difference can be attributed to the stronger inductive effect of a methyl group, compared with an ethyl group.

As was mentioned, the C–N frequencies of the square-planar compounds are higher than those of the octahedral ones. While the reason for these higher frequencies in the carbonyl species can be explained by the ease of charge acceptance by the CO groups (and also by NO groups[2] as in $NOCo[S_2CN(CH_3)_2]_2$, $\nu_{C=N}$ = 1544 cm.$^{-1}$, mull, and $NOFe[S_2CN(CH_3)_2]_2$, $\nu_{C=N}$ = 1542 cm.$^{-1}$, mull), it is tempting to suggest that in the nickel derivatives electrons are being donated from the dithiocarbamate group into a nonbonding molecular orbital, consisting mainly of Ni p_z, thus permitting the C–N frequency to be exceptionally high.

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The Existence of the Re_3Cl_9 Cluster in Anhydrous Rhenium(III) Chloride and Its Persistence in Solutions of Rhenium(III) Chloride

By F. A. Cotton and J. T. Mague

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The crystal structure of anhydrous rhenium(III) chloride, prepared by vacuum sublimation, has been determined by single crystal X-ray work. The space group is $R\bar{3}m$, with 18 $ReCl_3$ per hexagonal unit cell. The structure is built up of well-defined Re_3Cl_9 units, each having rigorous C_{3v} symmetry, and approximately the same structure as the Re_3Cl_9 moieties previously found in $Cs_3Re_3Cl_{12}$ and $Re_3Cl_9[P(C_2H_5)_2C_6H_5]_3$. The Re_3Cl_9 groups are arranged in double layers perpendicular to the crystallographic *c* axis and joined together by chlorine atom bridges. This structure appears to account for all reported aspects of the behavior of rhenium(III) chloride, except the claim by Wrigge and Biltz that it is dimeric in glacial acetic acid. The spectra of rhenium(III) chloride in a variety of solvents are practically identical and essentially the same as spectra of systems in which the presence of Re_3Cl_9 units seems certain. It is therefore concluded that, in general, fresh solutions of rhenium(III) chloride (including the acetic acid solution) contain Re_3Cl_9 units. A molecular weight measurement in sulfolane confirms this.

Introduction

The homophilicity[1] of Re(III) has been well-established.[2] One manifestation of this property is the important role which the Re_3X_9 (X = Cl, Br) clusters play in its chemistry. It has been observed in this laboratory[2] that whenever compounds of Re(III) are prepared directly (*i.e.*, without change in oxidation state or the use of strenuous reaction conditions) from rhenium(III) chloride, the products contain the rhenium solely in the form of Re_3Cl_9 clusters and derivatives thereof. We wish to emphasize that we are only reporting that degradation of the Re_3Cl_9 cluster has not *yet* been observed under mild conditions. While we think it likely that this is the general rule, exceptions may possibly be found in the future. Single crystal X-ray structure determinations have established the presence of such species in several cases.[2-6] On the basis of this observation, as well as the observations reported later in this paper concerning the spectra of rhenium(III) chloride in a variety of solvents, it appeared likely that the Re_3Cl_9 cluster would be present in anhydrous rhenium(III) chloride itself. A single-crystal X-ray structure determination was therefore undertaken. The results, which will be described below, have shown that rhenium(III) chloride does, in fact, consist of Re_3Cl_9 clusters.

Experimental

A sample of resublimed rhenium(III) chloride was very kindly supplied by Dr. R. H. Busey of the Oak Ridge National Laboratory. This material was obtained by Dr. Busey and his associates in the following way.[7] A small portion of a batch of very pure rhenium(III) chloride (*Anal.* Calcd. for $ReCl_3$: Cl, 36.35. Found: Cl, 36.33 ± 0.03) used previously in heat capacity measurements was transferred in an argon-filled vacuum-type drybox to a two-bulb quartz sublimation tube and the latter sealed under vacuum. The sample was slowly sublimed at *ca.* 400° into the second bulb, some residue remaining in the first bulb. The tube was then opened in the argon-filled drybox and selected crystals were placed in a second quartz sublimation tube. This tube was then connected to a high vacuum system equipped with a diffusion pump and liquid N_2 trap. Approximately half of the contents was sublimed (at *ca.* 500°) into the second bulb, at which point it was noted that the remaining unsublimed material appeared nicely crystalline, whereas the sublimate was depositing as a layer. The remaining unsublimed material was sealed off and sent to us for the crystallographic work.

