occupy approximately the same position relative to the $ReCl_6$ octahedra in a sheet as the potassium atoms in K_2ReCl_6. The average N–Cl distance is 3.59 A; that of K–Cl is 3.49 A. The average N–Re distance is 4.38 A; that of K–Re is 4.29 A.

Magnetic exchange is still possible in $(TH)_2ReCl_6$ since the nearest neighbor Re–Re distance (six nearest neighbors, average distance 6.94 A) is about the same as that in K_2ReCl_6 (6.98 A, 12 nearest neighbors). The nearest neighbor nonbonded Cl–Cl distances (not in the same octahedra) average 3.73 A in $(TH)_2ReCl_6$ and are 3.63 A in K_2ReCl_6.

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Some Reactions of the Octahalodirhenate(III) Ions. III. The Stability of the Rhenium–Rhenium Bond toward Oxygen and Sulfur Donors[1]

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The reactions of the $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$ ions with several carboxylic acids and sulfur ligands have been studied. The following carboxylates were prepared and their spectral properties investigated: $Re_2(O_2CCH_3)_2X_4 \cdot 2L$, $Re_2(O_2CCH_3)_3Br_3 \cdot H_2O$, $Re_2(O_2CR)_2(O_2CCl_3)_2Cl_2$, and $Re_2(O_2CCCl_3)_2Cl_4$, where L = H_2O or pyridine, X = Cl or Br, and R = CH_3 or $(CH_3)_3C$. Evidence for their dinuclear structures is presented. The $Re_2X_8^{2-}$ ions react with thiourea (tu) and tetramethylthiourea (tmtu) in acidified methanol to yield the complexes $[ReX_3(tu)_3]$ and $[ReX_3(tmtu)]_n$, respectively. In acetone the thiourea reaction gave the acetone solvates $ReX_3(tu)_3 \cdot {}^1/_3(CH_3)_2CO$. The thiourea complexes are believed to be true complexes of the type ReX_3L_3, only two of which have previously been reported in the literature. Spectral evidence in the case of $[ReX_3(tmtu)]_n$ suggests that $n = 2$ and that these complexes contain a Re–Re bond. $[(C_6H_5)_4As]_2[Re_2(C_2S_2(CN)_2)_4]$ is only the second compound reported in which a *cis*-1,2-disubstituted ethylene-1,2-dithiolate ligand is bonded to rhenium. The reaction of 2,5-dithiahexane (DTH) with $Re_2X_8^{2-}$ yields the complexes $[ReX_3(DTH)]_n$, $Re_2Cl_5(DTH)_2$, or $[ReBr_2(DTH)]_n$ depending upon the reaction conditions. Possible structures are suggested for these complexes on the basis of diffuse reflectance and infrared spectral studies. From their infrared spectra it is concluded that 2,5-dithiahexane assumes its *gauche* conformation on coordination. The infrared spectrum of the polymeric complex $Re_3Cl_9DTH_{1.5}$ is also reported and the ligand shown to have the *trans* conformation. This is the first example where this molecular form has been stabilized by complex formation. The complexes $ReCl_3(bipy)$ and $ReCl_3(CEP)_2 \cdot C_2H_5OH$, where CEP = tris(2-cyanoethyl)phosphine, have also been prepared and characterized.

Introduction

The reactivity and stability of the trimeric rhenium(III) halides is now well understood.[2] However, although the octahalodirhenate(III) ions $Re_2X_8^{2-}$, where X = Cl or Br, have been isolated,[3] and their electronic[4] and molecular[5,6] structures investigated, little information is yet available on their stability and reactivity. The most significant results of the earlier studies[4,6] are that the $Re_2X_8^{2-}$ species contain a Re–Re quadruple bond and an eclipsed rotational configuration.

We are at present investigating the reactions of these ions with a variety of donor molecules in an attempt to isolate new complexes in which the Re–Re bond may be broken, retained, or modified. A study of those complexes which contain a Re–Re bond should then provide information on such factors as the relationship between bond multiplicity and the molecular configuration (eclipsed or staggered).

Previous papers in this series have described the reactions of $Re_2X_8^{2-}$ with phosphines[7] and carboxylic acids.[8] A Re–Re bond is believed to be present in several of these phosphine complexes,[7] as is almost certainly the case with the tetracarboxylatodirhenate(III) species $Re_2(O_2CR)_4X_2$.[8] In the latter complexes the bridging nature of the carboxylate groups would be expected to favor the retention of a Re–Re bond.[9] In the present work further reactions of the octahalodirhenate(III) ions are reported and several new complexes containing rhenium–sulfur bonds described.

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[1] Research supported by the United States Atomic Energy Commission under Contract AT(30-1)-1965 and the National Science Foundation under grant No. GP-4329.

[2] F. A. Cotton and R. A. Walton, *Inorg. Chem.*, **5**, 1802 (1966), and earlier references therein.

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

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

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

[6] F. A. Cotton and W. R. Robinson, to be published.

[7] F. A. Cotton, N. F. Curtis, and W. R. Robinson, *Inorg. Chem.*, **4**, 1696 (1965).

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

[9] A recent structure determination of the benzoate complex $Re_2(O_2CC_6H_5)_4Cl_2$ has confirmed that a Re–Re bond is present and that it is essentially a quadruple bond: W. R. Robinson, to be published upon completion of crystallographic refinement.

In addition to this we have prepared and characterized a number of substituted rhenium(III) carboxylates of the general formula $[Re(O_2CR)(O_2CR')X]_2$ and $[Re(O_2CR)X_2 \cdot H_2O]_2$.

Experimental Section

The compounds $[(n\text{-}C_4H_9)_4N]_2Re_2X_8$, where X = Cl or Br, were prepared as previously described.[3]

Tris(2-cyanoethyl)phosphine was supplied by the American Cyanamid Co., through the kindness of Dr. Martin Grayson, and sodium *cis*-1,2-dicyanoethylene-1,2-dithiolate was prepared by a standard literature method.[10] All other reagents and solvents were commercially available.

Analyses were performed by S. M. Nagy, Massachusetts Institute of Technolgy, and the Galbraith Microanalytical Laboratories, Knoxville, Tenn.

Preparation of Carboxylate Derivatives. $Re_2(O_2CCH_3)_2X_4 \cdot 2H_2O$ (X = Cl or Br).—$[(n\text{-}C_4H_9)_4N]_2Re_2X_8$ (1 g) was added to a mixture of 30 ml of acetic anhydride and 10 ml of 48% fluoroboric acid, and the reaction mixture was stirred under nitrogen for 30 min. The solution was then filtered and placed in a vacuum desiccator over KOH and $CaCl_2$. As the solvent slowly evaporated blue crystals of the complex separated. These were filtered off, washed with pentane, and air dried.

Anal. Calcd for $C_4H_{10}O_6Re_2Cl_4$: C, 7.19; H, 1.49; Cl, 21.26. Found: C, 7.30; H, 1.49; Cl, 21.08. This compound had a molecular weight of 668 in acetone solution (calcd 700).

Calcd for $C_4H_{10}O_6Re_2Br_4$: C, 9.96; H, 1.66; Br, 33.19. Found: C, 9.93; H, 1.57; Br, 32.97.

When the above bromide complex was warmed with acetic acid for ~1 hr on a steam bath under nitrogen, the solution turned blue and on standing deposited orange crystals of $Re_2(O_2CCH_3)_3Br_3 \cdot H_2O$.

Anal. Calcd for $C_6H_{11}O_7Re_2Br_3$: C, 11.89; H, 1.36; Br, 29.74. Found: C, 11.98; H, 1.36; Br, 29.79.

On dissolving $Re_2(O_2CCH_3)_2X_4 \cdot 2H_2O$ in acetic acid and refluxing under nitrogen for 12 hr, the previously reported[8,11] complexes of the type $Re_2(O_2CCH_3)_4X_2$, where X = Cl or Br, were formed.

$Re_2(O_2CCH_3)_2Cl_4 \cdot 2py$.—$Re_2(O_2CCH_3)_2Cl_4 \cdot 2H_2O$ (0.2 g) was dissolved in a small volume of water, and pyridine was added dropwise until no further precipitation occurred. The blue complex was filtered off, washed freely with water, and dried *in vacuo* over P_2O_5.

Anal. Calcd for $C_{14}H_{16}N_2O_4Re_2Cl_4$: C, 21.26; H, 2.78; N, 3.54. Found: C, 21.80; H, 2.74; N, 3.51.

