Important peaks in the mass spectrum of VIa were assigned to CNF_2Cl (parent peak, 96%), CNFCl, CFCl, CNF_2 (100%), CNF, and CF. Isomer VIb displayed important peaks attributable to CNF_2Cl (parent peak, 100%), CNFCl, CFCl, CNF_2, CNF, and CF.

Fluorination of C-Bromodifluoromethylenimine.—A 12-ml infrared gas cell equipped with NaCl windows was charged with IIIb (2.2 mg, 0.015 mmole) and C_4F_8-2 (1.1 mg, 0.005 mmole). After freezing these reactants into the side arm of the cell, it was pressurized with fluorine (20 mm, 0.013 mmole). Immediately upon warming to room temperature (5 min) the infrared spectrum of the mixture was examined. On the basis of this spectrum, the conversion of IIIb was estimated at 23% and the yield of IV was

estimated at 70%. Other products of the reaction were COF_2, CF_4, C_4F_{10}, and CF_3COF. No C_4F_8-2 remained in the mixture.

Some Reactions of the Octahalodirhenate(III) Ions.
II.   Preparation and Properties of Tetracarboxylato Compounds[1]

BY F. A. COTTON, C. OLDHAM, AND W. R. ROBINSON

The conditions under which tetracarboxylatodirhenate(III) species, $Re_2(O_2CR)_4X_2$, may be prepared, directly or indirectly, from the $Re_2X_8^{2-}$ species have been explored and effective methods of preparation developed. A number of new compounds have been prepared and characterized. Certain features of the infrared and visible spectra of these molecules are discussed in relation to the structure and bonding. It is proposed that the terminal X groups may exert a weakening effect on the Re–Re bond comparable to the *trans* effect known in other, more classical complexes.

Introduction

Since the discovery and formulation[2–4] of species containing a quadruply bonded pair of Re(III) atoms, namely the $Re_2X_8^{2-}$ ions in which X = Cl or Br, several years ago, investigations of their chemistry have been carried out. One objective has been to determine the range of chemical behavior possible for the unique diatomic species, Re_2, including ligand substitution reactions, oxidation–reduction behavior, and stability. Another purpose has been to obtain compounds with which experiments shedding more light on the metal–metal bonding and electronic structure could be carried out. A previous paper has reported some reactions of the $Re_2X_8^{2-}$ species with phosphines.[5]

In this paper we describe in more detail the chemical relationship of the $Re_2X_8^{2-}$ species to the $Re_2(O_2CR)_4X_2$ species which were originally prepared by others[6–8] in various ways. It has previously been shown[2] that

the $Re_2X_8^{2-}$ and $Re_2(O_2CR)_4X_2$ species can be interconverted. It should also be noted that the Russian workers[7,8] have incorrectly formulated their compounds, which were the acetates only, as $Re_2(CH_3COOH)_4X_2$; the implication of this formula, for which there has never been any evidence given, is that Re(I) is present. This is undoubtedly an error unless, despite all appearances, the Russian workers were dealing with different materials than ours.

Experimental Section

$[(n-C_4H_9)_4N]_2Re_2Cl_8$ was prepared in 40% yield and converted to $[(n-C_4H_9)_4N]_2Re_2Br_8$ in 98% yield as previously described.[5]

Preparation of the Alkanoates.—A mixture of tetra-n-butylammonium octachlorodirhenate(III) (1.0 g), acetic acid (40 ml), and acetic anhydride (10 ml) was refluxed gently under nitrogen with a slow stream of nitrogen passing through the solution to prevent bumping and to sweep out the HCl formed. After 1 hr the supernatant liquid was essentially colorless and orange crystals of $Re_2(O_2CCH_3)_4Cl_2$ had been deposited. The crystals were separated by filtration in air, washed with three 20-ml portions of alcohol, then with 20 ml of diethyl ether, and dried under vacuum. The yield was 95%.

The bromo dimer, $Re_2(O_2CCH_3)_4Br_2$, was prepared in an analogous way using $[(n-C_4H_9)_4N]_2Re_2Br_8$.

