On the other hand, it is not clear why neither SO_4^{2-} nor H_2O should be coordinated. Clearly, this compound requires further study.

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Reactions of Rhenium(III) Chloride with 2,2'-Bipyridyl, 1,10-Phenanthroline, and Other Bidentate Donor Molecules[1]

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The reactions of rhenium(III) chloride with the bases (B) 2,2'-bipyridyl, 1,10-phenanthroline, 1,2-bis(diphenylphosphino)ethane, and 2,5-dithiahexane have been studied. Under mild reaction conditions the complexes $Re_3Cl_9B_{1.5}$ were isolated with all the above bidentate ligands except 1,10-phenanthroline. Their visible spectra are consistent with the presence of the Re_3Cl_9 cluster, and the complexes are believed to contain bridging bidentate donor molecules. These results are at variance with some earlier work. Products containing a higher proportion of ligand were isolated by carrying out the reactions under more forcing conditions. In addition, the complexes $Re_3Cl_9L_3$, where L = acetonitrile, benzonitrile, aniline, *o*- and *p*-phenylenediamines, and 1,4-thioxane have been isolated; their properties and structures are discussed. A novel reaction occurs on refluxing acetonitrile solutions of rhenium(III) chloride (or bromide) and 2,2'-bipyridyl. Under these conditions, products of empirical formula $Re_2X_5(\text{bipy})\cdot CH_3CN$ can be isolated.

Introduction

Studies in these laboratories[2-5] and elsewhere[6-8] have shown that the reactions of rhenium(III) chloride and bromide with halide ions and a variety of monodendate donor molecules invariably lead directly to the formation of complexes in which the trimeric Re_3X_9 cluster is retained. Only when forcing reaction conditions are used or oxidation is favored does a breakdown of these species appear to occur.

We are currently investigating the reactions of the octahalodirhenium(III) ions $(Re_2X_8)^{2-}$ with phosphorus,[9] nitrogen,[10] and sulfur[10] ligands and were prompted to study the reactivity of the trinuclear rhenium(III) halides toward bidentate donor molecules. Several of these systems have previously been investigated by other workers,[11] but this work was carried out at a time when the stereochemistry of rhenium(III) was not well understood and the correct formulation of the products therefore difficult. Consequently, we considered it worthwhile to investigate these and other systems further and in detail. In particular we were intrigued by the reported[8,11] isolation of complexes of empirical formula Re_2X_4B, where X = Cl or Br and B = 2,2'-bipyridyl or 1,10-phenanthroline, from the direct reaction of the trihalides with these amines. This behavior did not appear to be consistent with the known or expected behavior of the rhenium(III) chloride and bromide entities, Re_3Cl_9 and Re_3Br_9.

Since molecular models show that bidentate ligands are unlikely to be bonded to two rhenium atoms in the same cluster,[12] we were interested to know the mode of ligand bonding and the stability of the complexes so formed. The present communication describes the results of these studies.

Experimental Section

Rhenium(III) Chloride.—This compound was obtained from the H. W. Shattuck Co. and was used as supplied after being allowed to stand for a day in an atmosphere saturated with water vapor. This treatment gave a product which, after pumping *in vacuo* at 80°, readily dissolved in suitable solvents.

Rhenium(III) Bromide.—This halide was prepared as previously described.[6]

1,2-Bis(diphenylphosphino)ethane (diphos).—This phosphine was prepared by the method of Chatt and Mann.[13] Bipyridyl (bipy) was a commercial sample.

Analyses were performed by the Galbraith Microanalytical Laboratories, Knoxville, Tenn. Low chlorine analyses were obtained (up to 3% less than that required by theory), but in all cases these figures were sufficient to enable alternative formulations to be differentiated. These low analyses presumably result from an incomplete decomposition of the Re_3Cl_9 cluster.

Infrared spectra were recorded in the range 4000–400 cm^{-1} on a Perkin-Elmer Model 337 spectrophotometer. Visible spectra were obtained with a Beckman DU spectrophotometer. Conductivities were measured at 23 ± 2° with a commercial Wheat-

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[1] Research supported by the United States Atomic Energy Commission under Contract AT(30-1)-1965.

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

[10] F. A. Cotton, C. Oldham, and R. A. Walton, to be published.

[11] R. Colton, R. Levitus, and G. Wilkinson, *J. Chem. Soc.*, 4121 (1960).

[12] Complex formation occurs by breakdown of the "loose" intermolecular chlorine atom bridges in the trichloride[4] and coordination to the three in-plane, nonbridging positions. The bridging and terminal halogen atoms of the Re_3X_9 cluster then impose stringent steric requirements that will almost certainly prevent coordination of both donor atoms of the bidentate ligand to the same cluster.

[13] J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1378 (1960).

stone bridge circuit. The magnetic susceptibility of the complex Re_2Cl_5(bipy)·CH_3CN was measured at room temperature (300°K) on a Gouy balance.

Re_3Cl_9(bipy)$_{1.5}$.—To a solution of 0.10 g of rhenium(III) chloride (0.011 mmole) in 10 ml of acetone was added 0.17 g of 2,2′-bipyridyl (1.09 mmoles) dissolved in the minimum volume of acetone. A blue-purple solid immediately precipitated and was filtered off, washed freely with acetone and ether, and dried *in vacuo* at 80° for several hours.

Anal. Calcd for $C_{15}H_{12}N_3Re_3Cl_9$ (Re_3Cl_9(bipy)$_{1.5}$): C, 16.67; H, 1.12; N, 3.89; Cl, 29.49. Found: C, 16.3; H, 1.55; N, 3.70; Cl, 28.5. Calcd for $C_{10}H_8N_2Re_2Cl_4$, *i.e.*, Re_2Cl_4(bipy):[11] C, 17.92; H, 1.20; N, 4.18; Cl, 21.16.

