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A Spectroscopic Study of the Behavior of Rhenium(III) Chlorides in Molten Salts[1]

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The visible and ultraviolet spectra have been used to study the behavior of some Re(III) chloride species in melts. Re_3Cl_9 is stable in molten dimethyl sulfone, but in the presence of chloride ions, or when added as the chloro complex $[Re_3Cl_{12}]^{3-}$, it is converted to $[Re_2Cl_8]^{2-}$ and an as yet unidentified product. The same reaction occurs in molten diethylammonium chloride. In the LiCl–KCl eutectic, Re(III) disproportionates to Re(0) and $[ReCl_6]^{2-}$. A new method of preparing salts of $[Re_2Cl_8]^{2-}$ in good yield and high purity from the decomposition reaction in molten diethylammonium chloride is described.

Introduction

Since the discovery[2,3] that the stoichiometric compound $CsReCl_4$ actually contains the trinuclear cluster $[R_3Cl_{12}]^{3-}$ in which there is metal–metal bonding between the rhenium atoms, a considerable number of polynuclear Re(III) compounds have been prepared and characterized. It is now known that Re(III) forms at least three series of $[ReX_4]_n^{n-}$ complexes.[4] Generally the use of rhenium trichloride as starting material has led to products containing the Re_3Cl_9 group (which is the basic structural unit of $ReCl_3$), probably due to the mild conditions employed. Thus it seemed worthwhile to study the effects of more severe conditions, in this case molten salt solvents, on this cluster. Spectrophotometric measurements are well suited for this purpose, since the spectra of the various complexes are well known and dissimilar.[5–8] In this paper we report the results of studies in molten dimethyl sulfone, diethylammonium chloride, and the LiCl–KCl eutectic, including a new synthesis of compounds containing the $[Re_2Cl_8]^{2-}$ ion.

Experimental Section

Spectra were recorded with a Unicam SP700 spectrophotometer; the furnace assembly and the method of preparation of solutions in the LiCl–KCl eutectic have been reported previously.[9] Fused quartz cells of 0.1- and 1-cm path length were used, sealed under vacuum for the LiCl–KCl eutectic, and stoppered for the organic melts. With the latter melts, weighed amounts of solute and solvent were added to the cells, which were then repeatedly evacuated and flushed with dry nitrogen.

The dimethyl sulfone used was the commercial product recrystallized from methanol. Diethylammonium chloride was prepared by passing HCl gas into a solution of freshly distilled diethylamine in reagent grade benzene. The rhenium(III) chloride used was S. W. Shattuck material resublimed *in vacuo*.

Authentic samples of $Cs_3[Re_3Cl_{12}]$ were prepared by precipitation with CsCl from a solution of Re_3Cl_9 in 12 *N* HCl; and of $[(C_4H_9)_4N]_2[Re_2Cl_8]$ by the hypophosphorous acid reduction method.[7]

Rhenium was determined by the method of Meloche, Martin, and Webb[10] using a Beckman DU spectrophotometer, while the chloride analyses, when required, were done by the Mohr method.

Synthesis of Salts of $[Re_2Cl_8]^{2-}$.—Three methods of preparation of salts of $[Re_2Cl_8]^{2-}$ are known,[7] with highest yields being 35–40%. The method using Re_3Cl_9 as starting material produces yields of only ~10%, whereas with the method described here, a rhenium recovery of 60% can be attained.

The apparatus is shown in Figure 1. It consists of a glass tube, about 20 mm in diameter, with a fritted disk near one end. Below this is a side arm for gas inlet or vacuum and a length of narrower tubing to serve as a collecting vessel. This may be all in one piece as shown, or attached by a standard taper joint with a Teflon sleeve.