$Re_2(O_2CCl_3)_2Cl_4$.—$[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ (1 g) was dissolved in 2.0 g of molten trichloroacetic acid, the melt was cooled, and any excess free acid was dissolved by carefully washing the cooled melt with ether. The blue solid remaining on the filter pad was then air dried prior to analysis.

Anal. Calcd for $C_4O_4Re_2Cl_{10}$: C, 5.72; H, 0.00; Cl, 42.3. Found: C, 5.94; H, 0.4; Cl, 41.7.

$Re_2(O_2CR)_2(O_2CCl_3)_2Cl_2$ (R = CH_3 or $(CH_3)_3C$).—$Re_2(O_2CR)_4Cl_2$[8] (0.1 g) and 2.0 g of trichloroacetic acid were melted together, and the melt was refluxed gently under nitrogen for 10 min. The blue melt was then cooled, the excess trichloroacetic acid was carefully extracted with ether (the blue complex is also somewhat ether soluble), and the remaining blue solid was dissolved in and reprecipitated from chloroform–ether solution.

Anal. Calcd for $C_8H_{16}O_{13}Re_2Cl_8$ (*i.e.*, $Re_2(O_2CCH_3)_2(O_2CCl_3)_2Cl_2 \cdot 5H_2O$): C, 9.83; H, 1.64. Found: C, 9.93; H, 1.64.

Calcd for $C_{14}H_{18}O_8Re_2Cl_8$ (*i.e.*, R = $(CH_3)_3C$): C, 17.32; H, 1.86; Cl, 29.28. Found: C, 17.01; H, 1.97; Cl, 28.62.

Complexes with Sulfur Ligands. $ReCl_3(tu)_3 \cdot {}^1/_3(CH_3)_2CO$ (tu = thiourea).—On mixing acetone solutions of $[(n\text{-}C_4H_9)_4N]$-Re_2Cl_8 (0.10 g) and thiourea (0.15 g) the initial blue-green solution rapidly became cloudy and a dark red-orange solid separated. The reaction mixture was allowed to stand overnight and filtered, and the red complex was washed with acetone and ether and dried *in vacuo* at 80°.

Anal. Calcd for $C_3H_{12}N_6S_3ReCl_3 \cdot (C_3H_6O)_{0.33}$: C, 8.89; H, 2.61; N, 15.56; S, 17.81; Cl, 19.70. Found: C, 8.97; H, 2.77; N, 15.74; S, 17.69; Cl, 19.61.

A product of this same composition was isolated in five separate preparations.

Solubility.—This complex is soluble in water and slightly soluble in absolute ethanol; it is insoluble in acetone, acetonitrile, tetrahydrofuran, nitromethane, and chloroform.

The use of acetonitrile as solvent gave a product with identical diffuse reflectance and infrared spectra (except that a band at 1700 cm^{-1}, of medium intensity, was absent) to that isolated from acetone solution. However, the analytical data could not be fitted to any reasonable formulation and were not generally reproducible between products from different preparations.

Anal. Found: C, 8.57; H, 2.49; N, 14.41; S, 16.23.

$ReBr_3(tu)_3 \cdot {}^1/_3(CH_3)_2CO$.—This red compound was prepared in a manner analogous to that for the chloride using acetone as solvent. The complex was dried *in vacuo* at 70° prior to analysis and like the chloride showed no tendency to lose the associated acetone even on prolonged pumping.

Anal. Calcd for $C_3H_{12}N_6S_3ReBr_3 \cdot (C_3H_6O)_{0.33}$: C, 7.13; H, 2.08; N, 12.48; S, 14.26. Found: C, 7.20; H, 2.13; N, 12.53; S, 14.25.

$ReCl_3(tu)_3$.—$[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ (0.20 g) was dissolved in 12 ml of methanol, containing 0.3 ml of 12 *M* HCl to repress hydrolysis, and 0.10 g of thiourea was added. An immediate red coloration was produced but no complex precipitated. The solution was evaporated to low bulk on a steam bath and then to dryness at room temperature. The dark red residue was washed sparingly with acetone and then with ether, and the insoluble red complex was dried *in vacuo* at 80°.

Anal. Calcd for $C_3H_{12}N_6S_3ReCl_3$: C, 6.92; H, 2.32; N, 16.14; S, 18.47. Found: C, 7.30; H, 2.54; N, 15.92; S, 18.22.

Solubility.—The solubility is the same as for the analogous acetone solvate.

$ReBr_3(tu)_3$.—This complex was obtained as dark red-brown crystals by a similar method to that described for its chloride analog.

Anal. Calcd for $C_3H_{12}N_6S_3ReBr_3$: C, 5.50; H, 1.83; N, 12.84. Found: C, 5.47; H, 1.92; N, 12.41.

$[ReCl_3(tmtu)]_n$ (tmtu = tetramethylthiourea).—This complex precipitated on mixing acidified (with HCl) methanol solutions of $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ and excess tetramethylthiourea. The green reaction mixture was stirred for 15 min at room temperature until precipitation of the green-yellow product was complete; the mixture was filtered and the complex washed with methanol and ether and then dried *in vacuo*.

Anal. Calcd for $C_5H_{12}N_2SReCl_3$: C, 14.14; H, 2.85; N, 7.55; S, 6.60. Found: C, 13.70; H, 2.79; N, 7.23; S, 6.60.

Solubility.—This complex is insoluble in acetone, ethanol, acetonitrile, and nitromethane.

$[ReBr_3(tmtu)]_n$.—The chocolate-brown complex was prepared from $[(n\text{-}C_4H_9)_4N]_2Re_2Br_8$ and tetramethylthiourea in acidified (HBr) methanol solution.

Anal. Calcd for $C_5H_{12}N_2SReBr_3$: C, 10.76; H, 2.17; N, 5.02; S, 5.74. Found: C, 11.18; H, 2,03; N, 4.91; S, 5.57.

$[(C_6H_5)_4As]_2[Re_2(C_2S_2(CN)_2)_4]$.—$[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ (0.1 g) and 0.075 g of sodium *cis*-1,2-dicyanoethylene-1,2-dithiolate were suspended in 20 ml of absolute ethanol, and the reaction mixture was shaken and warmed on a steam bath. The initial dark green solution rapidly turned deep brown on warming. The reaction mixture was filtered, and 0.12 g of $[(C_6H_5)_4As]Cl$ was added to the filtrate. On allowing the filtrate to stand at room temperature, the complex slowly separated as a dark brown powder. It was filtered off and redissolved in 1:1 acetone–ethanol, and the solution was left to evaporate slowly at room temperature to yield the almost black microcrystalline complex.

Anal. Calcd for $C_{56}H_{40}N_4S_4As_2Re_2$: C, 45.23; H, 2.37; N, 6.59; S, 15.10. Found: C, 45.68; H, 2.70; N, 6.48; S, 14.85.

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[10] A. Davison and R. H. Holm, *Inorg. Syn.*, in press.

[11] F. Taha and G. Wilkinson, *J. Chem. Soc.*, 5406 (1963).

Solubility.—This complex is soluble in acetone, acetonitrile, tetrahydrofuran, and nitromethane; it is insoluble in water and ether.

[ReCl$_3$(DTH)]$_n$ (DTH = 2,5-dithiahexane).—2,5-Dithiahexane (1.0 ml) was added to a solution containing 0.10 g of [(n-C$_4$H$_9$)$_4$N]$_2$Re$_2$Cl$_8$ dissolved in 10 ml of methanol and 0.5 ml of 12 *M* HCl. The reaction mixture was warmed for a few minutes on a steam bath and then allowed to cool to room temperature, whereupon the green-brown complex precipitated. When crystallization was complete the complex was filtered off, washed with methanol and ether, and dried *in vacuo* at 80°.

Anal. Calcd for $C_4H_{10}S_2ReCl_3$: C, 11.59; H, 2.43; S, 15.46; Cl, 25.65. Found (for separate preparations): C, 11.98, 11.01; H, 2.45, 2.54; S, 15.57, 15.06; Cl, 25.49.

Solubility.—This complex is insoluble in acetone and tetrahydrofuran but slightly soluble in acetonitrile. It was soluble in nitromethane on warming but the solution rapidly became cloudy, presumably due to some decomposition.

The complex [ReCl$_3$(DTH)]$_n$ was also prepared by addition of 2,5-dithiahexane to the deep blue solution obtained from the concentrated hydrochloric acid–hydrogen reduction of potassium perrhenate.[3] The green-yellow salt K$_2$ReCl$_6$ was filtered off prior to the addition of 2,5-dithiahexane.