Solubility.—The compound is slightly soluble in acetonitrile, virtually insoluble in acetone, tetrahydrofuran, and ethanol, and insoluble in hydrocarbon and ethers.

An identical product was isolated by carrying out the reaction in a *small* volume of acetonitrile (less than 5 ml), washing the product with acetonitrile (5 ml) and ether, and drying *in vacuo* at 80°.

Anal. Found: C, 16.7; H, 1.62; N, 4.03.

The above complex, Re_3Cl_9bipy$_{1.5}$, was isolated by mixing the reactants at *room temperature* in the appropriate solvent (acetone or acetonitrile). When the reaction was carried out above room temperature, different products were isolated as described below. In view of the dependence of the products upon the reaction conditions, we recommend a strict adherence to the preparation details given.

(a) On mixing warm acetone solutions of the reactants and then heating the reaction mixture on a steam bath for about 5 min, an insoluble product, similar in appearance and properties to Re_3Cl_9(bipy)$_{1.5}$, was obtained. However, the analytical data were consistent with a product of composition approximating to Re_3Cl_9(bipy)$_2$. (These are virtually the reaction conditions reported[11] to give Re_2Cl_4(bipy). The analytical figures approximate more closely to those for Re_3Cl_9(bipy)$_2$ than to those (*vide infra*) for Re_2Cl_4(bipy), but are nonetheless rather poor. It is possible that neither of these formulations is appropriate.)

Anal. Calcd for $C_{20}H_{16}N_4Re_3Cl_9$ (Re_3Cl_9(bipy)$_2$): C, 20.19; H, 1.36; N, 4.71. Found (for separate preparations): C, 19.13, 20.09; H, 1.65, 1.70; N, 4.33, 4.27.

(b) On carrying out the reaction in *ca.* 20 ml of boiling acetonitrile, a small amount of fine purple precipitate separated. Refluxing the reaction mixture soon dissolved this precipitate and gave a clear wine-red solution, from which a purple powder could be precipitated on addition of a large excess of ether. This was filtered off, washed with benzene and ether, and dried *in vacuo* at 80°.

Anal. Calcd for $C_{12}H_{11}N_3Re_2Cl_5$ (Re_2Cl_5(bipy)·CH_3CN): C, 19.31; H, 1.49; N, 5.63; Cl, 23.76. Found (for separate preparations): C, 20.89, 20.26; H, 2.06, 2.19; N, 5.78, 5.69; Cl, 23.63, 23.61.

Dissolving this complex in acetone containing an excess of 2,2′-bipyridyl and refluxing the solution for several hours failed to affect the composition of the product, which could be reprecipitated unchanged by the addition of an excess of ether.

Solubility.—The compound is soluble in acetonitrile, acetone, nitromethane, and tetrahydrofuran and insoluble in hydrocarbons and ethers. Solutions in nitromethane rapidly changed color on standing, but the cause of this has not been elucidated.

This complex was soluble in acidified methanol to form a red solution from which purple crystalline product of composition *approximating* to Re_2Cl_6(bipy)·CH_3CN was isolated on evaporation of the solvent.

Anal. Calcd for $C_{12}H_{11}N_3Re_2Cl_6$: C, 18.43; H, 1.42; N, 5.37; Cl, 27.20. Found: C, 17.7; H, 1.92; N, 4.88; Cl, 28.0.

Re_3Cl_9(bipy)$_3$.—An attempt was made to repeat the preparation of the complex $ReCl_3$(bipy) by the method of Colton, *et al.*;[11] 0.15 g of Re_3Cl_9(bipy)$_{1.5}$ was suspended in 15 ml of acetone and 0.20 g of 2 2′-bipyridyl added. A stream of chlorine gas was passed into the suspension for 30 min. Colton *et al.*,[11] report that the initial complex dissolves to form a red solution and that the reaction could be stopped after 30 min. No such behavior was observed in the present work. After passage of chlorine for a few minutes a white precipitate rapidly formed (presumably bipyridinium hydrochloride) and after 2 hr a red solution had still not formed. The dark red insoluble solid remaining was filtered from the pale yellow solution, washed repeatedly with acetone and ether, and dried by pumping *in vacuo* at 80° when a further quantity of bipyridinium hydrochloride sublimed from this material.

Anal. Calcd for $C_{30}H_{24}N_6Re_3Cl_9$: C, 26.77; H, 1.80; N, 6.24. Found: C, 24.7; H, 2.78; N, 5.43.

This product was not investigated further.

Re_3Br_9(bipy)$_{1.5}$.—This complex was prepared by a method similar to that described for the chloride analog. A brown precipitate formed on mixing acetone solutions of the reactants and was filtered off, washed with acetone and ether, and dried *in vacuo* at 80°.

Anal. Calcd for $C_{15}H_{12}N_3Re_3Br_9$: C, 12.04; H, 0.80; N, 2.78. Found: C, 12.1; H, 1.26; N, 3.07.

Reaction in boiling acetonitrile yielded a product of empirical formula Re_2Br_5(bipy)·CH_3CN on addition of excess ether to the deep brown solution. The brown complex was filtered off, washed with benzene and ether, and dried *in vacuo*.

Anal. Calcd for $C_{12}H_{11}N_3Re_2Br_5$ (Re_2Br_5(bipy)·CH_3CN): C, 14.87; H, 1.25; N, 4.34. Found: C 14.8; H, 1.88; N, 4.47.

Re_3Cl_9(diphos)$_{1.5}$.—Rhenium(III) chloride (0.10 g, 0.011 mmole) and 0.10 g of diphosphine (0.215 mmole) were mixed in acetone or tetrahydrofuran. A pale red powder precipitated immediately and was filtered off and washed with acetone and ether. The red complex was dried *in vacuo* at 80°.

Anal. Calcd for $C_{26}H_{24}P_2Re_3Cl_9$: C, 32.76; H, 2.54; P, 6.50; Cl, 22.31. Found: C, 32.8; H, 2.60; P, 6.39; Cl, 20.6.

