$ReOCl_3$(bipy).**—Mixing acetone solutions of the reactants gave a brown precipitate and red-brown solution. The insoluble product was removed by filtration, and excess of 12 *N* HCl was added to the filtrate, which turned dark green in color. The solvent was evaporated to low bulk when a heterogeneous green-yellow solid separated. This was filtered off and extracted with boiling acetone to give a green soluble product and a bright yellow insoluble residue.

Soluble product. *Anal.* Calcd for $C_{10}H_8N_2OReCl_3$: C, 25.84; H, 1.95; N, 6.03. Found (for separate preparations): C, 25.43, 26.09; H, 1.58, 1.82; N, 5.91, 6.54.

Insoluble product. *Anal.* Calcd for $C_{10}H_9N_2OReCl_4$ (*i.e.*, [bipyH]$ReOCl_4$): C, 23.96; H, 1.81; N, 5.59. Found (for separate preparations): C, 22.82, 23.68; H, 1.91, 1.97; N, 5.56, 5.60.

In the infrared spectrum of $ReOCl_3$(bipy), $\nu(Re{=}O)$ was assigned to a strong band at 975 cm^{-1}. No such band was observed in the spectrum of [bipyH]$ReOCl_4$. This latter product was insoluble in common polar and nonpolar solvents.

The filtrate from the reaction of $ReCl_4$ with 2,2′-bipyridyl was allowed to evaporate slowly at room temperature without the addition of HCl. A blue-green insoluble powder precipitated and was filtered off and washed with hot acetone and ether.

Anal. Calcd for $C_{20}H_{18}N_4Re_2Cl_8$ (*i.e.*, [bipyH]$_2Re_2Cl_8$): C, 24.76; H, 1.87; N, 5.78; Cl, 29.25. Found: C, 26.55; H, 2.01; N, 6.33; Cl, 28.32.

The remaining filtrate was evaporated further to yield a small amount of the green-yellow complex $ReOCl_3$(bipy), which was filtered off and washed sparingly with cold acetone and ether.

Anal. Found: C, 25.80; H, 1.70; N, 6.33.

(8) **Pyridine.** **$Re_2O_3(C_5H_5N)_4Cl_4$.**—$ReCl_4$ was dissolved in acetone and excess of pyridine added dropwise with stirring. The pale green precipitate that formed was filtered off and washed with acetone and ether.

Anal. Found: C, 18.16; H, 1.89; N, 2.90; Cl, 33.14.

A portion of it was suspended in acetone containing a few milliliters of 12 *N* HCl, and the mixture was refluxed for 1 hr. The blue-green insoluble powder was filtered off, washed with acetone and ether, and dried *in vacuo*.

Anal. Calcd for $C_{10}H_{12}N_2Re_2Cl_8$: C, 14.66; H, 1.73; N, 3.42. Found: C, 14.66; H, 1.50; N, 3.70.

The infrared spectrum of this product was identical with that of the sample of $[C_5H_5NH]_2Re_2Cl_8$ prepared previously and showed only bands characteristic of the pyridinium cation.

The original filtrate, which remained after removal by filtration of the pale green insoluble product, was now treated with a few drops of 30% hydrogen peroxide. The solution turned blue and then violet and bright green crystals slowly separated. These were filtered off, washed with acetone and ether, and dried *in vacuo*.

Anal. Calcd for $C_{20}H_{20}N_4O_3Re_2Cl_4$: C, 27.34; H, 2.30; N, 6.38; Cl, 16.14. Found: C, 27.34; H, 2.60; N, 6.62; Cl, 16.65.

The infrared spectrum of this complex was identical with that of the product of the same composition prepared from $ReCl_5$ (see later).

$[ReO_2(C_5H_5N)_4]Cl \cdot 2H_2O$.—Excess of pyridine was added to an acetone solution of $ReCl_4$ and the reaction mixture refluxed for 5 hr. After this time the insoluble green product was filtered off and washed with acetone and ether.