Anal. Found: C, 11.86; H, 3.02.

The infrared and diffuse reflectance spectra of this product were virtually identical with those of an authentic sample of [ReCl$_3$(DTH)]$_n$.

[ReBr$_3$(DTH)]$_n$.—This brown complex was prepared by a method similar to that described for its chloride analog.

Anal. Calcd for $C_4H_{10}S_2ReBr_3$: C, 8.76; H, 1.84; Br, 43.73. Found: C, 8.96; H, 2.19; Br, 43.67.

Solubility.—This complex is virtually insoluble in all common polar and nonpolar organic solvents.

Re$_2$Cl$_5$(DTH)$_2$.—This complex was prepared by two slightly different methods.

a.—[(n-C$_4$H$_9$)$_4$N]$_2$Re$_2$Cl$_8$ (0.10 g) was dissolved in 15 ml of acetonitrile (containing 2 ml of 2,2-dimethoxypropane), and 1.0 ml of 2,5-dithiahexane was added to this deep blue solution. The reaction mixture was then refluxed under nitrogen for 70 hr, during which time large red-black dichroic crystals of the complex separated. These were filtered off, washed with acetonitrile, acetone, and ether, and dried *in vacuo* at 80°.

Anal. Calcd for $C_8H_{20}S_4Re_2Cl_5$: C, 12.10; H, 2.54; S, 16.14; Cl, 22.35. Found: C, 12.20; H, 2.50; S, 16.49; Cl, 23.10.

b.—Using acidified methanol (10 ml of CH$_3$OH and 0.5 ml of 12 *M* HCl) as solvent and refluxing under nitrogen for 50 hr again afforded black crystals of the complex.

Anal. Found: C, 12.02; H, 2.66.

Solubility.—This complex was insoluble in acetone, ethanol, acetonitrile, tetrahydrofuran, and nitromethane and apparently unaffected by water and concentrated hydrochloric acid.

[ReBr$_2$(DTH)]$_n$.—[(n-C$_4$H$_9$)$_4$N]$_2$Re$_2$Br$_8$ (0.2 g) was dissolved in 40 ml of methanol containing a few drops of 48% hydrobromic acid, 2 ml of 2,5-dithiahexane was added, and the reaction mixture was refluxed under nitrogen for 50 hr. During this time the brown insoluble complex separated and was filtered off, washed with ethanol and ether, and dried *in vacuo*.

Anal. Calcd for $C_4H_{10}S_2ReBr_2$: C, 10.26; H, 2.15; S, 13.70; Br, 34.14. Found: C, 10.22; H, 2.06; S, 13.95; Br, 32.44.

Solubility.—The solubility is similar to that of Re$_2$Cl$_5$(DTH)$_2$.

Oxo Complexes of the Type ReOCl$_3$L$_2$.—A convenient method for the preparation of complexes of the type ReOCl$_3$L$_2$ was developed, using the solution obtained from the potassium iodide reduction[12] of potassium perrhenate. Potassium perrhenate (4 g), 250 ml of concentrated hydrochloric acid, and 50 ml of water were heated together, 7 g of potassium iodide was added, and the reaction mixture was boiled until no more iodine was evolved. The solution was then evaporated until K$_2$ReCl$_6$ began to precipitate and then filtered, and the filtrate was diluted to 300 ml with 20% hydrochloric acid.

A portion of the brown solution was treated with excess thiourea to precipitate a complex of composition approaching ReCl$_3$(tu)$_4$·4H$_2$O.

Anal. Calcd for $C_4H_{24}N_8O_4S_4ReCl_3$: C, 7.18; H, 3.62; N, 16.75. Found: C, 7.43; H, 3.49; N, 16.63.

On warming, the brown solution turned green and addition of 2,5-dithiahexane, 1,4-thioxane, or triphenylphosphine to this solution precipitated the green oxo species, ReOCl$_3$L$_2$.

Anal. Calcd for $C_4H_{10}S_2OReCl_3$ (*i.e.*, ReOCl$_3$(DTH)): C, 11.16; H, 2.33; S, 14.88. Found: C, 11.15; H, 2.37; S, 15.16. The infrared spectrum of this complex confirmed the presence of the ReO group (ν(ReO) at 980 cm^{-1}).

Calcd for $C_8H_{16}O_2SReCl_3$ (*i.e.*, ReOCl$_3$(C$_4$H$_8$OS)$_2$): C, 17.52; H, 2.92. Found: C, 17.60; H, 3.08.

The infrared spectrum of this complex was typical of sulfur-bonded 1,4-thioxane[13] and also showed a strong band at 976 cm^{-1}, assigned to ν(ReO).

Calcd for $C_{36}H_{30}OP_2ReCl_3$ (*i.e.*, ReOCl$_3$[(C$_6$H$_5$)$_3$P]$_2$): C, 51.92; H, 3.61. Found: C, 53.69; H, 3.98.

The infrared spectrum of this product was identical with that of an authentic sample of ReOCl$_3$[(C$_6$H$_5$)$_3$P]$_2$.

Reactions with Other Ligands. (a). **Tris(2-cyanoethyl)-phosphine (CEP).**—[(n-C$_4$H$_9$)$_4$N]$_2$Re$_2$Cl$_8$ (0.08 g) was refluxed under nitrogen with 0.10 g of CEP, dissolved in 15 ml of absolute ethanol. After 3 hr reflux the red, insoluble product was filtered off and washed freely with absolute ethanol and ether. This red solid was then dissolved in acetone, the deep red acetone solution was filtered, and the filtrate was evaporated to low bulk. Excess of absolute ethanol was then added, and the precipitated red complex was filtered off, washed with ethanol and ether, and dried *in vacuo* at 80°.

Anal. Calcd for $C_{20}H_{30}N_6OP_2ReCl_3$ (*i.e.*, ReCl$_3$(CEP)$_2$·C$_2$O$_5$OH): C, 33.14; H, 4.17; N, 11.60. Found (for separate preparations): C, 33.15, 33.55; H, 4.18, 4.10; N, 11.35, 11.40.

Solubility.—This complex is slightly soluble in acetone, acetonitrile, and nitromethane; it is insoluble in ethanol, tetrahydrofuran, chloroform, and water.

(**b**) **2,2′-Bipyridyl.**—[(n-C$_4$H$_9$)$_4$N]$_2$Re$_2$Cl$_8$ (0.10 g) was suspended in 15 ml of 1-butanol, 0.10 g of 2,2′-bipyridyl was added, and the reaction mixture was refluxed under nitrogen for 2 hr. The resulting dark blue insoluble product was filtered from the blue solution, washed with butanol, acetone, and ether, and dried *in vacuo* at 80°.

Anal. Calcd for $C_{10}H_8N_2ReCl_3$: C, 26.77; H, 1.80; N, 6.25. Found (for separate preparations): C, 26.36, 26.29; H, 1.97, 2.05; N, 5.85, 6.13.

Reaction of [(n-C$_4$H$_9$)$_4$N]$_2$Re$_2$Cl$_8$ with 2,2′-bipyridyl in acidified methanol gave an immediate precipitate of blue [bipyH]$_2$Re$_2$Cl$_8$.

Anal. Calcd for $C_{20}H_{18}N_4Re_2Cl_8$: C, 24.76; H, 1.87; N, 5.78. Found: C, 24.82; H, 1.72; N, 5.65.

(**c**).—The reaction of [(n-C$_4$H$_9$)$_4$N]$_2$Re$_2$Cl$_8$ with pyridine (sealed tube), molten bipyridyl, molten picolinic acid, and 4-cyanopyridine gave impure products of nonreproducible analyses. No reaction occurred with triphenylarsine, 1,4-thioxane, or diphenyl sulfide.

The reaction of [(n-C$_4$H$_9$)$_4$N]$_2$Re$_2$Cl$_8$ with urea in 1:1 acetone–ethanol gave blue crystals on allowing the solution to stand for several days at room temperature.

Anal. Found (for separate preparations): C, 9.46, 9.84; H, 2.46, 2.26; N, 14.96, 13.74.

This product was not investigated further.

(**d**). **Iodide.**—[(n-C$_4$H$_9$)$_4$N]$_2$Re$_2$Cl$_8$ (0.10 g) was dissolved in acetone, excess of sodium iodide was added, and the reaction mixture was warmed and shaken for 15 min. Any insoluble products were filtered off and 0.20 g of triphenylphosphine, dissolved in the minimum volume of methanol, was added to the purple-black filtrate. The solution turned red-brown and then straw-colored as yellow crystals of ReOI$_2$(OCH$_3$)·2P(C$_6$H$_5$)$_3$ separated.