Solubility.—The compound is insoluble in all common polar and nonpolar solvents and unaffected by boiling hydrochloric acid.

$Re_3Cl_9[(CH_3SCH_2-)_2]_{1.5}$.—This complex was prepared by refluxing an acetone solution of 0.10 g of rhenium(III) chloride containing 0.5 ml of 2,5-dithiahexane (DTH) for *ca.* 15 min. A dark purple microcrystalline solid rapidly precipitated from the red solution and was filtered off, washed with acetone and ether, and dried *in vacuo* at 80°.

Anal. Calcd for $C_6H_{15}S_3Re_3Cl_9$: C, 6.79; H, 1.43; S, 9.07. Found: C, 6.34; H, 1.34; S, 8.85.

Solubility.—This complex is appreciably soluble in acetonitrile and tetrahydrofuran but only very slightly soluble in acetone; it is insoluble in the usual nonpolar solvents.

By using a larger excess of 2,5-DTH and longer reflux times, products containing a higher proportion of ligand could be isolated, as illustrated in the following examples.

(a) Refluxing 0.10 g of rhenium(III) chloride with 0.5 ml of DTH in acetone for 1–2 hr gave a crop of red crystals.

Anal. Calcd for $C_8H_{20}S_4Re_3Cl_9$ (Re_3Cl_9(DTH)$_2$): C, 8.57; H, 1.80; S, 11.42. Found (for separate preparations): C, 8.14, 8.21; H, 1.81, 1.65; S, 12.3, 11.0.

(b) Dark red crystals were obtained on refluxing 0.10 g of rhenium(III) chloride with 1.4 ml of DTH in acetone for 3 hr.

Anal. Calcd for $C_{12}H_{30}S_6Re_3Cl_9$ (Re_3Cl_9(DTH)$_3$): C, 11.59; H, 2.43; S, 15.46. Found: C, 10.7; H, 2.22; S, 14.5.

Analytical data were not always very reproducible between different runs, but by using the above conditions products *approximating* to Re_3Cl_9(DTH)$_2$ and Re_3Cl_9(DTH)$_3$ could be isolated.

An attempt was made to repeat the preparation of ($ReCl_3$-DTH)$_n$ as described by Colton, *et al.*[11] (these workers assumed $n = 1$). Rhenium(III) chloride (0.1 g) and 2.5 ml of DTH were refluxed in 10 ml of acetone for 1 hr. The red solution so obtained was filtered and a large excess of ether added to precipitate a pale red solid. This product was washed with ether and pumped *in vacuo* for several hours at 80°.

Anal. Found: C, 10.0; H, 1.87; S, 13.0.

$Re_3Cl_9(C_6H_5NH_2)_3$.—To a suspension of 0.10 g of rhenium(III) chloride in 5 ml of benzene was added *ca.* 1 ml of aniline. The chloride quickly dissolved to form a cherry-red solution which was heated for 30 min and filtered while hot. Ether was then added to the filtrate to precipitate a dark brown powder which was washed with benzene and ether and dried *in vacuo*.

Anal. Calcd for $C_{18}H_{21}N_3Re_2Cl_9$: C, 18.69; H, 1.83; N, 3.63. Found: C, 18.3; H, 2.08; N, 3.20.

The insoluble residue remaining on the filter pad after the initial filtration of the hot solution was extracted with mixed benzene–chloroform. Evaporating this solvent left a white crystalline solid whose infrared spectrum was identical with that of an authentic sample of aniline hydrochloride.

$Re_3Cl_9[(p\text{-}C_6H_4(NH_2)_2)]_3$.—The reaction of 0.08 g of rhenium(III) chloride with 0.10 g of *p*-phenylenediamine in tetrahydrofuran gave a red solution from which a red complex could be isolated by addition of a large excess of ether.

Anal. Calcd for $C_{18}H_{24}N_6Re_3Cl_9$: C, 17.99; H, 2.01. Found: C, 17.4; H, 1.95.

$Re_3Cl_9[(o\text{-}C_6H_4)NH_2)_2)]_3$.—A similar method to that described above gave the red complex, which was precipitated from solution by addition of cold pentane.

Anal. Calcd for $C_{18}H_{24}N_6Re_3Cl_9$: C, 17.99; H, 2.01. Found: C, 17.2; H, 1.96.

$Re_3Cl_9(C_4H_8OS)_3$.—Rhenium(III) chloride (0.08 g) was dissolved in 10 ml of tetrahydrofuran, and 0.5 ml of 1,4-thioxane was added to the solution. After refluxing for 2 hr the cherry-red solution was filtered and the filtrate evaporated to low bulk. As the solution cooled to room temperature dark red needles separated, and these were filtered off, washed with ether, and dried *in vacuo* at 80°.

Anal. Calcd for $C_{12}H_{24}O_3S_3Re_3Cl_9$: C, 12.12; H, 2.03; S, 8.08. Found: C, 12.9; H, 2.12; S, 7.63.

This product is probably contaminated with a trace of "free" 1,4-thioxane, since even after pumping for 12 hr at 80°, the complex still smelled strongly of 1,4-thioxane.

$Re_3Cl_9(CH_3CN)_3$.—This complex was obtained as dark purple crystals by evaporating to dryness an acetonitrile solution of rhenium(III) chloride.

Anal. Calcd for $C_6H_9N_3Re_3Cl_9$: C, 7.20; H, 0.91; N, 4.20. Found: C, 7.59; H, 1.18; N, 4.10.

Prolonged pumping *in vacuo* at 80° resulted in some loss of coordinated acetonitrile.

$Re_3Cl_9(C_6H_5CN)_3$.—This complex was obtained by a similar method to that described for its acetonitrile analog.