Anal. Found: C, 15.95; H, 2.00; N, 3.67.

The analytical data and infrared spectrum of this product suggested it was impure $[C_5H_5NH]_2Re_2Cl_8$.

The red filtrate remaining after the removal of this insoluble green powder was allowed to evaporate slowly at room temperature to yield a mixture of green and orange crystals. These were separated by hand, the green crystals were discarded (Re_2O_3(py)$_4Cl_4$?), and the orange product was washed with acetone and ether.

Anal. Calcd for $C_{20}H_{24}N_4O_3ReCl$: C, 39.63; H, 3.99; N, 9.25. Found: C, 39.78; H, 4.25; N, 9.03.

The infrared spectrum of these orange crystals confirmed their formulation as $[ReO_2(py)_4]Cl \cdot 2H_2O$ (see later).

(9) **Other Reactions.** (a).—$ReCl_4$ was treated with triphenylphosphine and $[(C_6H_5)_4As]Cl$ after the halide had been allowed to stand for 1 week in contact with the atmosphere.

The sticky brown-black residue was dissolved in acetone, and excess of triphenylphosphine was added. The green-yellow complex $[ReCl_3P(C_6H_5)_3]_n$ slowly precipitated.

Anal. Calcd for $C_{18}H_{15}PReCl_3$: C, 38.95; H, 2.72. Found: C, 40.91; H, 3.19.

Reaction with $[(C_6H_5)_4As]Cl$ in acidified acetonitrile solution gave the blue-green crystalline salt, $[(C_6H_5)_4As]_2Re_2Cl_8$.

Anal. Calcd for $C_{48}H_{40}As_2Re_2Cl_8$: C, 40.51; H, 2.84. Found: C, 40.99; H, 2.93.

(b). **The Reaction of Rhenium(V) Chloride with Pyridine.**—Johnson, *et al.*,[24] have reported the preparation of the complex $Re_2O_3(py)_4Cl_4$ from the reaction of $ReCl_5$ with pyridine in acetone. We were unable to repeat their preparation procedure, although $Re_2O_3(py)_4Cl_4$ and $[ReO_2(py)_4]Cl \cdot 2H_2O$ were isolated from the reaction mixture.

The reaction of $ReCl_5$ with pyridine in acetone solution (using the recommended quantities of reagents)[24] gave a violet solution and a dark green insoluble powder. This insoluble product was filtered off, but found to be completely insoluble in dichloromethane contrary to the reports of Johnson, *et al.*[24] It is therefore not $Re_2O_3(py)_4Cl_4$ as was anticipated.

The reaction was then repeated using a sample of $ReCl_5$ which had been allowed to age for a further week. This gave an insoluble green product and a green solution. After filtration, the filtrate was allowed to evaporate slowly at room temperature to give a mixture of green and orange crystals which could be separated by hand.

Green crystals. *Anal.* Calcd for $C_{20}H_{20}N_4O_3Re_2Cl_4$: C, 27.34; H, 2.30; N, 6.38. Found: C, 27.75; H, 2.42; N, 6.25.

---

[24] N. P. Johnson, F. I. M. Taha, and G. Wilkinson, *J. Chem. Soc.*, 2614 (1964).

This complex was insoluble in ethanol but slightly soluble in acetone, acetonitrile, and nitromethane.

Orange crystals. *Anal.* Calcd for $C_{20}H_{24}N_4O_2ReCl$: C, 39.63; H, 3.99; N, 9.25. Found: C, 40.23; H, 4.13; N, 9.64.

Physical Measurements.—The visible and ultraviolet spectra of solutions were run on a Cary Model 14 recording spectrophotometer using 1.0-cm matched quartz cells. Diffuse reflectance spectra were obtained with a Beckman DU spectrophotometer. Infrared spectra of Nujol mulls were recorded from 4000 to 650 cm^{-1} using Perkin-Elmer Model 337 and 237B grating spectrophotometers.