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(12) L. I. Evteev, *Russ. J. Inorg. Chem.*, **9**, 336 (1964).

(13) R. A. Walton, *Inorg. Chem.*, **5**, 643 (1966).

TABLE I

VISIBLE ABSORPTION SPECTRA AND CONDUCTIVITY DATA FOR RHENIUM(III) CARBOXYLATE COMPLEXES

Compound	Absorption maxima, mμ[a,b]				Λ_M,[c] ohm^{-1} cm^2
$Re_2(O_2CCH_3)_2Cl_4\cdot 2H_2O$	635 (755)	472 (94)	322 (6000)	252 (29,600)	4.4
$Re_2(O_2CCH_3)_2Cl_4\cdot 2py$	633	473	312	255	...
$Re_2(O_2CCH_3)_2Br_4\cdot 2H_2O$	656	383			1.5
$Re_2(O_2CCH_3)_3Br_3\cdot H_2O$	570	388		251	...
$Re_2(O_2CCH_3)_2(O_2CCCl_3)_2\cdot 5H_2O$	635 (455)	470 (47)	318 (3830)	247 (7260)	8.0
$Re_2(O_2CC(CH_3)_3)_2(O_2CCCl_3)_2$	633	428	318	210	

[a] Solutions in chloroform. [b] ϵ_{max} values in parentheses. [c] $\sim 10^{-3}$ *M* solutions in acetonitrile.

Anal. Calcd for $C_{37}H_{33}O_2P_2ReI_2$: C, 43.92; H, 3.29; P, 6.13. Found: C, 44.48; H, 3.48; P, 6.25.

The infrared spectrum of this complex had a strong band at 938 cm^{-1} assigned to ν(ReO).

Attempts to prepare other phosphine complexes by halide ion replacement followed by addition of excess phosphine failed to yield pure products.

Physical Measurements.—Infrared spectra were recorded in the range 4000–400 cm^{-1} using Perkin-Elmer 237B and 337 grating spectrophotometers. Visible and ultraviolet spectra were obtained with Beckman DU and Cary Model 14 spectrophotometers. Conductances were measured at room temperature with a commercial Wheatstone bridge circuit.

Results and Discussion

(a) Carboxylate Complexes.—The preparation of $Re_2X_4(O_2CCH_3)_2\cdot 2H_2O$ and $Re_2Br_3(O_2CCH_3)_3\cdot H_2O$ from the octahalodirhenate(III) ions is illustrated in Figure 1, together with their probable structures. These complexes are soluble in a variety of polar and nonpolar solvents, and conductivity data for their acetonitrile solutions (Table I) confirm their nonionic nature. Since they are precursors in the preparation of the previously reported $Re_2(O_2CR)_4X_2$[8,11,14] there can be little doubt as to their dinuclear nature.[9] They thus provide further examples of carboxylate derivatives of rhenium of which a large number are already known.[8,11,14] It seems likely that all these complexes contain bridging carboxylate molecules.[15]

Some interesting comparisons may now be made between the present work and several earlier observations reported by Russian workers.[17] The blue solution of "$H_2ReCl_4\cdot 2H_2O$," obtained by the hydrogen reduction of perrhenate at 300°, is reported[17] to react with carboxylic acids according to Scheme I.

Since we have shown[3,8] that the $Re_2X_8{}^{2-}$ ions react directly with acetic acid at 250° to form the orange dinuclear rhenium(III) carboxylates $Re_2(O_2CCH_3)_4X_2$ (formulated by the Russians[17] as I, *i.e.*, $Re_2X_2\cdot 4CH_3COOH$)[18] it seemed unlikely that the above series of compounds (II and III) were intermediates in this reaction. Although we were unable to repeat the original[17] preparation of the compound written as $[ReCl_2\cdot CH_3COOH\cdot H_2O]$, this complex, which we write as $Re_2Cl_4(O_2CCH_3)_2\cdot 2H_2O$, could be obtained more conveniently by the reaction of acetic anhydride in fluoroboric acid with $Re_2X_8{}^{2-}$. By solution of the chloride or bromide of this complex in acetic acid and either warming to 100° or refluxing at 240° it was possible to prepare $Re_2(O_2CCH_3)_3X_3\cdot H_2O$ and $Re_2(O_2CCH_3)_4X_2$, respectively. Pumping *in vacuo* at 130° for 50 hr failed to remove the two molecules of water in $[Re(O_2CCH_3)_2Cl_4]\cdot 2H_2O$, although they could be readily displaced by pyridine to give $[Re(O_2CCH_3)_2Cl_4]\cdot 2py$.

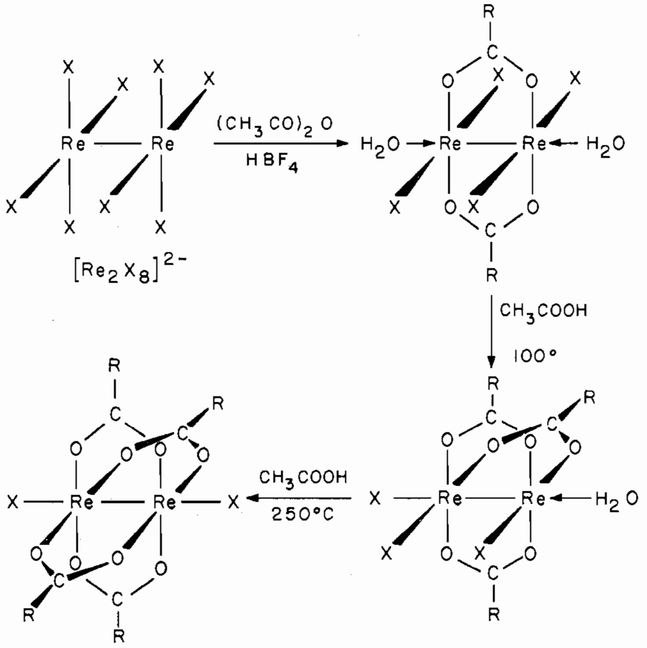
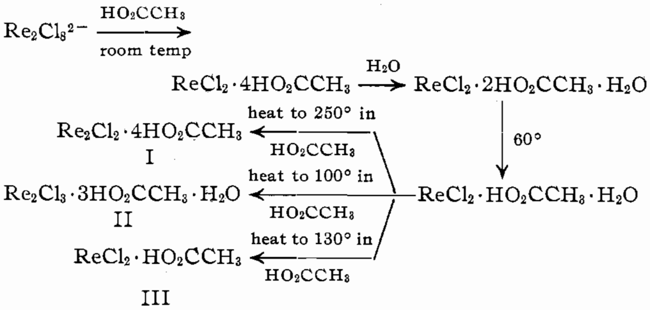


Figure 1.—Reaction scheme and probable structures of rhenium(III) carboxylates.

SCHEME I



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(14) G. Rouschias and G. Wilkinson, *J. Chem. Soc., Sect. A*, 465 (1966).

(15) The structures recently proposed[14] for the complexes $Re_2Cl_3(O_2CR)_2[P(C_6H_5)_3]_2$ and $Re_2OX_5(O_2CR')[P(C_6H_5)_3]_2$ appear to us to be unlikely. Both were formulated as dimers, the former containing two bridging carboxylate molecules and a single Re–Cl–Re bridge, while the latter complexes were suggested to have a single carboxylate bridge in addition to chlorine and oxygen bridges. In view of the known bridging nature of the acetate group in the copper acetate dimer,[16] for example (the O–O distance is 2.20 A), and assuming a Re–Cl distance of ~2.5 A, it seems unlikely that a carboxylate molecule can bridge two rhenium atoms already bridged by a chlorine atom. Similar considerations apply to $Re_2OX_5(O_2CR')[P(C_6H_5)_3]_2$.

(16) J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **6**, 227 (1953).

(17) A. S. Kotelnikova and G. A. Vinogradova, *Zh. Neorgan. Khim.*, **9**, 168 (1964), and references therein.

(18) It should be noted that the Russian workers[17] formulated the carboxylate derivatives as carboxylic acid "adducts," which would then make $Re_2Cl_2\cdot 4CH_3COOH$ a complex of rhenium(I).