Anal. Calcd for $C_{21}H_{15}N_3Re_3Cl_9$: C, 21.27; H, 1.28; N, 3.55. Found: C, 22.4; H, 1.66; N, 3.02.

$ReOCl_3$(bipy).—To a suspension of oxotrichlorobistriphenylphosphinerhenium(V)[6] in acetone was added 0.05 g of 2,2′-bipyridyl, and the mixture was heated on a steam bath until a deep yellow-brown solution was formed. This was filtered to remove any undissolved $ReOCl_3[P(C_6H_5)_3]_2$, and ether was added to the filtrate to precipitate a yellow-brown solid, which was washed with ether. It was then suspended in acidified (HCl) methanol and warmed on a steam bath for ~10 min. The bright yellow powder was filtered off, washed with acidified methanol and ether, and finally dried *in vacuo*.

Anal. Calcd for $C_{10}H_8N_2OReCl_3$: C, 25.84; H, 1.95; N, 6.03. Found: C, 25.9; H, 2.00; N, 5.72.

The infrared spectrum of this complex showed a strong band at 983 cm^{-1} (ν(Re–O)), in addition to the usual bipyridyl absorptions.

Reaction of Rhenium(III) Chloride with 1,10-Phenanthroline.—Attempts to repeat the reported preparation[11] of Re_2Cl_4(phen) were unsuccessful. In no instance did we isolate this complex, but in all cases we obtained purple insoluble products of composition $Re_3Cl_9(phen)_x$, where x had values ranging from 2 to ~2.8. Reaction was carried out using acetone, tetrahydrofuran, or acetonitrile as solvents. In the latter solvent the product $Re_3Cl_9(phen)_2$ could be isolated.

Anal. Calcd for $C_{24}H_{16}N_4Re_3Cl_9$: C, 23.89; H, 1.34; N, 4.64. Found: C, 23.5; H, 1.62; N, 4.55.

We have confirmed,[8] however, that any of the above products can readily be converted into dark red (o-phenH)Re_3Cl_{11} by warming with an acidified methanol solution (~1 ml of 12 *N* HCl in 3 ml of methanol) of phenanthroline. The complex halide crystallizes from the red solution.

Anal. Calcd for $C_{24}H_{18}N_4Re_3Cl_{11}$: C, 21.97; H, 1.37; N, 4.27. Found: C, 20.6; H, 1.74; N, 4.04.

Results

All the complexes prepared in the present study are listed in Table I, together with those physical properties which we have investigated. In all instances the products isolated were purple-red in color and insoluble in nonpolar solvents, but in some instances slightly soluble in acetonitrile and other polar solvents. Their insolubility in suitable solvents precluded the measurement of molecular weights in solution. Figures 1 and 2 show the visible spectra of several of the complexes in the region 1200–350 mμ.

Complexes with Bidentate Ligands. (a) **2,2′-Bipyridyl.**—Rhenium(III) chloride and bromide react at room temperature with this ligand in acetone, acetonitrile, or tetrahydrofuran solutions to give the insoluble complexes $Re_3X_9(bipy)_{1.5}$. In the case of the chloride, reaction under reflux in acetone resulted in the formation of products of composition approximating to $Re_3Cl_9(bipy)_2$, whose appearance and properties are similar to those of $Re_3Cl_9(bipy)_{1.5}$.

Complexes of empirical formula $Re_2X_5(bipy)\cdot CH_3CN$ could be isolated by refluxing acetonitrile solutions of rhenium(III) chloride or bromide and 2,2′-bipyridyl. The chloride complex had a room-temperature magnetic moment of ~0.9 (±0.1) BM per dimer. The reaction of $Re_2Cl_5(bipy)\cdot CH_3CN$ with hydrochloric acid yielded a purple product analyzing fairly closely to $Re_2Cl_6(bipy)\cdot CH_3CN$.

The infrared spectra of all the above 2,2′-bipyridyl complexes were virtually identical in the 4000–650 cm^{-1} range and showed peaks characteristic of coordinated bipyridyl.[14,15] The absence of bands associated with the rhenium–oxygen stretching vibrations was confirmed by comparison with the infrared spectrum of $ReOCl_3$(bipy), which has a strong band at 983 cm^{-1} assigned to ν(Re—O). The spectra of $Re_2X_5(bipy)\cdot CH_3CN$ had no bands at ~2250 cm^{-1} characteristic of $\nu(C{\equiv}N)$ of free or coordinated acetonitrile. However, medium-weak absorptions were observed at ~3200 cm^{-1} which may be associated with N—H stretching vibrations; no such bands were found in the spectra of $Re_3X_9(bipy)_{1.5}$ and $ReOCl_3$(bipy).

(b) **1,10-Phenanthroline.**—The products obtained from the reaction of rhenium(III) chloride with 1,10-phenanthroline were similar in appearance to the analogous bipyridyl complexes. Analytical data showed them to have compositions ranging from $Re_3Cl_9(phen)_2$ to $Re_3Cl_9(phen)_{2.8}$ depending upon the reaction conditions. Solution of these blue-purple powders in acidified methanol (HCl) afforded the red complex halide (o-phenH)Re_3Cl_{11}.

(c) **1,2-Bis(diphenylphosphino)ethane.**—The red

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[14] A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem.*, **9**, 211 (1959).

[15] R. G. Inskeep, *ibid.*, **24**, 763 (1962).