A series of about twenty fragments, which were picked from the sample and mounted in sealed capillaries in a drybox, were examined on a precession camera before one was found which was not cracked or twinned. From precession pictures of the *hk*0–

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[1] The words *homophilicity* and *homophilic* have previously[2] been proposed to designate the tendency of an atom (or ion) to form bonds to other identical atoms (or ions) in comparison to its tendency to form bonds to different atoms (*heterophilicity*).

[2] F. A. Cotton, N. F. Curtis, C. B. Harris, B. F. G. Johnson, S. J. Lippard, J. T. Mague, W. R. Robinson, and J. S. Wood, *Science*, in press.

[3] J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *J. Am. Chem. Soc.*, **85**, 1349 (1963); *Inorg. Chem.*, **2**, 1106 (1963).

[4] W. T. Robinson, J. E. Fergusson, and B. R. Penfold, *Proc. Chem. Soc.*, 116 (1963).

[5] J. E. Fergusson, B. R. Penfold, and W. T. Robinson, *Nature*, **201**, 181 (1964).

[6] F. A. Cotton and J. T. Mague, *Inorg. Chem.*, **3**, 1094 (1964).

[7] This procedure, explained to us in detail by Dr. Busey, is recorded here in case it might later turn out that $ReCl_3$ is polymorphic.

*hk*3 and 0*kl* zones, the crystal was found to be trigonal and was indexed on the basis of a hexagonal unit cell with $a = 10.33 \pm 0.02$ and $c = 20.36 \pm 0.02$ Å. The following systematic absence was observed: *hkil* for $-h + k + l \neq 3n$.

Using the density of 4.66 g./cc. as measured pycnometrically in *m*-xylene and 1,2-dibromoethane and the measured cell dimensions, the number of $ReCl_3$ moieties per unit cell was calculated to be 18.1. This indicates that the rhenium atoms lie on one of the 18-fold special positions of this space group.

The crystal used for collecting intensity data had the form of a triangular plate. Intensity data were recorded photographically on a precession camera using Mo Kα radiation. Using the *hk*0–*hk*3 and 0*kl*–1*kl* layers, 136 independent reflections were recorded. The relative intensities were recorded visually by comparison with an intensity wedge prepared from the same crystal. Absorption, Lorentz, and polarization corrections were made, using the program ECIT, written for the IBM 7094 computer by Dr. A. B. Blake and modified by R. C. Elder, both of this Laboratory. In order to use the absorption correction portion of this program, the crystal was approximated by a cylinder of radius 0.15 mm. This gave a value of μr for Mo Kα radiation of 4.34.

Spectra.—Visible absorption spectra were recorded on a Cary Model 14 spectrophotometer, using 1.0 and 5.0 cm. cells. Mulls of solid samples were held between glass microscope slides.

Molecular Weight Measurements.—These were done in sulfolane (tetrahydrothiophene sulfone), which was obtained from the Shell Chemical Company. The sulfolane was prepurified by distillation from sodium hydroxide pellets. The apparatus consisted of a three-neck glass flask equipped with a magnetic stirrer, a Beckmann thermometer, and a side vessel for introducing the sample. The sulfolane was first distilled from sodium hydroxide pellets directly into this flask using the third neck.[8a]

In each run, the freezing points of the solvent and the solution were measured repeatedly over a period of time, usually about 60 min., until they became constant. For the first run: g. of $ReCl_3$, 0.055; g. of $C_4H_8SO_2$, 166.9; ΔT, 0.023°. For the second run: g. of $ReCl_3$, 0.063; g. of $C_4H_8SO_2$, 170.4; ΔT, 0.030°. Using the cryoscopic constant for sulfolane reported by Burwell and Langford,[8b] these results give 950 and 820, respectively, for the molecular weight. The average of these, 885, may be compared with the weight of Re_3Cl_9, which is 887.