TABLE II

PROPERTIES OF RHENIUM(III) COMPLEXES

Compound	Medium	Visible absorption maxima, mμ[a]				Λ_M,[b] ohm^{-1} cm^2
$[ReCl_3(DTH)]_n$	Solid	785	(625)	500		84.0[c] (0.61×10^{-3})
	CH_3NO_2		680	466	320	12.0[d] (0.55×10^{-3})
$[ReOCl_3(DTH)]$	Solid	925	670			...
$[ReBr_3(DTH)]_n$	Solid	825	(640)	440		...
$Re_2Cl_5(DTH)_2$	Solid	795	615	(470)	(415)	...
$[ReBr_2(DTH)]_n$	Solid	875	620	520	430	...
$ReCl_3(tu)_3 \cdot {}^1/_3(CH_3)_2CO$	Solid	~950	~775	520	470	...
$ReBr_3(tu)_3 \cdot {}^1/_3(CH_3)_2CO$	Solid	(~950)	(~780)	525	470	...
$ReCl_3(tu)_3$	Solid	850	770	(540)	460	...
$ReBr_3(tu)_3$	Solid	(~870)	750	(540)	480	...
$[ReCl_3(tmtu)]_n$	Solid	740	580	460		...
$[ReBr_3(tmtu)]_n$	Solid	800	(625)?	440		...
$[(C_6H_5)_4As]_2[Re_2(C_2S_2(CN)_2)_4]$	Solid	870	540	440		309[d] (0.22×10^{-3})
	CH_3CN	850 (4630)[f]	550 (5090)[f]	415 (11,900)[f]		
$ReCl_3(CEP)_2 \cdot C_2H_5OH$	Solid	955	(~600)	500		15.7[e] (0.40×10^{-3})
$ReCl_3(bipy)$	Solid	690	575	(500)		...

[a] Bands in parentheses only observed as shoulders. [b] Concentrations given in parentheses (*M*). [c-e] Conductivities measured in (*c*) nitromethane, (*d*) acetonitrile, or (*e*) acetone. [f] Molar extinction coefficients.

In addition to the isolation of these intermediates, it was found possible to achieve partial carboxylate ligand replacement to give the previously reported blue complexes $Re_2(O_2CR)_2(O_2CCl_3)_2X_2$, where X = Cl or Br and R = CH_3 or $(CH_3)_3C$. However, attempts to prepare $Re_2(O_2CCCl_3)_4Cl_2$ were unsuccessful although $Re_2(O_2CCCl_3)_2Cl_4$ was isolated from the reaction of $Re_2Cl_8^{2-}$ with molten trichloroacetic acid.

Table I summarizes the electronic absorption spectra of the above carboxylate complexes for which some general trends may be noted. In the series of compounds $Re_2(O_2CR)_2X_4 \cdot 2L$, where X = Cl or Br and L = H_2O or pyridine, no bands were observed in the 14,000–12,500 cm^{-1} region which has previously been assigned[4] to a transition from the δ-bonding orbital to one of the nonbonding σ orbitals. This would suggest[8] that the L groups are bonded to the terminal positions of the dimer, along the line of the Re–Re bond. In the benzoate complexes, $Re_2(O_2CC_6H_5)_4X_2$, where X = Cl or Br,[8] a crystallographic investigation of the chloride complex[9] has shown that the chlorine atoms are strongly bonded to these terminal positions and in keeping with this these complexes have no visible absorption bands at frequencies below 18,000 cm^{-1}. For the complexes $Re_2(O_2CCH_3)_2X_4 \cdot 2L$ described in the present work, the appearance of absorption bands in the 15,000–16,000 cm^{-1} region would imply that the terminal groups are more weakly bonded. These complexes appear to be of the same type as $Re_2(O_2CC_3H_7)_4SO_4 \cdot 2H_2O$,[8] which has an absorption band at 15,700 cm^{-1}. Finally, we note that the lowest energy band of $Re_2Br_3(O_2CCH_3)_3 \cdot H_2O$ occurs at 17,500 cm^{-1}, consistent with one or two bromine atoms being bonded to the terminal positions (Figure 1).

Replacement of the O_2CCH_3 groups by the more inductive O_2CCCl_3 in the series $Re_2(O_2CR)_4Cl_2$ causes a pronounced shift of this axial substituent-sensitive band: this band moves from 20,000 to 17,900 to 15,750 cm^{-1} in the series $Re_2(O_2CCH_3)_4Cl_2$,[8] $Re_2(O_2CCH_2Cl)_4Cl_2$,[8] and $Re_2(O_2CCH_3)_2(O_2CCCl_3)_2Cl_2$, confirming the suggestion[8] that this band is sensitive to both the nature of the axial substituent and the inductive effect of the substituent on R.

(b) **Complexes with Sulfur Ligands.**—Table II lists the complexes prepared from the reaction of 2,5-dithiahexane (DTH), thiourea (tu), tetramethylthiourea (tmtu), and sodium *cis*-1,2-dicyanoethylene-1,2-dithiolate with $Re_2X_8^{2-}$ (or solutions believed to contain these species), together with several of their physical properties.

Previous studies have shown[7] that the $Re_2X_8^{2-}$ ions react with phosphines to yield complexes in which the Re–Re bond may be either retained or broken. In the latter case, complexes of the type $ReOCl_3(LL)$ or $[ReX_2(LL)_2]Y$, where LL = 1,2-bis(diphenylphosphino)ethane, can be isolated. Sulfur donors also react with $Re_2X_8^{2-}$ to yield several new characterizable complexes, whereas triphenylarsine and most nitrogen ligands (with the exception of 2,2′-bipyridyl) either show little tendency to react or yield impure products with nonreproducible compositions.

Thiourea Complexes.—The reactions of $Re_2X_8^{2-}$ with thiourea in acidified methanol afforded the complexes $ReX_3(tu)_3$, whereas the use of acetone as a solvent gave the solvates $ReX_3(tu)_3 \cdot {}^1/_3(CH_3)_2CO$. The diffuse reflectance spectra of these four complexes were very similar (Table II and Figure 2), although the low-energy absorption maxima (below ~14,000 cm^{-1}) in $ReX_3(tu)_3$ were apparently more intense than in the solvated species. The presence of one-third of a molecule of acetone per rhenium was indicated by the analytical data and confirmed by a band at 1700 cm^{-1} (C=O stretching vibration) in the infrared spectra of $ReX_3(tu)_3 . {}^1/_3(CH_3)_2CO$ that was absent in $ReX_3(tu)_3$.

In all cases the infrared spectra of the thiourea complexes were typical of sulfur-bonded thiourea.[19] The following ligand band modifications were taken as characteristic of such bonding: (i) The free ligand

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[19] A. Yamaguchi, R. B. Penland, S. Mizushima, T. J. Lane, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **80**, 527 (1958).

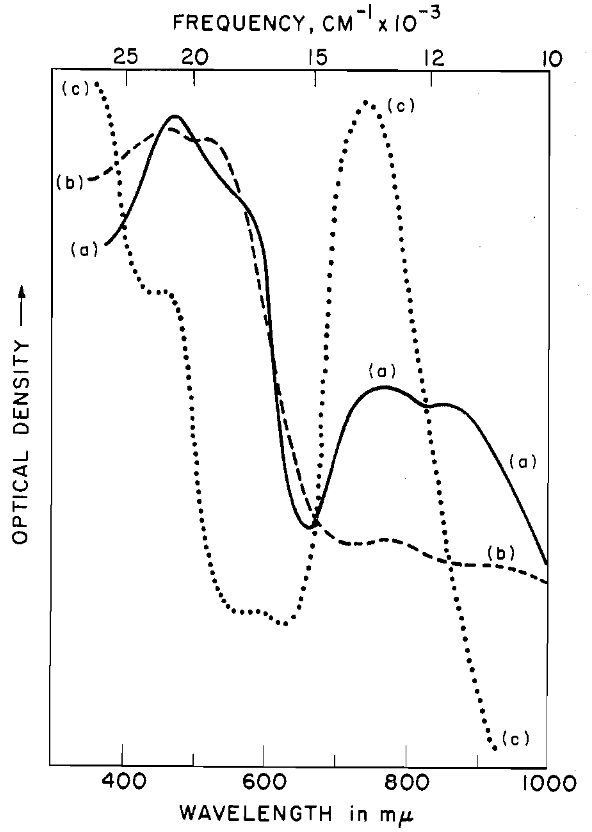


Figure 2.—Diffuse reflectance spectra (1000–350 mμ) of (a) $ReCl_3(tu)_3$; (b) $ReCl_3(tu)_3 \cdot {}^1/_3(CH_3)_2CO$; (c) $[ReCl_3(tmtu)]_n$.