TABLE I

PROPERTIES OF RHENIUM(III) COMPOUNDS

Compound	Color	Visible absorption bands		Λ_M, ohm^{-1} cm^2 [b]
		Medium	Peak positions, mμ[a]	
$Re_3Cl_9(bipy)_{1.5}$	Blue-purple	Solid	935 ~560 br	130
		CH_3CN	~870 (180) 550 (1430)	
$Re_2Cl_5(bipy)\cdot CH_3CN$	Purple	Solid	875 br 550	110
		CH_3CN	820 (250) 540 (1160)	61[c]
$Re_2Cl_6(bipy)\cdot CH_3CN$	Purple	Solid	840 560	106
$Re_3Br_9(bipy)_{1.5}$	Brown	Solid	910 560 ~400 sh	166
		CH_3CN	~880 sh 560 (1700)	
$Re_2Br_5(bipy)\cdot CH_3CN$	Brown	Solid	~800 sh, br 570	
		CH_3CN	~800 sh, br 570 (840)	
$Re_3Cl_9(CH_3CN)_3$	Purple	Solid	840 550	6.2
		CH_3CN	800 (410) 535 (1750)	
$Re_3Cl_9(C_6H_5CN)_3$	Purple	Solid	900 565	
$Re_3Cl_9(C_6H_5NH_2)_3$	Brown	Solid	~950 br ~550 sh	
$Re_3Cl_9[(p\text{-}C_6H_4(NH_2)_2)]$	Red	Solid	800 535	
$Re_3Cl_9(diphos)_{1.5}$	Red	Solid	840 555 ~440 sh	Insol
$Re_3Cl_9(DTH)_{1.5}$	Purple	Solid	810 535	
$Re_3Cl_9(DTH)_2$	Red	Solid	775 520	
$Re_3Cl_9(DTH)_{>2.5}$	Red	Solid	750 515	17
$Re_3Cl_9(C_4H_8OS)_3$	Red	Solid	805 535	

[a] ϵ_{max} in parentheses. [b] Molar conductance of ~0.001 *M* solutions in CH_3CN. [c] Measured in acetone: 1:1 electrolytes have Λ_M ~120 ohm^{-1} cm^2 in this solvent.

complex $Re_3Cl_9(diphos)_{1.5}$ was precipitated from acetone or tetrahydrofuran solutions of the reactants. In the region 4000–650 cm^{-1} the infrared spectrum of this complex was typical of coordinated diphosphine.

(d) **2,5-Dithiahexane (2,5-DTH).**—The product from the reaction of rhenium(III) chloride with this ligand was dependent upon the experimental conditions. Thus the use of a moderate excess of ligand and a reaction time of about 10 min favored the formation of $Re_3Cl_9(DTH)_{1.5}$. Longer reaction times and a larger excess of ligand gave products of composition approximating to $Re_3Cl_9(DTH)_2$ or $Re_3Cl_9(DTH)_3$. Exact reaction conditions for the reproducible isolation of complexes of these particular stoichiometries were difficult to ascertain and cannot at present be exactly specified.

All three compounds have very similar infrared spectra which closely resemble that of the rhodium(III) complex $RhCl_3(DTH)$. In all instances the spectra were dominated by a strong band at 960 cm^{-1}, which is also present in the spectrum of the free ligand.[16] For this reason we believe it is not associated with a Re–O stretching vibration. The possibility that ν(Re–O) is coincident with this ligand vibration cannot, of course, be ruled out, but the absence of a corresponding band in the infrared spectra of the other complexes of Re_3X_9 suggests this is very unlikely. The free ligand symmetric C–S stretching vibration (738 cm^{-1}) is drastically reduced in intensity on complex formation, while the antisymmetric stretching vibration (686 cm^{-1}) is lowered in frequency by about 10 cm^{-1}.

Complexes with Other Ligands.—Rhenium(III) chloride dissolves in acetonitrile and benzonitrile and from these solutions the complexes $Re_3Cl_9(RCN)_3$ can be isolated. The presence of coordinated nitrile was confirmed by the infrared spectra of the complexes, which showed bands at 2280 ($R = CH_3$) and 2250 ($R = C_6H_5$) cm^{-1}, associated with the C≡N stretching

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(16) Measured as a liquid film (1300–650 cm^{-1}): 1284 sh, 1269 mw, 1206 ms, 1133 mw, 1025 vw, 1010 vw, 975 sh, 960 m, 840 vw, 738 mw, 686 m.

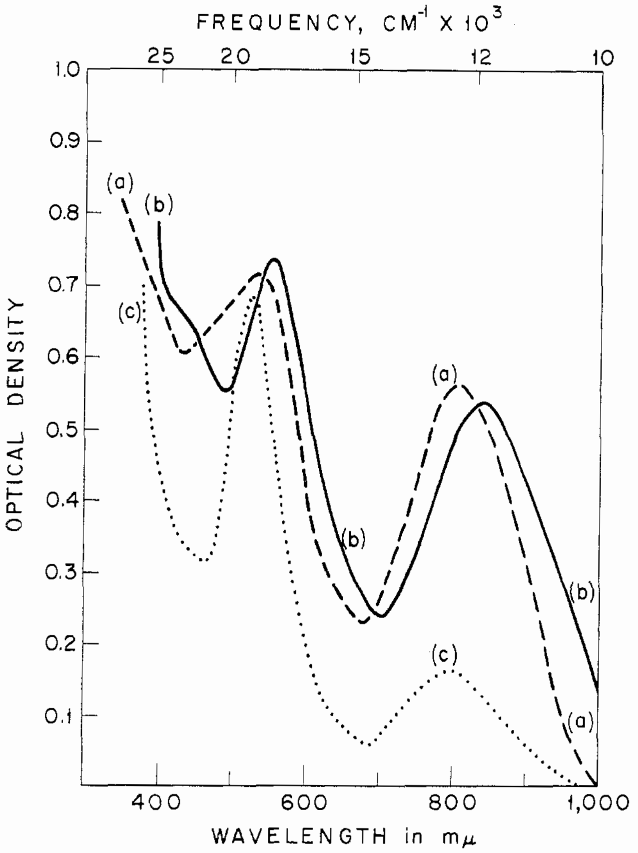

Figure 1.—Diffuse reflectance spectra (1000–350 mμ) of (a) $Re_3Cl_9(DTH)_{1.5}$ and (b) $Re_3Cl_9(diphos)_{1.5}$; solution spectrum of (c) $Re_3Cl_9(CH_3CN)_3$ in acetonitrile.

vibrations. These vibrations suffer the usual increase in frequency (compared to the free ligand)[17] that is characteristic of bonding from the lone pair on the nitrile nitrogen atom. The combination band ($\nu_3 + \nu_4$), which occurs at 2293 cm^{-1} in free acetonitrile,[18] close to ν(C≡N), is shifted to 2310 cm^{-1} in $Re_3Cl_9(CH_3CN)_3$.