Higher alkyl carboxylate chloride and bromide dimers were prepared similarly using the corresponding carboxylic acid and, when available, the anhydride. Due to the solubility of these higher homologs and their sensitivity in solution to traces of oxygen, it was necessary to use carefully deoxygenated solvents and extended reflux periods (up to 48 hr). In each case the orange product was isolated by cooling the dark final solution to about $-5°$ and filtering the product under nitrogen. Yields

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

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

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

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

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

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

(7) A. S. Kotel'nikova and V. G. Tronev, *Zh. Neorgan. Khim.*, **3**, 1016 (1958).

(8) A. S. Kotel'nikova and G. A. Vinogradova, *Russ. J. Inorg. Chem.*, **9**, 168 (1964).

TABLE I

ANALYTICAL AND SPECTRAL DATA FOR THE COMPOUNDS

Compound	Color	C, % Found	C, % Theory	H, % Found	H, % Theory	Cl, Br, or S, % Found	Cl, Br, or S, % Theory	Absorption spectra[a,b,c] (maxima in mμ with molar extinction in parentheses)				
1 $Re_2(O_2CCH_3)_4Cl_2$	Orange	14.3	14.14	1.81	1.78	10.3	10.43				420	500
2 $Re_2(O_2CCH_3)_4Br_2$	Red-brown	12.4	12.50	1.51	1.57	20.6	20.78		347		420 sh	507
3 $Re_2(O_2CC_2H_5)_4Cl_2$	Orange	19.5	19.58	2.75	2.72	9.37	9.64			274 (16,400)	396 (167)	497 (157)
4 $Re_2(O_2CC_2H_5)_4Br_2$	Brown	17.2	17.48	2.61	2.44	...	...	253 sh		304 (14,200)	419 (125)	509 (203)
5 $Re_2(O_2CC_3H_7)_4Cl_2$	Orange	24.4	24.27	3.72	3.56	9.15	8.96	276 (18,000)			404 (150)	507 (156)
6 $Re_2(O_2CC_3H_7)_4Br_2$	Brown	21.7	21.82	3.23	3.20	...	...	252 sh		306 (15,600)	417 (156)	508 (153)
7 $Re_2(O_2CC_3H_7)_4I_2$	Brown	19.7	19.72	2.94	2.90	...	...	247 (50,000)	270 sh	386 (17,500)	415 sh	512 (790)
8 $Re_2(O_2CC(CH_3)_3)_4Cl_2$	Red-brown	28.9	28.33	4.53	4.25	8.24	8.36	276 (24,000)			401 (106)	498 (160)
9 $Re_2(O_2CC_6H_5)_4Cl_2$	Red	36.1	36.24	2.28	2.17	7.68	7.68	245 (28,700)	307 (12,900)	321 (11,600)	415 sh	533 (218)
10 $Re_2(O_2CC_6H_5)_4Br_2$	Red-brown	31.3	33.07	2.04	1.98	16.0	15.72					
11 $Re_2(o\text{-}CH_3C_6H_4CO_2)_4Cl_2$	Red	38.9	39.05	2.98	2.84	7.62	7.22	267 (7050)	314 (5530)	330 (5200)	450 sh	542 (168)
12 $Re_2(m\text{-}CH_3C_6H_4CO_2)_4Cl_2$	Red	38.8	39.05	2.78	2.84	7.98	7.22	278 (2840)	309 (4740)	322 (4270)	445 sh	536 (171)
13 $Re_2(p\text{-}CH_3C_6H_4CO_2)_4Cl_2$	Red	38.4	39.05	2.73	2.84	7.33	7.22	262 (6410)	313 (5070)	326 (4760)	448 sh	542 (168)
14 $Re_2(O_2CC_6H_5)_4(SCN)_2$	Orange	37.5	37.02	2.52	2.02	6.56	6.59			310 (16,800)		505 (54)
15 $Re_2(O_2CC_3H_7)_4SO_4(H_2O)_2$	Blue	22.6	22.48	3.84	3.81	...	...	235 (26,200)	255 sh		478 (12)	636 (121)
16 $Re_2(O_2CCH_2C_6H_5)_4Cl_2$	Orange	39.2	39.04	2.95	2.85	6.82	7.22	270			404	505
17 $Re_2(O_2CCH_2Cl)_4Cl_2$	Light orange	12.0	11.76	1.01	0.99	26.0	26.02				418	560

[a] Solutions in acetonitrile. [b] sh means shoulder. [c] When no extinction coefficients are given, spectrum was measured by reflectance from 300 to 800 mμ.

varied between 10 and 40%. All elemental analyses are given in Table I.