In use, a mixture of Re_3Cl_9 and diethylammonium chloride (about 1:15 by weight) is placed above the fritted disk. Total amounts of up to 30 g can be handled conveniently; larger amounts would require a larger diameter tube. Dry nitrogen gas is passed through the side arm to flush air from the system; this is the main requirement in the preparation. The mixture is heated to just above the melting point of the diethylammonium chloride by means of a small furnace placed around the tube and controlled by a variable transformer. The stream of nitrogen is allowed to continue stirring the solution for 5 min after melting, and the melt is filtered through the fritted disk. It is allowed to solidify and when cool detached from the larger tube and dissolved in a minimum of 6 *N* HCl. This solution is also filtered through fritted glass. Salts of the $[Re_2Cl_8]^{2-}$ ion can be precipitated by the suitable cation added as the chloride. We have prepared the tetra-*n*-butylammonium salt in 60% yield. *Anal.* Calcd: Cl, 24.9; Re, 32.7. Found (without recrystallization): Cl, 24.8; Re, 33.7. The tetraethylammonium, tetraphenylarsonium, and cesium compounds were also obtained and characterized spectroscopically.

Another product, a brown solid insoluble in water but quite soluble in acetone, is obtained on filtration of the initial HCl solution. This product shows qualitative tests for Re and Cl, but its infrared spectrum does not show evidence for the diethylammonium cation. No definite bands could be found in the visible or ultraviolet spectrum of the acetone solution of this material, so that its presence could not interfere with the identi-

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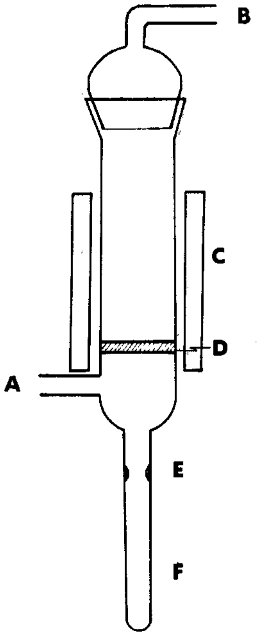

Figure 1.—Apparatus for the preparation of compounds of $[Re_2Cl_8]^{2-}$ in molten salts: A, side arm for nitrogen inlet or vacuum; B, nitrogen outlet; C, furnace; D, frit; E, seal-off point (or standard taper joint); F, receiving tube.

fication of the other product. Further studies in this laboratory are attempting to determine the nature of this species.

Results and Discussion

The spectra obtained are shown in Figures 2–5, with the band positions listed in Tables I and II. Our ambient temperature spectral data are in general agreement with those previously reported,[5–8] except that we observe a shoulder at 27,000–28,000 cm^{-1} for the $[ReCl_8]^{2-}$ ion, both that formed in our reactions and that prepared by the method of Cotton, *et al.*[7]

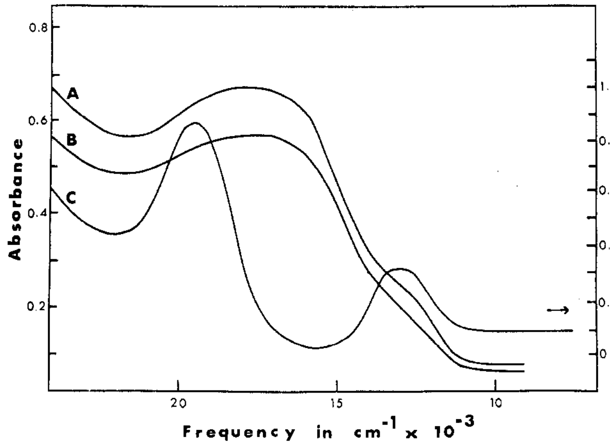

Figure 2.—A, Re_3Cl_9 in dimethyl sulfone, 140°; B, Re_3Cl_9 in dimethyl sulfone, 200°; C, Re_3Cl_9 in 6 *N* HCl.