From the reaction of rhenium(III) chloride with aniline and *o*- and *p*-phenylenediamines, the complexes Re_3Cl_9(amine)$_3$ could be isolated. In the latter two reactions, the complexes were quickly isolated from the reaction mixtures to avoid the formation of aminolyzed products. The isolation of aniline hydrochloride from the reaction with aniline showed that some solvolysis of rhenium(III) chloride had occurred during this reaction.

The solution of rhenium(III) chloride in 1,4-thioxane afforded red needles of $Re_3Cl_9(C_4H_8OS)_3$. The infrared spectrum of this complex was virtually identical with that of the free ligand.[19] The symmetric and antisymmetric C–O–C stretching vibrations, which occur at 1105 and 834 cm^{-1} in the free ligand, were unaltered in frequency and relative intensity on complex formation. As previously discussed[19] this is indicative of sulfur-bonded 1,4-thioxane.[20]

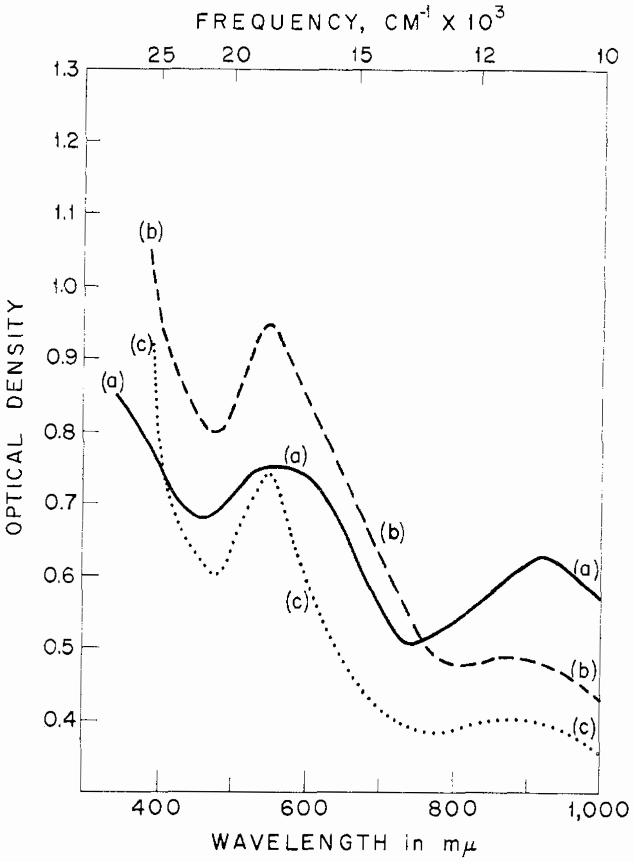

Figure 2.—Diffuse reflectance spectra (1000–350 mμ) of (a) $Re_3Cl_9(bipy)_{1.5}$ and (b) $Re_2Cl_5(bipy)\cdot CH_3CN$; solution spectrum of (c) $Re_3Cl_9(bipy)_{1.5}$ in acetonitrile.

Discussion

We have found that under mild reaction conditions rhenium(III) chloride reacts with 2,2′-bipyridyl, 1,2-bis(diphenylphosphino)ethane, and 2,5-dithiahexane to give complexes of empirical formula $Re_3Cl_9(B)_{1.5}$. The diphosphine complex is completely insoluble in all common solvents, whereas $Re_3Cl_9(DTH)_{1.5}$ forms a nonconducting solution in acetonitrile. The $Re_3X_9(bipy)_{1.5}$ (X = Cl, Br) compounds are slightly soluble in this latter solvent, and conductivity and spectral measurements (Table I) suggest that the soluble species may be $Re_2X_5(bipy)\cdot CH_3CN$, complexes that we have prepared by reaction of rhenium(III) halides with 2,2′-bipyridyl in boiling acetonitrile.

In all instances the diffuse reflectance and solution spectra of the complexes (Table I) were typical of species containing the $[Re_3X_9]$ cluster. Bands at ~550 and 800–950 mμ, the former being the more intense, were consistent with the presence of this trinuclear species. A comparison may usefully be made with spectral data previously reported for complexes of the type $Re_3X_9L_3$,[5,8] where L represents a monodentate donor molecule. While the position of the 550 mμ band is essentially independent of the coordinating species, the band at longer wavelength is particularly sensitive to the donor molecules and appears to occur at longest wavelengths for nitrogen donors. It occurs at a somewhat shorter wavelength (800 mμ) in $Re_3Cl_9[(p$-

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[17] R. A. Walton, *Quart. Rev.* (London), **19**, 126 (1965).

[18] P. Venkateswarlu, *J. Chem. Phys.*, **19**, 293 (1951).

[19] R. A. Walton, *Inorg. Chem.*, **5**, 643 (1966).

[20] This is not unexpected as rhenium(III) chloride shows little or no tendency to form complexes with ethers such as tetrahydrofuran and 1,4-dioxane.

$C_6H_4(NH_2)_2]_3$, for which there is no obvious explanation.