Preparation of the Compounds Containing Aromatic Acids.—
The benzoates were prepared by fusing, under nitrogen, 5 g of benzoic acid mixed with 1 g of the $Re_2(O_2CCH_3)_4X_2$ compound, giving an orange melt. Gentle boiling of this solution for about 5 min caused a color change to red. On cooling, a pink solid was obtained. Excess benzoic acid was removed by washing with ether. The pink residue was recrystallized from chloroform to give red crystals; yield 85%.

The compounds containing the toluic acids (compounds 11, 12, and 13 in Table I) were prepared in the same way.

$Re_2(O_2CCH_2C_6H_5)_4Cl_2$ and $Re_2(O_2CCH_2Cl)_4Cl_2$ were also prepared by carboxyl displacement from the acetate, $Re_2(O_2CCH_3)_4$-Cl_2.

$Re_2(O_2CC_6H_5)_4(SCN)_2$ was prepared from $Re_2(O_2CC_6H_5)_4Cl_2$ by stirring 1 g of the latter with 1 g of AgSCN in 50 ml of chloroform under nitrogen. The resulting orange solution was filtered to separate AgCl and excess AgSCN, and the filtrate was evaporated under vacuum to yield the product as a brown powder.

$Re_2(C_3H_7CO_2)_4(H_2O)_2SO_4$.—This compound was prepared as described by Taha and Wilkinson.[6] Under nitrogen, 1.0 g of $Re_2(C_3H_7CO_2)_4Cl_2$ was stirred with 2.0 g of silver sulfate in 40 ml of 3:1 acetone–water. Silver chloride and excess silver sulfate were filtered from the solution and the blue compound was isolated by evaporation of the solvent under vacuum.

$Re_2(C_3H_7CO_2)_4I_2$.—To the blue solution obtained in the above preparation of the sulfate was added 40 ml of freshly distilled 55% HI. A brown precipitate resulted which was filtered and washed with 55% HI in order to remove silver iodide. The product was washed with 5 ml of ethanol (in which it is slightly soluble) and 20 ml of ether, then dried; yield 75%.

All elemental analyses are given in Table I.

Absorption Spectra.—Optical spectra were recorded in a Cary Model 14 or Beckman DU spectrophotometer. Typical spectra are given in Figure 1, and all peak maxima and extinction coefficients are listed in Table I.

Infrared spectra of these compounds, mulled in hydrocarbon oil, showed the absorptions expected for carboxylate groups. A few other features indicative of structure in particular cases will be noted subsequently.

Discussion

Preparation and General Properties.—The present study has confirmed and extended the earlier[2] observation that the $Re_2X_8{}^{2-}$ complexes react with carboxylic acids according to eq 1. We believe that this reac-
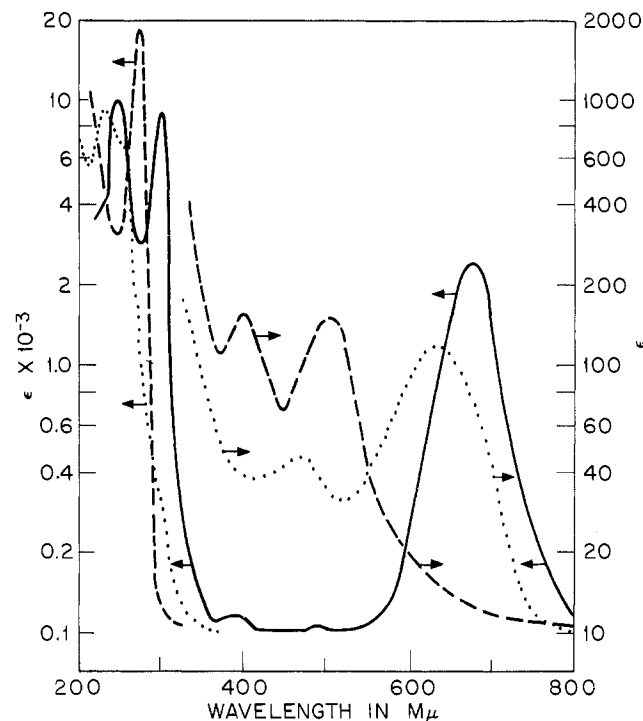
$$Re_2X_8{}^{2-} + 4RCOOH = Re_2(O_2CR)_4X_2 + 4HX \quad (1)$$