The molar susceptibility of $[(C_6H_5)_4As]_2Re_2Cl_9$ was measured at room temperature by the Gouy method. The molar susceptibility, corrected for diamagnetism (-630×10^{-6}) was 482×10^{-6} cgs unit at 302°K; using the Curie law, this leads to μ_{eff} = 1.08 BM.

Results and Discussion

Although several rhenium(IV) complexes of the types $ReCl_4L_2$[25-27] and $ReCl_6^{2-}$[28] are known, they are invariably prepared by oxidation or reduction procedures on other rhenium complexes. The present work has shown that β-rhenium(IV) chloride reacts to give complexes of rhenium(III) and/or rhenium(V). There is evidence for the stabilization of rhenium(IV) in one of the complexes isolated in the present work, but the simple adducts $ReCl_4L_2$ were not isolated.

Chemical evidence that this halide is not a mixture of rhenium(III) chloride (Re_3Cl_9) and rhenium(V) chloride is provided by its insolubility in acetonitrile (Re_3Cl_9 is very soluble[11]) and its failure to form complexes of the type $Re_3Cl_9L_3$.[11] It is unstable thermally[22] and in solution with respect to its disproportionation into rhenium(III) and rhenium(V) chlorides. On the other hand, Brown and Colton[20,29] report that on heating α-rhenium(IV) chloride, it decomposes into rhenium(VI) chloride. The α form is also soluble in acetone and in dry acetonitrile to give reddish brown solutions, whereas β-rhenium(IV) chloride, although soluble in acetone to give a green solution, is insoluble in acetonitrile. From the available evidence it appears that two different forms of this halide exist.

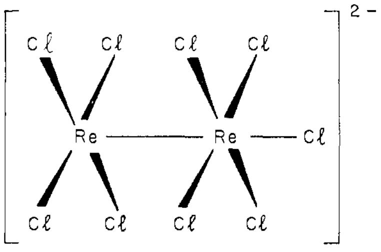
From acidified methanol solutions of β-rhenium(IV) chloride the dimeric rhenium(III) complexes $[ReCl_3(DTH)]_n$, where DTH = 2,5-dithiahexane, and $M_2Re_2X_8$, where M = $(n\text{-}C_4H_9)_4N^+$, $(C_6H_5)_4As^+$, or $C_5H_5NH^+$ and X = Cl or Br, can be isolated. Similarly, from the reaction of this halide with acetic acid, the previously reported[3,9,10] binuclear acetates $Re_2(O_2CCH_3)_4Cl_2$ and $Re_2(O_2CCH_3)_2Cl_4 \cdot 2H_2O$ were prepared. Thus, dissolving rhenium(IV) chloride in acid solution almost certainly yields a dimeric rhenium(III) species, in addition to any oxidized rhenium products (*e.g.*, rhenium(V)).

Triphenylphosphine and triphenylarsine gave the insoluble green complexes $[ReCl_3P(C_6H_5)_3]_n$[7] and $[ReCl_3As(C_6H_5)_3]_n$ when added to freshly prepared acetone solutions of rhenium(IV) chloride. Unfortunately these products were contaminated with small amounts of the analogous oxorhenium(V) complexes $ReOCl_3L_2$. Acetone solutions of this halide oxidize on standing, as evidenced by the isolation of $ReOCl_3[P(C_6H_5)_3]_2$ rather than the monophosphine rhenium(III) complex. As discussed previously,[10] $[ReCl_3L]_n$ complexes are almost certainly dinuclear[29a] and are identical (infrared and diffuse reflectance spectra) with the products obtained from the direct reaction of the $Re_2X_8^{2-}$ ions with L.[7,10]

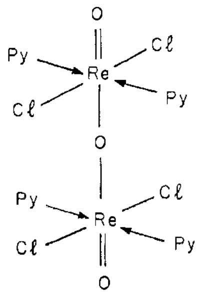
The diffuse reflectance spectra of $[ReCl_3P(C_6H_5)_3]_n$ and $[ReCl_3As(C_6H_5)_3]_n$ were almost identical (Figure 1) and closely resemble those of other nontrinuclear complexes of the type $[ReCl_3L]_n$.[10]