N—C—N stretching vibration (B_1) at 1470 cm^{-1} increased to ~1505 cm^{-1} on coordination. (ii) The band at 730 cm^{-1}, assigned[19] to the C=S + N—C—N bending vibrations (A_1), decreased to ~680 cm^{-1} in $ReX_3(tu)_3$ and to 690 cm^{-1} in $ReX_3(tu)_3 \cdot {}^1/_3(CH_3)_2CO$.

The intensity of the band at ~1090 cm^{-1}, assigned[19] to a mode involving the N—C—N stretching, NH_2 rocking, and C=S stretching vibrations, was drastically reduced on coordination as has been reported[19] for other metal halide complexes of thiourea. The strong band at ~1410 cm^{-1} was not split on coordination so that the presence of bridging thiourea molecules can be ruled out.[20]

The infrared spectral studies provide no evidence for the presence of nonequivalent thiourea molecules. Also, the shifts of the infrared absorption bands on coordination are consistent with a reduction in the double-bond character of the S-C bond and enhanced double-bond character of the N-C bonds.

The insolubility of the thiourea complexes in suitable solvents precluded a study of their properties in solution, but it is reasonable to assume that they are true complexes of the type $ReX_3L'_3$, only two examples of which appear to have been reported in the literature.[21] Their diffuse reflectance spectra differ from those of $[ReX_3(tmtu)]_n$ (see below) and other complexes of the type $[ReX_3L]_n$, where *n* is probably 2, so we conclude that the Re-Re bond of $Re_2X_8^{2-}$ is readily broken on reaction with thiourea.

In contrast to this behavior, tetramethylthiourea (tmtu) reacts with $Re_2X_8^{2-}$ in acidified methanol to give the insoluble complexes $[ReX_3(tmtu)]_n$. It is not immediately obvious why further reaction does not occur, as in the reaction with thiourea, but this may be due to the extreme insolubility of the initial tetramethylthiourea adducts.

The infrared spectra of $[ReX_3(tmtu)]_n$ are virtually identical and closely resemble those of other tetramethylthiourea complexes of metal halides.[22] The increase in frequency of the antisymmetric N—C—N stretching vibration and decrease in frequency of the C=S stretching vibration (Table III) are characteristic of sufur-bonded tetramethylthiourea.

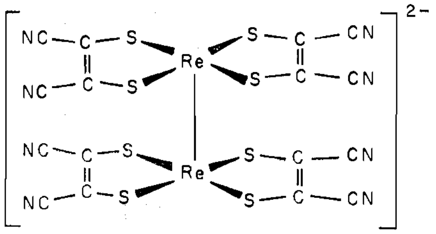
TABLE III

INFRARED SPECTRA (CM^{-1}) OF TETRAMETHYLTHIOUREA COMPLEXES

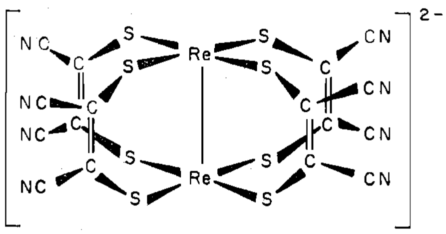
	Antisym N—C—N str	C=S str
tmtu (ref 22)	1504	1126
$[ReCl_3(tmtu)]_n$	1575 vs	1113 s
$[ReBr_3(tmtu)]_n$	1580 vs	1112 s

The diffuse reflectance spectra of $[ReX_3(tmtu)]_n$ (Table II and Figure 2) were very similar to those of $[ReX_3(P(C_6H_5)_3)]_n$[7,23] and $Re_2X_8^{2-}$ [3,23] and were characterized by a sharp band between 14,500 and 12,500 cm^{-1}, which is presumably associated with a transition of the type $\delta \rightarrow \sigma_n{}^4$, and an intense band at ~22,000 cm^{-1}. Further discussion of the spectral data will be deferred until the 2,5-dithiahexane complexes are considered.

$[(C_6H_5)_4As]_2[Re_2(C_4N_2S_2)_4]$.—This black crystalline complex appears to be only the second complex in which a *cis*-1,2-disubstituted ethylene-1,2-dithiolate ligand is bonded to rhenium. The first, tris(*cis*-1,2-diphenylethylene-1,2-dithiolate)rhenium, has been shown[24] to contain a trigonal prismatic coordination of



IV



V

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[20] G. Yagupsky, R. H. Negrotti, and R. Levitus, *J. Inorg. Nucl. Chem.*, **27**, 2603 (1965).

[21] J. Chatt and G. A. Rowe, *J. Chem. Soc.*, 4019 (1962).

[22] M. Schafer and C. Curran, *Inorg. Chem.*, **5**, 265 (1966).

[23] F. A. Cotton, W. R. Robinson, and R. A. Walton, to be published.

[24] R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **5**, 410 (1966).

TABLE IV

INFRARED SPECTRA OF 2,5-DITHIAHEXANE COMPLEXES IN THE REGION 1350–650 CM^{-1}

DTH (liquid)	$[\text{ReCl}_3(\text{DTH})]_n$	$[\text{ReBr}_3(\text{DTH})]_n$	$[\text{Re}_2\text{Cl}_5(\text{DTH})]_2$	$\text{Re}_2\text{Br}_2(\text{DTH})_n$	$\text{ReOCl}_3(\text{DTH})$	Assignment[a]
1320 m	1312 m	1316 m	1321 mw		1321 ms	CH_3 sym def (T,G)
1283 sh	1300 sh	1300 w	1312 w	1300 m	1312 ms	CH_2 wag (T,G)
1270 m	1260 w	1260 mw			~1250 w, br	CH_2 wag and twist (G)
1206 s						CH_2 wag (T)
	1170 w, br	1180 w	1175 m	~1160 w, br	~1175 w, br	
1134 m						CH_2 twist (T)
1120 sh	1143 w	1145 w	1133 mw	~1120 w	1130 ms	CH_2 twist (G)
1027 vw	1025 s	1033 s	1026 m	1015 w	1023 w	C–C str (T,G) and CH_2 rock (T)
1010 vw						?
975 sh	975 ms	982 s			980 vs[b]	CH_3 rock (T,G)
960 s	960 s	966 s	975 s	960 s	968 s	CH_2 rock (G), CH_3 rock (T,G)
	880 mw	888 mw	916 mw	875 mw	912 m	
840 w	833 mw	840 m	845 ms	835 m	846 s	CH_2 rock (G)
738 m						C–S str and CH_2 rock (T)
686 s						C–S str (T)
650 vw	654 vw 633 vw	660 mw	650 w		650 w	C–S str (G)

[a] From ref 28; T = *trans;* G = *gauche.* [b] $\nu(\text{Re}{=}\text{O})$.

six sulfur atoms around the rhenium. The tetraphenylarsonium salt of $[\text{Re}_2(\text{C}_4\text{N}_2\text{S}_2)_4]^{2-}$ behaves as a typical 2:1 electrolyte in acetonitrile (Table II) and its visible absorption spectrum in this solvent and diffuse reflectance spectrum are identical. A structure such as IV would appear to be very likely, but molecular models suggest that the structure V, in which the Re–Re bond is retained, can be ruled out. However, a dimer with sulfur bridges as has been found for bis(*cis*-1,2-bis(trifluoromethyl)ethylene-1,2-dithiolate)cobalt[25] is also possible. This complex will be worthy of further study.[26]

2,5-Dithiahexane Complexes.—The use of mild reaction conditions and acidified methanol as solvent gave the insoluble complexes $[\text{ReX}_3(\text{DTH})]_n$, where X = Cl or Br. The chloride complex was sufficiently soluble in nitromethane and acetonitrile to permit conductivity measurements (Table II). In the former solvent it appeared to behave as a 1:1 electrolyte, while in acetonitrile it gave an essentially nonconducting solution, although some reaction with the solvent was indicated by an increase in the conductivity of this solution with time. The chloride almost certainly reacts with nitromethane since the electronic spectrum of this solution was appreciably different from that of the pure solid; this may then account for the conductance of the nitromethane solution.