Figure 1.—The electronic absorption spectra of some $Re^{III}{}_2$ compounds, measured in acetonitrile: (———), $Re_2Cl_8{}^{2-}$; (- - - - -), $Re_2(O_2CC_3H_7)_4Cl_2$; (· · · · · ·), $Re_2(O_2CC_3H_7)SO_4(H_2O)_2$.

tion constitutes the best method for preparation of these carboxylate complexes. However, when the group R is aryl and certain other groups such as benzyl and chloromethyl, it is more convenient to use a two-step process, the first step being that in eq 1, with R = CH_3, and the second being a carboxyl exchange, eq 2.

$$Re_2(O_2CCH_3)_4X_2 + 4ArCOOH =$$
$$Re(O_2CAr)_4X_2 + 4CH_3COOH \quad (2)$$
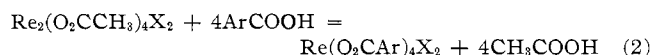
Of the alkanoates, the acetate can be prepared in the highest yield and with the greatest ease. In fact, small amounts of $Re_2(O_2CCH_3)_4Cl_2$ can be isolated even when the reaction is carried out in air. Presumably this stability of the acetate is due to its extreme insolubility

rather than any inherent structural difference from the other compounds. The other carboxylates are all stable toward air as solids but they are quite sensitive to oxygen when in solution. A formate has not been isolated, probably because of the high water content of formic acid.

In addition to the carboxyl interchange reaction, eq 2, in which a more volatile acid can be displaced by a less volatile one, reactions involving displacement of the end groups, as shown in the general reaction (3) can also be carried out. In several cases reported

$$Re_2(O_2CR)_4X_2 + 2Y^- = Re_2(O_2CR)_4Y_2 + 2X^- \qquad (3)$$
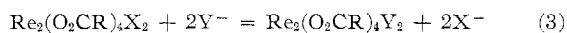
here this provided the only way of obtaining a particular compound. Thus, reactions of type 1 starting with $Re_2(NCS)_8{}^{2-}$, a new $Re_2X_8{}^{2-}$ species whose preparation will be described elsewhere,[9] do not lead readily to isolable amounts of $Re_2(O_2CR)_4(NCS)_2$ species. However, the compound $Re_2(O_2CC_6H_5)_4(NCS)_2$ was obtained by a reaction of type 3 using AgSCN as a source of SCN^-. Similarly, the sulfato complex, $Re_2(O_2CC_3H_7)_4SO_4(H_2O)_2$, and the iodide, $Re_2(O_2CC_3H_7)_4I_2$, were obtained by exchange of Cl in $Re_2(O_2CC_3H_7)_4Cl_2$. Reactions of type 1 are not at present possible in these cases since neither $Re_2(SO_4)_4{}^{2-}$ nor $Re_2I_8{}^{2-}$ is known.