The complexes $[ReCl_3P(C_6H_5)_3]_n$ and $[(C_6H_5)_4As]_2Re_2Cl_8$ were also prepared from a sample of rhenium(IV) chloride which had been exposed to moist air. The most likely explanation of this stabilization of rhenium(III) even in the hydrolyzed halide is that hydrochloric acid, formed by hydrolysis, reacts with any rhenium(III) species to form $Re_2Cl_8^{2-}$, or a related chloro complex. This then resists further attack by air and moisture.

The violet compound $[(C_6H_5)_4As]_2Re_2Cl_9$, which has a room-temperature magnetic moment of ~1.1 BM, can reasonably be formulated as a dinuclear anionic complex containing rhenium in two oxidation states (+3 and +4). A structure such as I, based upon the dimeric $Re_2Cl_8^{2-}$ ion[19] (which is known to be diamagnetic), may account for the observed magnetic moment, although a bi-octahedron structure (like that of $W_2Cl_9^{3-}$) must also be considered. The



I



II

---

(25) V. G. Tronev and G. K. Babeshkina, *Zh. Neorgan. Khim.*, **10**, 2484 (1965).

(26) V. G. Tronev and G. K. Babeshkina, *Russ. J. Inorg. Chem.*, **7**, 108 (1962).

(27) J. Chatt, J. D. Garforth, N. P. Johnson, and G. A. Rowe, *J. Chem. Soc.*, 601 (1964).

(28) R. Colton, "The Chemistry of Rhenium and Technetium," John Wiley and Sons, New York, N. Y., 1965, p 87.

(29) D. Brown and R. Colton, *J. Chem. Soc.*, 714 (1964).

(29a) Note Added in Proof.—This has now been proved (single crystal X-ray study) for $[ReCl_3(C_2H_5)_3P]_2$, which has an eclipsed, dinuclear structure (symmetry, C_{2h}).

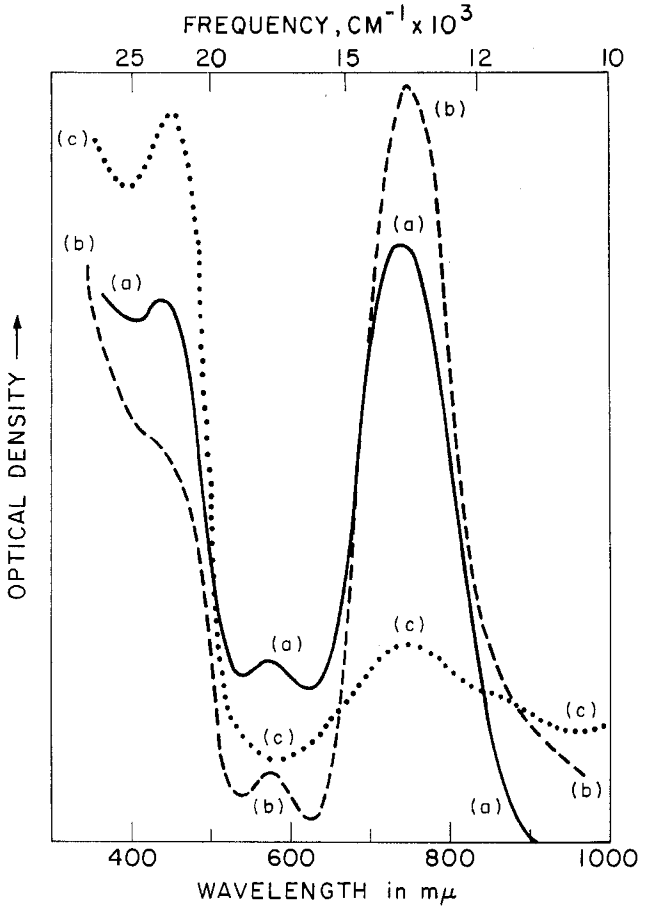


Figure 1.—Diffuse reflectance spectra (1000–350 mμ) of (a) $[ReCl_3 \cdot As(C_6H_5)_3]_n$; (b) $[ReCl_3 \cdot P(C_6H_5)_3]_n$; (c) $ReOCl_3[P(C_6H_5)_3]_2$.