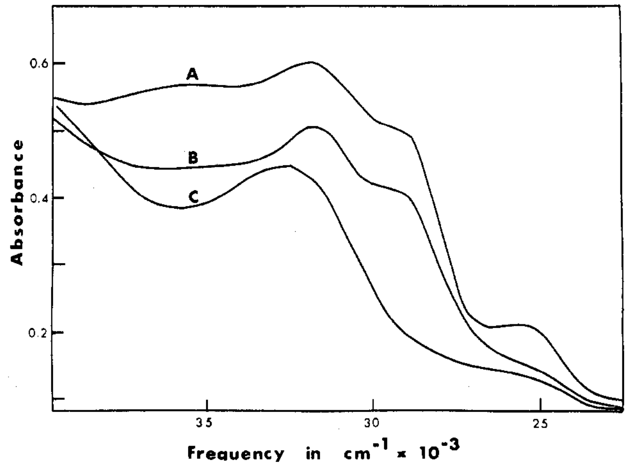

Figure 3.—A, Re_3Cl_9 in 3 *N* HCl; B, $Cs_3[Re_3Cl_{12}]$ in 12 *N* HCl; C, Re_3Cl_9 in dimethyl sulfone, 140 and 200°.

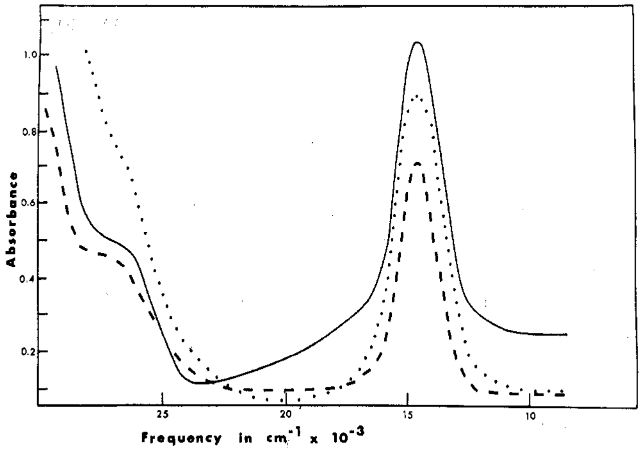

Figure 4.—. . . . , Re_3Cl_9 in diethylammonium chloride, 255°; ———, $[(C_4H_9)_4N]_2[Re_2Cl_8]$ in diethylammonium chloride, 255 and 285°; – – – –, $[(C_4H_9)_4N]_2[Re_2Cl_8]$ in dimethyl sulfone, 140 and 185°.

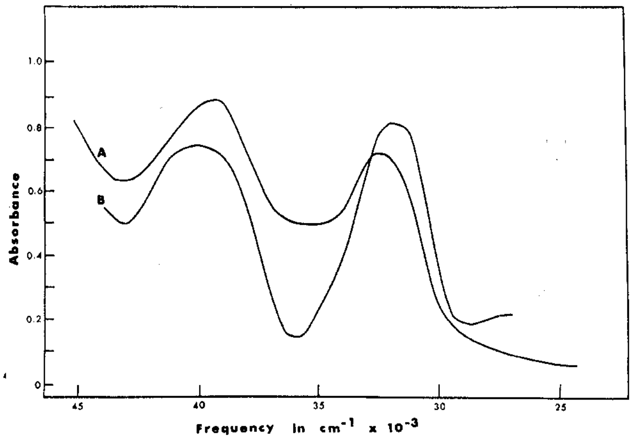

Figure 5.—A, $[(C_4H_9)_4N]_2[Re_2Cl_8]$ in CH_3OH; B, $[(C_4H_9)_4N]_2$-$[Re_2Cl_8]$ in dimethyl sulfone, 140°.

The visible spectrum of Re_3Cl_9 in dimethyl sulfone (Figure 2) shows considerable broadening, with a red shift of the most intense band of some 1800 cm^{-1} as compared to the spectrum in $CHCl_3$ at room temperature. It appears that this should be attributed strictly to temperature effects, since the visible spectrum of $Re_3Cl_9X_n$ has been shown[5] to be relatively insensitive to the nature or to the absence of X.