With regard to the linkages present in the SCN^- compounds, infrared data provide some information. The SCN^- compound has $\nu(CN)$ at 2020 ± 5 cm^{-1}, $\nu(C-S)$ at 755 cm^{-1}, and $\delta(SCN)$ at 470 ± 5 cm^{-1}. The first of these is low for either N- or S-bonded thiocyanate[10] and is even lower than that for the uncoordinated ion ($\sim$2060 cm^{-1}). $\nu(C-S)$ is close to that for the uncoordinated ion ($\sim$745 cm^{-1}), but at the border line of the accepted ranges for N- and S-bonded thiocyanate. $\delta(SCN)$ is not resolvably split and occurs at a value considered[10] to correspond to N bonding, although again it is also similar to that for the uncoordinated ion ($\sim$470 cm^{-1}). Thus, from the infrared data alone it appears that SCN is probably not S bonded but might be N bonded or uncoordinated.

Electronic Spectra.—The electronic absorption spectra of most of the compounds have been recorded. The numerical data are collected in Table I and several of the spectra are shown in Figure 1. At present, detailed interpretation of these spectra appears impossible, but certain trends and correlations may be noted. As a basis for even a superficial discussion, it should be stated that the structures of the $Re_2(O_2CR)_4X_2$ compounds are all presumably as shown in Figure 2. This is the type of structure originally suggested by Taha and Wilkinson[6] and for $Re_2(O_2CC_6H_5)_4Cl_2$ it has been confirmed by a single crystal X-ray diffraction study.[11] Of particular importance, the Re–Re distance found is similar to that in $Re_2Cl_8{}^{2-}$, thus confirming our earlier suggestion[4] that the $Re_2(O_2CR)_4X_2$ compounds contain the quadruple bond between the Re atoms, although there may well be differences in
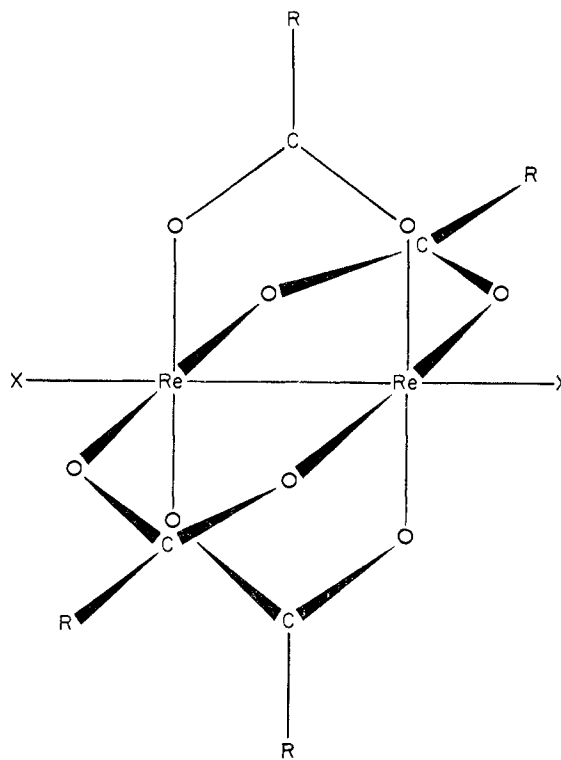

Figure 2.—The molecular structure assumed for all $Re_2(O_2CR)_4X_2$ compounds on the basis of X-ray results for $Re_2(O_2CC_6H_5)_4Cl_2$.

quantitative detail between the Re–Re interactions in the $Re_2X_8{}^{2-}$ and in the $Re_2(O_2CR)_4X_2$ compounds.

Indeed, it is to be expected that the π systems of the carboxyl groups will interact with the valence orbitals of the rhenium atoms. These carboxyl π orbitals can combine to give a large number of molecular orbitals ($2E_u$, $2A_{2g}$, $2B_{2g}$, E_g, A_{1u}, B_{1u}), some of which are of the same symmetry types as the Re–Re orbitals which are presumably involved in optical transitions (B_{1u}, A_{2u}, A_{1g}, B_{2g}, E_g). Thus, no simple predictions as to how the transitions of the $Re_2X_8{}^{2-}$ species[4] should be perturbed by substituting the $8X^-$ by $4RCOO^-$ are possible. A detailed discussion of the spectral assignments should therefore await the completion of molecular orbital calculations on the $Re_2(O_2CR)_4X_2$ species.