presence of rhenium(III) and rhenium(IV) species (we are here assuming a charge localization) would result in the loss of one electron from the filled δ orbital in the molecular orbital diagram of $Re_2Cl_8^{2-}$,[13] and consequently the presence of one unpaired electron per dimer. It is uncertain at present whether this would result in an eclipsed (as in $Re_2Cl_8^{2-}$) or staggered molecular configuration. This proposed structure is evidently a reasonable one, since this salt is readily converted into the $Re_2Cl_8^{2-}$ dimer under very mild reaction conditions (see Experimental Section). Thus $Re_2Cl_9^{2-}$ is almost certain to be dinuclear. Its isolation from methanol solution evidently results from the stabilization of some rhenium(IV) species under the *weakly* acidic reaction conditions; addition of more acid gave the expected dimer $[(C_6H_5)_4As]_2Re_2Cl_8$. Salts of the dinuclear rhenium(IV) species, $Re_2X_9^-$, have recently been isolated,[22] so that $Re_2Cl_9^{2-}$ could conceivably be an unstable intermediate in the oxidation of $Re_2X_8^{2-}$ to $Re_2X_9^-$. The formation of dinuclear rhenium compounds of mixed, or mean fractional, oxidation states appears to be quite extensive. Thus the recent crystal structure determination[30] of the Re(III)–Re(II) dimer $[Re_2Cl_5(DTH)_2]$, and the polarographic reduction[31] of $Re_2(NCS)_8^{2-}$ to $Re_2(NCS)_8^{3-}$ and $Re_2(NCS)_8^{4-}$ and $Re_2Cl_8^{2-}$ to $Re_2Cl_8^{3-}$ and $Re_2Cl_8^{4-}$, have revealed the existence of other dinuclear species with formally mixed oxidation states.

The diffuse reflectance spectra (Figure 2) of $Re_2Cl_9^{2-}$ and $Re_2Cl_8^{2-}$ are different, although both complex anions show a sharp band at ~720 mμ, characteristic of a dimeric rhenium halide species.[13] However, the solution spectrum of $Re_2Cl_9^{2-}$ in acetonitrile indicates (Table I) that in this solvent some decomposition to $Re_2Cl_8^{2-}$ occurs. The band maxima and extinction coefficients of a solution of rhenium(IV) chloride dissolved in acidified methanol (Table I) suggest that under these conditions $Re_2Cl_9^{2-}$ is present in the solution.