Another difference in the spectrum is that the band which appears at 29,200 cm^{-1} in HCl solution is not observed in dimethyl sulfone (Figure 3). There are three possible reasons for this: (a) it could be obscured

TABLE I

SPECTRA OF Re_3Cl_9 AND $Cs_3Re_3Cl_{12}$ IN VARIOUS SOLVENTS

Solution	Positions of absorption maxima, cm^{-1} (ϵ_{max})				
Re_3Cl_9 in 6 *N* HCl	13,100 (545)	19,500 (1940)	25,400 (1100)	29,200 (6450)	32,000 (9350)
Re_3Cl_9 in $CHCl_3$	13,000	19,600	25,400	29,500	32,200
Re_3Cl_9 in dimethyl sulfone, 140 and 200°	13,000 sh (1380)	140°, 17,700 (2350) 200°, 17,600 (2500)	25,000 sh		32,500
Re_3Cl_9 in diethylammonium chloride, 255°	14,600	27,000			
$Cs_3Re_3Cl_{12}$ in HCl	13,000 (460)	19,200 (1720)	25,000 sh (1320)	29,500 (7200)	31,700 (9150)
$Cs_3Re_3Cl_{12}$ in dimethyl sulfone, 140°[a]	13,000	19,000	26,000 sh		32,200

[a] Reacts.

TABLE II

SPECTRA OF $[(C_4H_9)_4N]_2Re_2Cl_8$ IN VARIOUS SOLVENTS

Solvent	Positions of absorption maxima, cm^{-1}			
CH_3OH[a]	14,750	27,800 sh	32,400	39,400
Dimethyl sulfone, 140 and 185°	14,600	28,000 sh	31,900	40,400
Diethylammonium chloride, 255 and 285°	14,600	27,400 sh		

[a] 1 ml of 12 *N* HCl per 100 ml.

by the broadening of the 32,500 cm^{-1} band, although this is unlikely from the appearance of the spectrum; (b) the intensity has decreased markedly relative to the 32,5000 cm^{-1} band due to the temperature change; or (c) this band is due to charge transfer involving X in $Re_3Cl_9X_n$,[6] and dimethyl sulfone, which is very weakly complexing,[11] does not coordinate to allow this. This last possibility appears to be eliminated due to the appearance of a shoulder at 29,500 cm^{-1} in the spectrum of Re_3Cl_9 in $CHCl_3$, where the chromophore should be Re_3Cl_9 since $CHCl_3$ does not act as an electron-pair donor.[6]

The spectrum of Re_3Cl_9 in diethylammonium chloride is markedly different from that in dimethyl sulfone; it is, in fact, essentially identical with that reported by Cotton, *et al.*,[7] for the $[Re_2Cl_8]^{2-}$ ion. The same results were obtained for a solution of $[(C_4H_9)_4N]_2$-$[Re_2Cl_8]$ in diethylammonium chloride. Moreover, while Re_3Cl_9 appears to be stable in dimethyl sulfone, on addition of some diethylammonium chloride $[Re_2Cl_8]^{2-}$ is formed at a rate which is dependent on the diethylammonium chloride concentration. The use of this reaction as a synthetic method is described in the Experimental Section.

$Cs_3[Re_3Cl_{12}]$ also reacts in dimethyl sulfone to yield the $[Re_2Cl_8]^{2-}$ ion. This reaction proceeds much more slowly than that of Re_3Cl_9 in diethylammonium chloride, and the rate is quite sensitive to temperature. The rate of reaction is increased on addition of some diethylammonium chloride to the $Cs_3[Re_3Cl_{12}]$–dimethyl sulfone solution.

The reaction in the melt involves a partial breakup of the Re_3Cl_9 unit (or of the $[Re_3Cl_{12}]^{3-}$ species, although the qualitative observations on the rate indicate that free chloride ions are important in the process), but does not destroy the interactions between two of the rhenium atoms. The second product of this decomposition has not yet been identified.

In the LiCl–KCl eutectic, Re_3Cl_9 disproportionates to rhenium metal and the hexachlororhenate(IV) ion, $[ReCl_6]^{2-}$. The spectrum is identical with that of $K_2[ReCl_6]$ in the LiCl–KCl eutectic.[12] The rhenium metal was identified by means of X-ray analysis. The same disproportionation is observed for salts of $[Re_3Cl_{12}]^{3-}$ in the solid state at elevated temperatures.[13] Some ReO_2 and other products were also formed, probably during extraction of the excess salt.

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