In terms of a simple bonding scheme,[4] the validity of which has since been supported by an LCAO–MO calculation,[12] the bands occurring in the $Re_2X_8{}^{2-}$ species at 700–800 mμ were assigned to a transition from the δ-bonding orbital to one of the nonbonding σ orbitals. In the $Re_2(O_2CR)_4X_2$ species, where the end groups, X, are bound by means of these orbitals,[13]

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

(10) *Cf.* A. Sabatini and I. Bertini, *ibid.*, **4**, 959 (1965), for a recent discussion of the thiocyanate complexes and earlier references.

(11) F. A. Cotton and W. R. Robinson, unpublished work.

(12) F. A. Cotton and C. B. Harris, to be published. A verbal presentation was made at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 31, 1966; *Cf.* Abstract H71.

(13) This may be an appropriate place to comment on the absence of end groups in the $Re_2X_8{}^{2-}$ species. Although suitably directed orbitals are available, they are inaccessible for steric reasons. Thus, using the reported[3] dimensions of the $Re_2Cl_8{}^{2-}$ ion and accepted van der Waals radii for Cl and O atoms, it can be calculated that the closest approach of a water molecule to an Re atom would give an Re–O distance of $\sim$2.9 Å, effectively preventing the formation of a stable bond. In the $Re_2(O_2CR)_4$ group, however, the smaller size of the O atoms and the fact that those in each set of four are essentially coplanar with the Re atom to which they are bound, instead of swept back, permits close approach of an additional ligand atom to each Re atom.

such transitions should be shifted to higher energies. In accord with this, it may be seen that (with the exception of $Re_2(O_2CC_3H_7)_4SO_4(H_2O)_2$, to be discussed below) none of the spectra of $Re_2(O_2CR)_4X_2$ compounds contains absorption bands at wavelengths beyond 500–550 mμ. Consequently, they have red, orange, or brown colors, rather than the blue and green colors of the $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$ ions.

One of the most striking features of the spectra is illustrated in Figure 3. For the series of compounds $Re_2(O_2CC_3H_7)_4X_2$, in which X is Cl, Br, I, there are intense bands in the near-ultraviolet, but their positions vary markedly. For the iodo compound there are two intense bands; the one at higher energy is probably due to a charge-transfer transition which lies at still higher energies in the bromo and chloro species. Therefore only the lower-energy band of the iodo compound will be considered in conjunction with the bands observed in the other compounds.

If the intense band in each compound is assumed to have a similar origin, the main questions are (1) what is this origin?, and (2) why does the energy of the transition shift in the observed manner?

We believe that an orbitally-allowed, strong δ–δ^* transition, analogous to that in $Re_2Cl_8^{2-}$, is to be expected in this part of the spectrum. Since, except as noted above for the iodo compound, no other strong band is found, this assignment is implied. The considerable shift (from $\sim$36,000 to $\sim$27,000 cm^{-1}) in the band position in going from the chloro to the iodo compound does, however, require comment. There is no obvious way in which this might be a direct consequence of the interaction of the halogen atoms with the δ or δ^* molecular orbitals.

However, if the interaction of the halogen atoms with the metal dπ orbitals increases from Cl to I so that the Re-to-Re π bonding is weakened, the Re–Re distance will increase. Since the δ–δ overlap is sensitive to distance[12] and the distance should be sensitive to the Re-to-Re π bonding because this accounts for more than half of the total Re–Re bond strength,[12] a lowering of the δ–δ^* transition in the observed direction would be anticipated. The proposed weakening of the Re-to-Re bond as the end groups are changed from Cl to Br to I can be viewed as manifestation of the *trans* effect and it follows the known order of Cl, Br, and I in the *trans* effect series.[14]