We believe that the complexes $Re_3X_9(B)_{1.5}$ are polymeric, with bridging bidentate molecules linking Re_3X_9 units. This is evidently reasonable in the case of the diphosphine and 2,5-DTH complexes, and although 2,2′-bipyridyl is not definitely known to bond in this manner, there are several instances where such bonding has been postulated.[21-23] Since 1,10-phenanthroline cannot bond in this way, the formation of $Re_3Cl_9(phen)_{1.5}$ would not be expected. We have confirmed this and found that only products of variable composition, with two or more phenanthroline molecules per Re_3Cl_9 unit, can be isolated. Coordination of monodentate donors to the Re_3X_9 cluster does not necessarily result in the occupation of all three donor sites,[8] and this probably accounts for the stoichiometry of the 1,10-phenanthroline products isolated in the present work. The diffuse reflectance spectra of these products confirmed the presence of the Re_3 metal atom cluster.

Reaction under more forcing conditions, in the case of the 2,2′-bipyridyl and 2,5-DTH reactions, then leads to the formation of products containing a higher proportion of ligand. This we believe is consistent with the breakdown of the polymer, which presumably results in the ligands acting as monodentate donors. In no instance did we isolate pure complexes of composition $Re_3X_9(B)_3$, and in all cases there were less than three molecules of ligand associated with each Re_3X_9 cluster.

The isolation of the complexes $Re_2X_5(bipy)\cdot CH_3CN$ is at first sight unexpected in view of the relatively mild reaction conditions used. Both complexes are soluble in polar solvents and form conducting solutions in acetonitrile and acetone (see Table I). The observed conductivities were generally appreciably less than those expected for typical 1:1 electrolytes in these solvents. On the basis of these data, the complexes could be formulated as $[Re_2X_4(bipy)_2]^+[Re_2Cl_6(CH_3CN)_2]^-$, although the conductivity data in acetonitrile would now be closer to that for a 1:2, rather than a 1:1, electrolyte.

The visible spectra of these complexes were characteristic of species containing the Re_3 cluster, yet $Re_2Cl_5(bipy)\cdot CH_3CN$ reacted with hydrochloric acid to form a complex of composition approximating to $Re_2Cl_6(bipy)\cdot CH_3CN$, rather than $(bipyH)_3ReCl_{12}$.[8] This former complex may be the salt $[bipyH][Re_2Cl_6\cdot CH_3CN]$, but unfortunately we were unable to prepare sufficient of this material for the determination of its magnetic moment by the Gouy method. Thus evidence for presence of a Re_3 cluster in these complexes is somewhat contradictory. In view of this we are currently attempting to prepare single crystals of $Re_2Cl_5(bipy)\cdot CH_3CN$ in the hope of carrying out an X-ray crystallographic investigation of this material.

Two further points of interest concern the complexes of empirical formula $Re_2X_5(bipy)\cdot CH_3CN$. First, although the analytical data are consistent with the presence of one molecule of acetonitrile per dimer, in the infrared spectra of both complexes there is an absence of bands associated with $\nu(C{\equiv}N)$ and the presence of weak bands at $\sim$3200 cm^{-1} which may be due to $\nu(N-H)$. In view of this, one might consider the possibility that the nitrile has been reduced to an *imine*. Second, the stoichiometry of the complexes and the magnetic moment of the chloride complex (0.9 BM) suggest that we may be dealing with rhenium in the formal oxidation state 2.5, *i.e.*, one unpaired electron per *dimer*. A similar oxidation state occurs in the technetium dimer $(NH_4)_3(Tc_2Cl_8)$,[24] and we have recently found evidence for the formation of species derived from the dimer $(Re_2Cl_8)^{3-}$.[25]

The isolation of aniline hydrochloride from the reaction of aniline with rhenium(III) chloride shows the susceptibility of the trihalides to aminolysis. No attempt was made to isolate the aminolyzed rhenium(III) species that must be present in the reaction mixture, although we did obtain the expected complex $Re_3Cl_9(C_6H_5NH_2)_3$.

The reaction of ammonia and the ethylamines with rhenium(III) chloride is reported[26] to give black powders of composition "$ReCl_3\cdot(amine)_4$," which we believe are mixtures of aminolysis products. Thus these workers report that aminolysis probably occurs when rhenium(III) chloride reacts with *liquid* diethylamine, yet they prepare "$ReCl_3(C_2H_5\cdot NH_2)_4$" from the corresponding reaction with monoethylamine. Since aminolysis is invariably greater with primary than secondary amines,[27] this material is presumably a mixture of aminolysis products.

Comparisons with Earlier Work.—Previous workers[8,11] have reported that 2,2′-bipyridyl and 1,10-phenanthroline react with rhenium(III) chloride and bromide to form the complexes $Re_2X_4\cdot B$. Rather surprisingly these novel formulations were based upon analytical data for only one of these complexes, *viz.*, $Re_2Cl_4(phen)$. Robinson and Fergusson[8] suggested that the complexes probably involved a trimeric rhenium(III) cluster since their visible spectra were very similar to those of complexes of the type $Re_3X_9L_3$. Colton, *et al.*,[11] on the other hand, postulated a dimeric structure in which rhenium atoms were present in both I and III oxidation states; other than the color of the complexes, no other evidence was given to support such a structure. From our results it is clear that the above formulation is incorrect. In all cases the Re_3 cluster is retained. However, the spectral data of Robinson and Fergusson[8] are essentially correct and we have confirmed that these complexes react with acid to form $Re_3X_{9+n}{}^{n-}$.

We were also unable to repeat the preparation of

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[21] G. W. A. Fowles, R. A. Hoodless, and R. A. Walton, *J. Inorg. Nucl. Chem.*, **27**, 391 (1965).

[22] A. S. Mufti and R. C. Poller, *J. Organometal. Chem.*, **3**, 99 (1964).

[23] B. F. G. Johnson and R. A. Walton, *Inorg. Chem.*, **5**, 49 (1966).

[24] F. A. Cotton and W. K. Bratton, *J. Am. Chem. Soc.*, **87**, 921 (1965).

[25] F. A. Cotton, W. R. Robinson, and R. A. Walton, unpublished results.