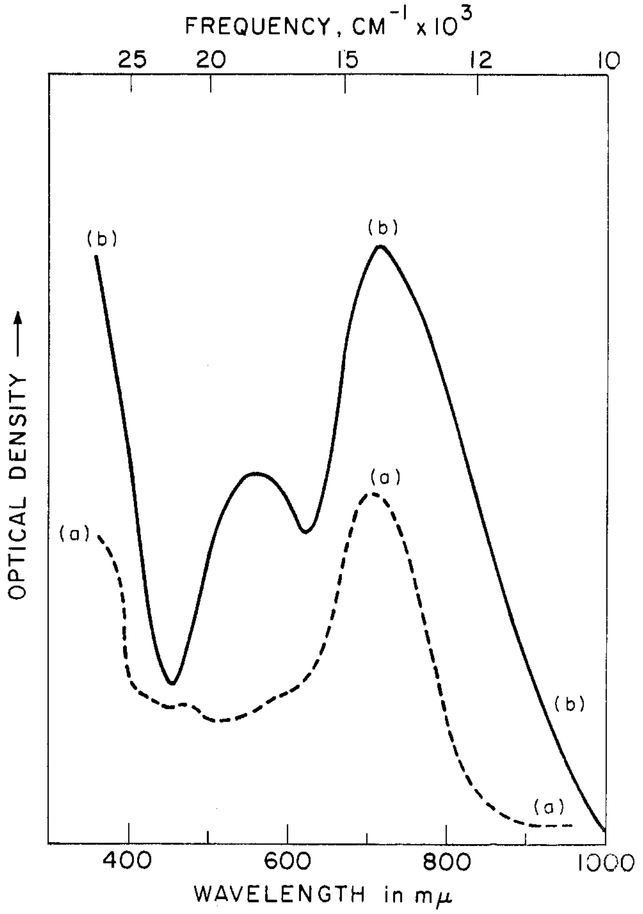


Figure 2.—Diffuse reflectance spectra (1000–350 mμ) of (a) $[C_5H_5NH]_2[Re_2Cl_8]$; (b) $[(C_6H_5)_4As]_2[Re_2Cl_9]$.

The reactions of rhenium(IV) chloride with 2,2′-bipyridyl and pyridine gave several oxorhenium(V) complexes, in addition to yielding $(bipyH)_2Re_2Cl_8$ or $(pyH)_2Re_2Cl_8$ under conditions which favored the formation of acidic solutions.

The green, acetone-soluble complex $ReOCl_3(bipy)$ was identical with that prepared from the reaction of $ReOCl_3[P(C_6H_5)_3]_2$ with 2,2′-bipyridyl,[11] and its diffuse reflectance spectrum (bands at 12,050, 12,820 (sh), and 23,260 cm^{-1}) was very similar to that of $ReOCl_3[P(C_6H_5)_3]_2$ (Figure 1). A yellow complex of composition approximating to $[bipyH]ReOCl_4$ was also isolated, but its infrared spectrum showed the absence

---

(30) M. J. Bennett, F. A. Cotton, and R. A. Walton, *J. Am. Chem. Soc.*, **88**, 3866 (1966).

(31) F. A. Cotton, W. R. Robinson, and R. A. Walton, *Inorg. Chem.*, in press.

Table I

Electronic Absorption Spectra

Compound	Medium	Absorption maxima, cm^{-1} [a]
$[(C_6H_5)_4As]_2Re_2Cl_9$	Solid	13,900, 17,700
$[C_5H_5NH]_2Re_2Cl_8$	Solid	14,080, ~16,700 sh?, 21,050 sh
$[(C_6H_5)_4As]_2Re_2Cl_9$	CH_3CN[b]	14,620 (0.09), 18,350 (0.03), 28,250, 31,950 (0.62), 36,900 (0.92),[c] 37,800 (1.0),[c] 38,760 (0.94)[c]
$[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$	CH_3CN	14,660 (2770), 27,030 (42), 32,260 (11,500), 39,530 (11,200), 46,300 (13,000)[d]
$ReCl_4$	CH_3OH–HCl[e]	13,990 (400), 18,730 (200), 29,850 sh, 31,550 sh, 36,500 (5000)

[a] Extinction coefficients in parentheses unless otherwise stated. [b] Relative ϵ_{max} values only. [c] Components of a closely spaced triplet. [d] This band has not previously been reported for $Re_2Cl_8^{2-}$ (ref 6). [e] 5.21 mg of sample dissolved in 10 ml of methanol and −0.05 ml of concentrated HCl.

of bands associated with the Re═O stretching vibration, suggesting that it could contain the polymeric anion $[OReCl_4]_n^-$. However, the absence of a band in its infrared spectrum which could be attributed to the bridging Re—O—Re group[32] does not support such a formulation. In view of the complete insolubility of this compound in polar and nonpolar solvents, it was not investigated further.