As Figure 3 also shows, the other, weak peaks in the spectra do not appear to have any simple dependence on variation in the terminal ligands; indeed the one around 20,000 cm^{-1} seems practically invariant in the Cl, Br, I series. These weaker absorption bands do show slight variation in position as the R groups are changed, and, as Figure 4 shows, their shifts correlate moderately well with the inductive potential of the R groups as measured by the Taft σ^* parameter.[15] The significance of this is not clear, but it perhaps suggests
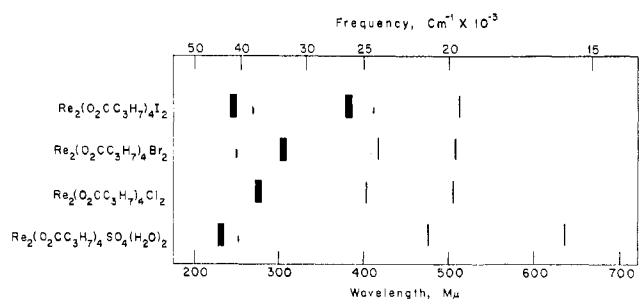
(14) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962).
(15) *Cf.* J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1962, pp 96–98.

Figure 3.—Schematic comparison of the spectra of a series of $Re_2(O_2CR)_4X_2$ compounds. Bands with ϵ >10^4 are represented by thick lines, others (with ϵ of 10–200) by thin lines. Short thin lines are shoulders.
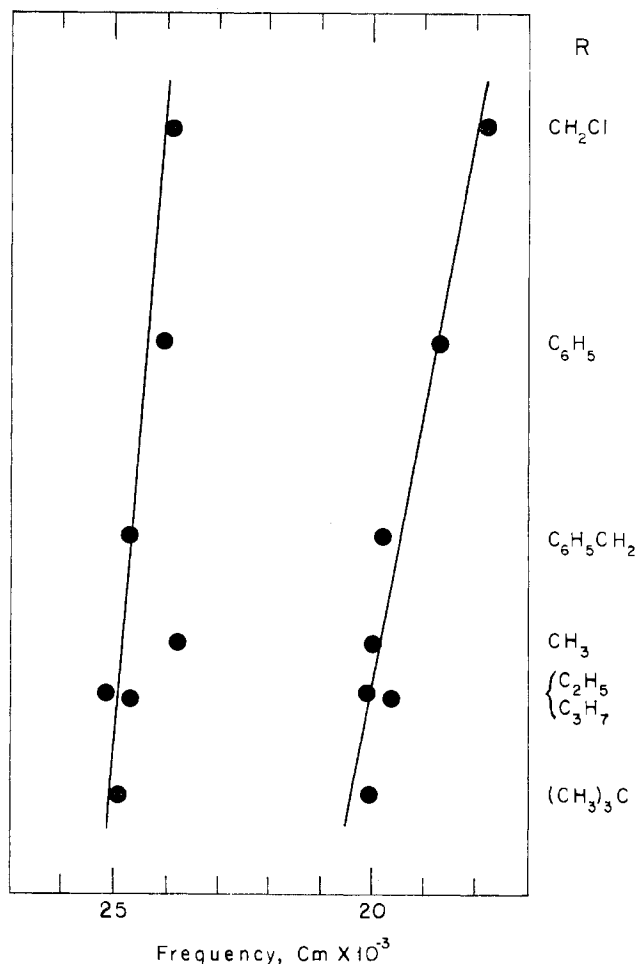

Figure 4.—Graph showing the dependence of the energies of several transitions upon variation of the R groups over a range of Taft's σ^* constant.

that orbitals of the carboxyl groups are directly involved in the transitions.

Finally, comment must be made on the compound $Re_2(O_2CC_3H_7)_4SO_4(H_2O)_2$, which is blue, due to the presence of a band near 17,000 cm^{-1}. If, indeed, the basic quadruply bridged $Re_2(O_2CR)_4^{2+}$ unit is present, this would seem to imply that there are no coordinated end groups. The position of the strong band tentatively assigned to a δ–δ^* transition, compared to the positions of this band in the Cl, Br, and I compounds (see Figure 3), is also consistent with this supposition.

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.

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

BY F. A. COTTON AND R. A. WALTON

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 $Re_2X_5(bipy)\cdot CH_3CN$ 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-phenanthro-

line, 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 $23 \pm 2°$ with a commercial Wheat-

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

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