$\text{Re}_2\text{Cl}_5(\text{DTH})_2$ and $[\text{ReBr}_2(\text{DTH})]_n$ were insufficiently soluble for solution studies and it would appear that all the 2,5-dithiahexane complexes are nonionic in the solid state. The formation of $\text{Re}_2\text{Cl}_5(\text{DTH})_2$ and $[\text{ReBr}_2(\text{DTH})]_n$ illustrates the rather surprising reducing potentialities of 2,5-dithiahexane in its reactions with $\text{Re}_2\text{X}_8^{2-}$. Certainly we know of no other instances where a stable oxidation state such as rhenium(III) is so readily reduced by this ligand.

The green rhenium(V) complex ReOCl_3DTH ($\nu(\text{Re}{=}\text{O})$ at 980 cm^{-1}) was isolated when 2,5-dithiahexane was added to a solution obtained by the potassium iodide reduction of potassium perrhenate. This solution is also suitable for the preparation of other oxorhenium(V) complexes, such as $\text{ReOCl}_3[\text{P}(\text{C}_6\text{H}_5)_3]_2$ and $\text{ReOCl}_3(\text{C}_4\text{H}_8\text{OS})_2$.

The principal infrared absorption bands of all the 2,5-dithiahexane complexes prepared in the present work are listed in Table IV, together with the probable band assignments.

In the gaseous and liquid states free 2,5-dithiahexane exists in both its *trans* and *gauche* conformers.[27–29] However, on coordination the ligand is believed to assume only the *gauche* conformation since the infrared spectral bands attributable to the *trans* conformer disappear on complex formation.[30,31]

Although there is some disagreement in the vibrational assignments of 2,5-dithiahexane in its liquid and gaseous states,[27,28,30] the same general conclusions have been reached as to which bands are due to the *gauche* and *trans* conformers, respectively. In particular the CH_2 rocking modes assigned by various workers do not agree.[28,30,32] The band most sensitive to the presence or absence of the *trans* isomer is the strong absorption at 1205 cm^{-1}, assigned to the CH_2 wagging mode of the *trans* isomer. An inspection of the absorption maxima listed in Table IV shows that without exception the

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(25) J. H. Enemark and W. N. Lipscomb, *Inorg. Chem.*, **4**, 1729 (1965).

(26) The redox behavior of this and other dimeric rhenium(III) complexes is currently under investigation as are their crystal structures and will be the subject of forthcoming publications.

(27) D. Welti and D. Whittaker, *J. Chem. Soc.*, 4372 (1962).

(28) M. Hayashi, Y. Shiro, T. Oshima, and H. Murata, *Bull. Chem. Soc. Japan*, **39**, 118 (1966).

(29) We refer to the molecular forms around the C–C bond: if we also consider the C–S bonds, then ten different isomers are expected.[28] However, as Hayashi, *et al.*,[28] have indicated, it is only from a study of the skeletal deformation modes (which occur below 450 cm^{-1}) that these ten isomers can readily be differentiated. Consequently in the following discussion we will only consider the isomerism that arises from rotations about the C–C bond of 2,5-dithiahexane.

(30) D. M. Sweeny, S. Mizushima, and J. V. Quagliano, *J. Am. Chem. Soc.*, **77**, 6521 (1955).

(31) R. J. H. Clark and W. Errington, *Inorg. Chem.*, **5**, 650 (1966).

(32) We have confirmed that the 900 cm^{-1} band, assigned by Sweeny, *et al.*,[30] to a CH_2 rocking mode of the *gauche* isomer, is probably due to an impurity as has been suggested by Hayashi, *et al.*[28]

1205 cm^{-1} band is absent. Also, the weak band at 840 cm^{-1} in liquid 2,5-dithiahexane, assigned to the CH_2 rocking mode of the *gauche* isomer, increases in intensity on complex formation, as does the band at ~1030 cm^{-1} in the free ligand, which is believed[28] to arise from several superimposed vibrations (Table IV), one of which, the C–C stretching vibration, is attributed to the *gauche* isomer. The present work seems to confirm the observation[31] that several of the weak absorptions due to the *gauche* isomer increase in intensity on complex formation. In addition, the *trans* isomer C–S stretching vibrations at 739 and 688 cm^{-1} disappeared on coordination of the ligand, whereas the analogous vibration at 650 cm^{-1}, attributed to the *gauche* isomer, is still observed. Thus we conclude that in all the complexes listed in Table IV the ligand takes the *gauche* conformation. Confirmation of this is provided by the crystal structure of $Re_2Cl_5(DTH)_2$,[33] in which both ligand molecules have been shown to have the *gauche* conformation.

We have recently prepared[2] the complex $Re_3Cl_9(DTH)_{1.5}$ and suggested that it is polymeric with bridging 2,5-dithiahexane molecules. Apparent confirmation of this is now available. If 2,5-dithiahexane acts as a bridge rather than a chelate it is reasonable to expect that the ligand will assume the more symmetric *trans* conformation. A comparison of the infrared spectrum of $Re_3Cl_9DTH_{1.5}$ (Table V and Figure 3) with that of the other 2,5-dithiahexane complexes (Table IV and Figure 3) indicates that this is the case and to our knowledge it is the first example where the *trans* isomer has been stabilized by complex formation. The following evidence seems to support conclusively the presence of the *trans* isomer: (i) The presence of a band of medium intensity at 1212 cm^{-1}, assigned to a CH_2 wagging mode of the *trans* isomer, that is not present in the complexes containing the *gauche* isomer (see Table IV and ref 30 and 31). (ii) Absence of a band at 840 cm^{-1} assigned to the *gauche* CH_2 rocking mode. (iii) The presence of medium–weak absorptions at 745 (C–S stretch), 730 (CH_2 rock), and 678 cm^{-1} (C–S stretch), all of which may be assigned to the *trans* isomer.[28]

TABLE V

INFRARED SPECTRUM OF $Re_3Cl_9(DTH)_{1.5}$ IN THE REGION 1350–650 CM^{-1}

Re_3Cl_9-$(DTH)_{1.5}$	Assignment[a]	Re_3Cl_9-$(DTH)_{1.5}$	Assignment[a]
1318 mw	CH_3 sym def (T,G)	960 s	CH_3 rock (T,G)
1273 w	CH_2 wag and twist (G)?	908 vw	?
1212 m	CH_2 wag (T)	770 w	
~1150 w, br	CH_2 twist (T)	743 m	C–S str (T)
1120 vw	?	730 w	CH_2 rock (T)
1020 m	C–C str (T,G) and CH_2 rock (T)	678 m	C–S str (T)
978 m	CH_3 rock (T,G)		

[a] From ref 28; T = *trans*; G = *gauche*.

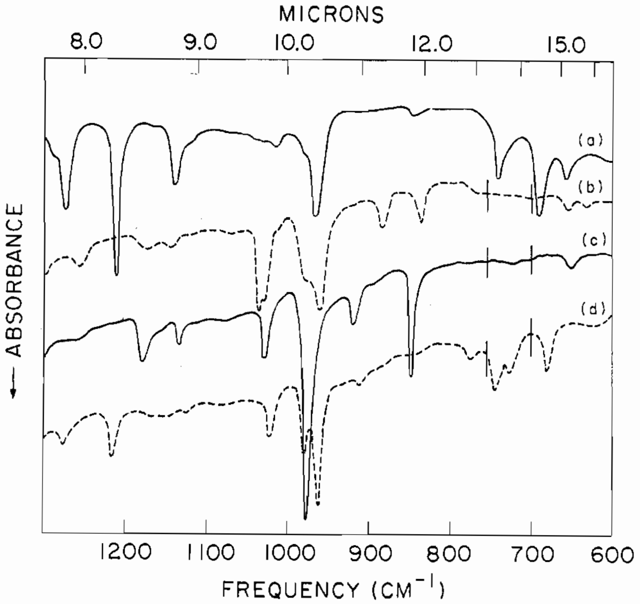
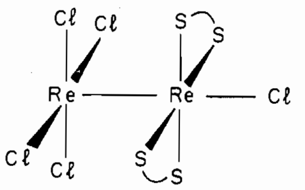


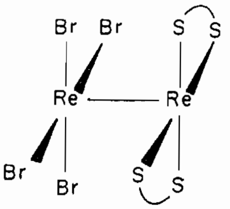
Figure 3.—Infrared spectra (1300–600 cm^{-1}) of (a) 2,5-dithiahexane (liquid film); (b) $(ReCl_3(DTH))_n$; (c) $Re_2Cl_5(DTH)_2$; (d) $Re_3Cl_9(DTH)_{1.5}$ as Nujol mulls. Between 750 and 700 cm^{-1} (b), (c), and (d) were recorded as hexachlorobutadiene mulls.