Under oxidizing conditions, *e.g.*, the addition of hydrogen peroxide or the free access of air, acetone solutions of rhenium(IV) chloride and pyridine gave the complexes $Re_2O_3(py)_4Cl_4$ (green) and $[ReO_2(py)_4]Cl \cdot 2H_2O$ (orange), both of which have previously been prepared from rhenium(V) chloride.[24] The single strong sharp band at 825 cm^{-1} in the infrared spectrum of $[ReO_2(py)_4]Cl \cdot 2H_2O$ is characteristic of the *trans* dioxo O═Re═O grouping.[4]

Johnson, *et al.*,[24] have reported that $Re_2O_3(py)_4Cl_4$ has a band at 970 cm^{-1} in its infrared spectrum, assigned to ν(Re═O), but none which they could attribute to the bridging Re—O—Re group. Previous work[32] has indicated that the antisymmetric M—O—M stretching mode of such a bridging group in *halo* complexes, *e.g.*, $Ru_2OCl_{10}^{4-}$, occurs as a strong band between 900 and 800 cm^{-1}. However, if the structure of $Re_2O_3(py)_4Cl_4$ is as shown in II, then the electron-withdrawing effect of the terminal Re═O groups should result in a relative weakening of the bridging Re—O bonds and consequently a reduction in the frequency of this mode. In keeping with this postulate, we observed a very strong broad band (710–675 cm^{-1}) in the infrared spectrum of $Re_2O_3(py)_4Cl_4$ which appeared to be at least a triplet. This we attribute to the overlap of ν(Re—O) of the bridging Re—O—Re group, with the pyridine out-of-plane deformation vibrations. This is clearly shown in Figure 3, where the infrared spectra of $[ReO_2(py)_4]Cl \cdot 2H_2O$ and $Re_2O_3(py)_4Cl_4$ are compared.

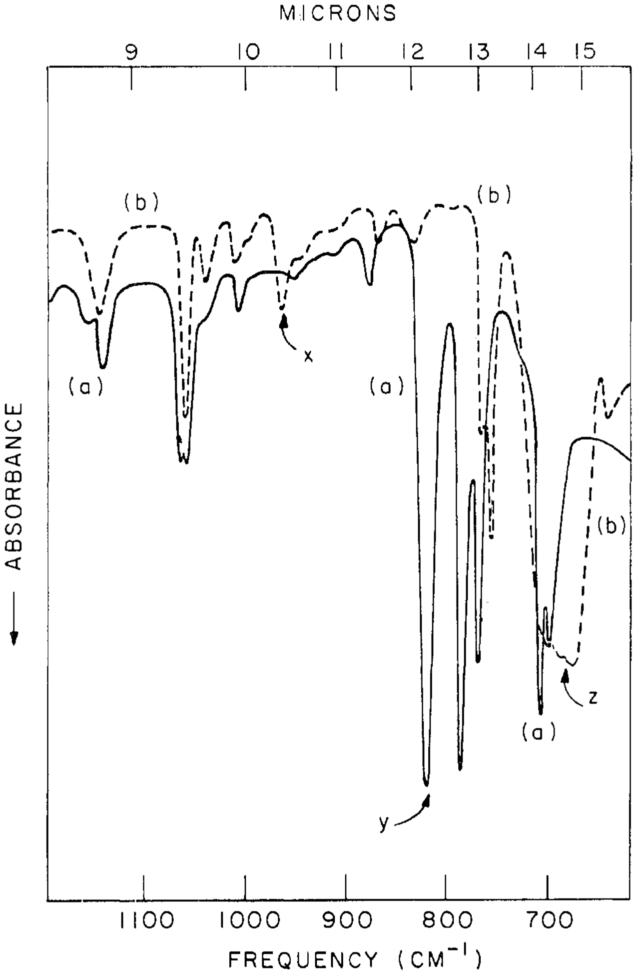


Figure 3.—Infrared spectra (1200–650 cm^{-1}) of (a) $[ReO_2(py)_4]Cl \cdot 2H_2O$ (y = ν(O═Re═O)); (b) $Re_2O_3(py)_4Cl_4$ (x = ν(Re═O) and z = ν(Re—O—Re)).

---

[32] D. J. Hewkin and W. P. Griffith, *J. Chem. Soc., Sect. A*, 472 (1966).