[26] M. Tsin-Shen and V. G. Tronev, *Russ. J. Inorg. Chem.*, **5**, 414 (1960).

[27] G. W. A. Fowles, *Progr. Inorg. Chem.*, **6**, 1 (1964).

"$ReCl_3 \cdot B$," where B = 2,5-DTH, 2,2′-bipyridyl, or 1,10-phenanthroline, as described by Colton, *et al.*[11] Not only were we unable to repeat the preparative details (see Experimental Section), but the products isolated were not of this stoichiometry. Thus, although prolonged reaction of rhenium(III) chloride with 2,5-DTH *sometimes* yields a product of composition approaching $Re_3Cl_9(DTH)_3$, usually less than three molecules of ligand were coordinated. Also the assertion[11] that "$ReCl_3 \cdot B$" are five-coordinate is clearly incorrect. Their visible spectra are consistent in all cases with a trimeric species.

CONTRIBUTION FROM THE U. S. GEOLOGICAL SURVEY, WASHINGTON, D. C., AND THE
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The Crystal Structures of Potassium and Cesium Trivanadates[1]

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Potassium and cesium trivanadates are monoclinic and isomorphous, space group $P2_1/m$, with the following dimensions ($Z = 2$): KV_3O_8, $a = 7.640$ A, $b = 8.380$ A, $c = 4.979$ A, $\beta = 96° 57'$; CsV_3O_8, $a = 8.176$ A, $b = 8.519$ A, $c = 4.988$ A, $\beta = 95° 32'$. The crystal structure of KV_3O_8 has been determined from $hk0$, $0kl$, and $h0l$ Weissenberg data with an R factor of 0.15. The structure of CsV_3O_8 has been refined with 1273 hkl Weissenberg data to an R factor of 0.089. The structures consist of corrugated sheets based on a linkage of distorted VO_6 octahedra. Two of the vanadium atoms lie in double, square-pyramid groups V_2O_8, which are linked through opposite basal corners into chains along the b axis. The chains are joined laterally along the c axis into sheets by the third vanadium atom in VO groups, also forming part of a square-pyramid coordination. Various aspects of these structures are compared with other known oxovanadate structures.

Introduction

A study of the crystal chemistry of vanadium in relation to the geochemistry of vanadium and uranium in the Colorado Plateau region has been carried on at the Geological Survey over the past decade. Several synthetic compounds have been analyzed by X-ray diffraction methods in order to learn more about the unusual coordination behavior of vanadium, especially in the higher valence states. Vanadium is deposited in the Colorado Plateau sandstones as lower valence oxides (for example, montroseite, VO(OH)), but under the influence of weathering conditions it is rapidly oxidized to the pentavalent state.[3] In this state readily soluble vanadates are formed, and many corresponding minerals have been found. Examples are the calcium metavanadate hydrate rossite, $Ca(VO_3)_2 \cdot 4H_2O$, the hexavanadate hewettite, $CaV_6O_{16} \cdot 9H_2O$, and the decavanadate pascoite, $Ca_3V_{10}O_{28} \cdot 17H_2O$. Alkali vanadate solutions also readily crystallize such compounds, but the natural products almost always contain an alkaline earth cation. Moderately acid potassium vanadate solutions produce crystals of decavanadates and hexavanadates but these are often accompanied, especially from warm solutions, by a light orange, crystalline phase of low solubility, potassium trivanadate KV_3O_8.[4] This seems to be a very stable phase but has not yet been found in nature.

As part of the general crystal chemical study the structure of KV_3O_8 was analyzed some time ago by Block.[5,6] Subsequently, considerably better data were obtained for the isomorphous compound cesium trivanadate CsV_3O_8, so that a more accurate description of the structure can now be presented. The present paper describes the study of both of these compounds.

Trivanadates and Vanadate Solutions

The complex behavior of vanadate solutions with respect to changes in pH has long been the subject of study by inorganic chemists, frequently with contradictory and inconclusive results. Jander and Jahr,[7] by means of diffusion-rate studies, were the first to delineate clearly the progressive condensation of vanadate anions into higher and higher molecular weight polyanions as the pH is lowered. More recently, careful studies by emf methods have been reported for sodium vanadate solutions over the pH range 7–10 by Brito and Ingri[8] and by Ingri and Brito,[9] and in the pH range 1–6.5 by Rossotti and Rossotti.[10] These authors have given reviews of previous work on these systems and no attempt will be made to give a comprehensive summary here.

According to Rossotti and Rossotti,[10] the main

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[1] Publication authorized by the Director, U. S. Geological Survey.

[2] (a) U. S. Geological Survey. (b) Johns Hopkins University; present address National Bureau of Standards, Washington, D. C.

[3] H. T. Evans, Jr., and R. M. Garrels, *Geochim. Cosmochim. Acta*, **15**, 131 (1958).

[4] For compounds with the O:V ratio <3, the names trivanadate, pentavanadate, hexavanadate, etc., are assigned arbitrarily according to the simplest formulation, except where a definite polyion is involved, such as decavanadate.

[5] S. Block, "Program and Abstracts of Pittsburgh Diffraction Conference and the American Crystallographic Association, Nov 3–5, 1954," p 15; Ph.D. Thesis, The Johns Hopkins University, Baltimore, Md., 1955.

[6] S. Block, *Nature*, **186**, 540 (1960). In Table 1 of this paper, x for O_4 is incorrectly given as 0.518 and should be 0.158.

[7] G. Jander and K. F. Jahr, *Z. Anorg. Allgem. Chem.*, **212**, 1 (1933).

[8] F. Brito and N. Ingri, *Anales Real Soc. Espan. Fis. Quim.* (Madrid), **B56**, 165 (1960).

[9] N. Ingri and F. Brito, *Acta Chem. Scand.*, **13**, 1971 (1959).

[10] F. J. C. Rossotti and H. Rossotti, *ibid.*, **10**, 957 (1956).