One interesting feature of the spectra of several of the complexes is the presence of a band of medium intensity at 978 cm^{-1}, previously noted[31] in the spectra of other complexes of *gauche*-2,5-dithiahexane. In addition to the strong band at 960 cm^{-1}, assigned to the CH_2 and CH_3 rocking modes of both the *trans* and *gauche* isomers, Hayashi, *et al.*,[28] also attributed a weak band at 972 cm^{-1} to the CH_3 rocking mode of the *trans* and *gauche* isomers. Thus the appearance of a band at ~980 cm^{-1} (in addition to that at 960 cm^{-1}) in the complexes of *trans*- and *gauche*-2,5-dithiahexane is consistent with such an assignment.

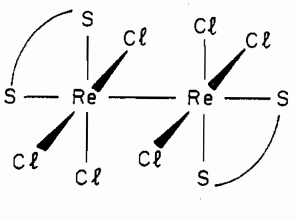
The diffuse reflectance spectra of $Re_2Cl_5(DTH)_2$ and $[ReBr_2(DTH)]_n$ (Table II and Figure 4) differ from those of $[ReX_3(DTH)]_n$, in keeping with the expected



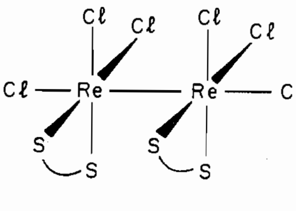
VI



VII



VIII



IX

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

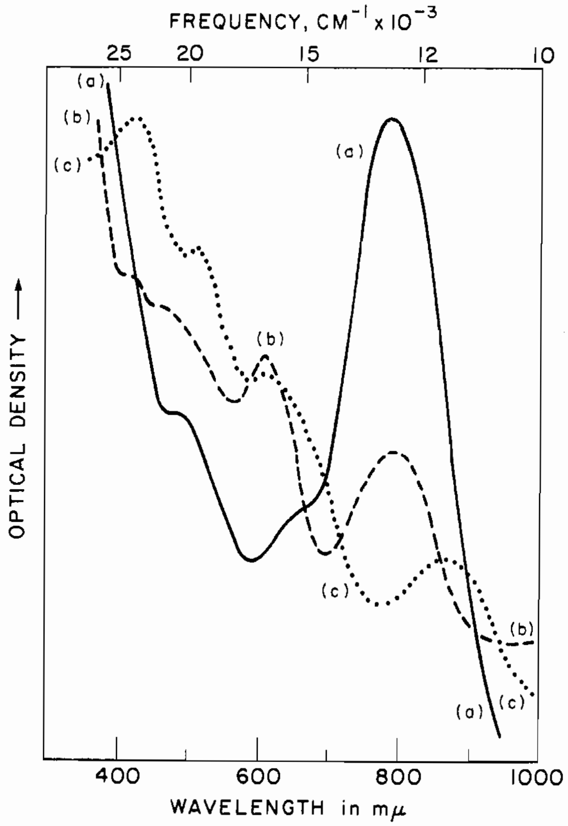

Figure 4.—Diffuse reflectance spectra (1000–350 mμ) of (a) $(ReCl_3(DTH))_n$; (b) $Re_2Cl_5(DTH)_2$; (c) $[ReBr_2(DTH)]_n$.

differences in molecular and electronic structures. The crystal structure of $Re_2Cl_5(DTH)_2$ is known[33] and is essentially as shown in VI with both rhenium(III) and rhenium(II) species. It is tempting to suggest that $[ReBr_2(DTH)]_n$ may be related to this (VII), since both are prepared by very similar methods. However, a polymer (or dimer) based upon the square-planar unit $[ReBr_2(DTH)]$ must also be considered possible. Few complexes of rhenium(II) have previously been reported, and virtually no structural data are yet available.

The structure of $[ReX_3(DTH)]_n$, like $ReCl_3$(diphos),[7] in unknown, although infrared and visible spectral studies have shed some light on the problem. Figure 5 shows a chart of the electronic absorption bands of several rhenium(III) complexes in which a Re–Re bond is known to exist or in which there is a strong possibility of such a dinuclear species. With the exception of $ReCl_3$(diphos), all the complexes show a sharp absorption band between 14,100 and 12,100 cm^{-1}, a weak band or shoulder between 18,200 and 15,400 cm^{-1}, and usually a further fairly intense absorption below 20,000 cm^{-1} (three bands in the case of $(pyH)_2Re_2Br_8$).[34] From the close similarity of the spectra we conclude that the Re–Re bond is retained on passing from $Re_2X_8^{2-}$ to $[ReX_3L]_n$, except possibly in $[ReCl_3$(diphos)].

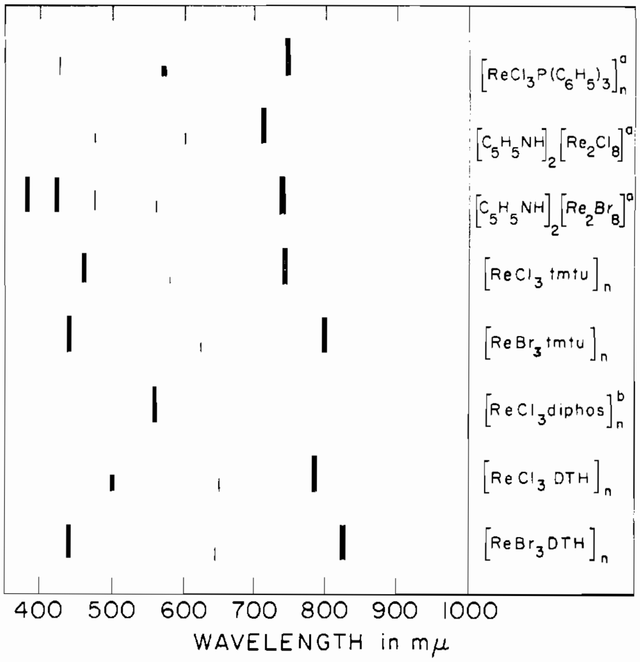

Figure 5.—Correlation chart of the diffuse reflectance spectra of complexes of the types $Re_2X_8^{2-}$ and $[ReX_3L]_n$. The relative intensity of a band is indicated by the length of the line representing it. Short thin lines are shoulders.

[a] F. A. Cotton, W. R. Robinson, and R. A. Walton, to be published. [b] Mull spectrum—see ref 7.

In the case where L = 2,5-dithiahexane, the ligand can bond either as a monodentate ligand or as a chelate; in the latter case two structures (VIII or IX) appear most likely.

Infrared spectral studies on $[ReX_3(DTH)]_n$ have shown that the ligand has the *gauche* conformation and is therefore almost certainly bidentate and chelating.[35] A structure similar to IX is then favored for the following reasons: (i) Axial substituents are known[8] to affect the position of the low energy (14,000–12,000 cm^{-1}) visible absorption band unless this interaction is weak. This would be consistent with the presence of long, weak terminal Re–Cl bonds. (ii) This might then explain the reaction of the chloride complex with nitromethane and acetonitrile since the terminal Re–Cl bonds would then be likely to be susceptible to solvolysis.

(c) **Other Complexes.**—Further reactions of $Re_2Cl_8^{2-}$ were studied in the hope of extending the known complexes of rhenium(III). As described in the Experimental Section, only 2,2′-bipyridyl of the nitrogen ligands investigated gave a pure complex. $ReCl_3$(bipy) was isolated as a dark blue powder and its infrared spectrum confirmed the absence of bands associated with the Re=O group. However, its electronic spectrum (Table II) differed from those of other com-

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(34) The intensities of the bands shown in Figure 5 refer only to the relative intensity of the absorptions in the diffuse reflectance spectra and do not necessarily reflect the absolute band intensities. For example, the solution spectrum of $Re_2Cl_8^{2-}$ has shown[3,4] that the 14,100–12,100 cm^{-1} band is associated with the $\delta \rightarrow \sigma_n$ transition, which is electric dipole forbidden and consequently of small oscillator strength. However, it occurs as a strong band in the diffuse reflectance spectra and could therefore have been incorrectly attributed to an allowed transition.

(35) The infrared spectrum of $Re_3Cl_9(DTH)_{\sim 3}$, in which the ligand is possibly bonded as a monodentate,[2] is very similar to that of $Re_3Cl_9DTH_{1.5}$, in which the ligand has the *trans* conformation (Table V and Figure 3). Consequently the *trans* conformation seems to be characteristic of bridging and monodentate 2,5-dithiahexane.

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.

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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

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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

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[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.

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