Solution of the Structure

The correct assignment of the space group constituted a nontrivial problem. The single observed extinction condition, $-h + k + l \neq 3n$, is characteristic for seven space groups, *viz.*, R3, R$\bar{3}$, R32, R3m, R3c, R$\bar{3}$m, and R$\bar{3}$c. However, R3c and R$\bar{3}$c also have a systematic absence $h\bar{h}0l$, $l \neq 2n$, which does not occur, thus excluding these. Further, the remaining five groups fall into two classes of Laue symmetry and the appearance of 12-fold symmetry in the *hk*0 net eliminates R3 and R$\bar{3}$. No choice among the three remaining ones was possible at this stage, but later the density of peaks on the Harker line x, x, 0 in the Patterson function eliminated R32, leaving only R3m and R$\bar{3}$m. A decision between these might, in principle, be made according to the accumulation of vectors in the Harker plane, x, $2x$, z, if the rhenium atoms do not occupy the 9b positions of R3m. However, some peaks did appear in this plane and no decision on this basis was considered reliable. After solution of the Patterson function for rhenium atom positions, a Fourier map was calculated, in such a way that the symmetry used was only triclinic. The positions of the chlorine atoms found were the 18h positions (x, $\bar{x}$, z) of R$\bar{3}$m within the limits of error, thus indicating this to be the correct space group. The least-squares refinements were then carried out using R$\bar{3}$m, leading to the positional parameters of Table I. As a final check on the space group, several cycles of least-squares refinement were carried out in R3m, starting with the parameters in Table I. Large interactions between the x and z coordinates of those atoms which would be centrosymmetrically related in R$\bar{3}$m immediately appeared, indicating again that R$\bar{3}$m is correct.

TABLE I

FRACTIONAL ATOM COORDINATES AND ISOTROPIC TEMPERATURE FACTORS FOR HEXAGONAL RHENIUM(III) CHLORIDE

Atom	x/a	σ_x	z/c	σ_z	β	σ_β
Re	0.2530	0.0006	0.3929	0.0005	2.2	0.2
Cl_1	0 2292	0.0030	0.2769	0.0026	1.9	1.3
Cl_2	0.2376	0.0031	0.5045	0.0028	2.7	1.4
Cl_3	0.0156	0.0040	0.3880	0.0045	4.7	[a]

[a] No σ since β for Cl_3 was held fixed in the final five cycles of full matrix least-squares refinement.

A three-dimensional Patterson synthesis was computed[9] for one-half of the unit cell. The appearance of a large peak on each of the Harker lines (0, $3x$, 0) and ($3x$, 0, 0) dictated the choice of the 18h special position for the rhenium atoms and provided the x coordinate. Finally, a large peak at ($2x$, x, $2z$) provided the z coordinate. Using these coordinates, all possible Re–Re vectors in the Patterson function could be located and a model of the rhenium atoms showed them to be in groups of three, as anticipated, with Re–Re distances of ~2.5 Å., in good agreement with Re–Re distances in the $[Re_3Cl_{12}]^{3-}$ ion,[4] $[Re_3Cl_{11}]^{2-}$ ion,[5] and $Re_3Cl_9[P(C_2H_5)_2C_6H_5]_3$.[6]

Structure factors were then calculated using only the rhenium atoms. Here and subsequently, atomic scattering factors were taken from the International Tables[8b] (Table 3.31A for Cl^0; Table 3.31B for Re^0). No correction for anomalous dispersion by Re was made. Using the phases thus obtained, a three-dimensional Fourier synthesis was computed[9] from which the parameters of the three independent chlorine atoms were determined. These also lie on 18h special positions. The program ECIT puts all the zones on a common scale, so only one scale factor was necessary in the subsequent refinement. Five cycles of least-squares refinement[10] were now run, in which the scale factor and the positional parameters of the four independent atoms were varied. At this point, the conventional residual

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

was 0.167. Next, the isotropic temperature factors of all atoms were allowed to vary and a new weighting scheme[11] of the form $w = 0.1/K$ was introduced. In

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(8) (a) We thank Professor C. H. Langford, Amherst College, for helpful advice on procedure; (b) R. L. Burwell, Jr., and C. H. Langford, *J. Am. Chem. Soc.*, **81**, 3799 (1959).

(9) Using W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende's ERFR-2, IBM 709–7090 Fourier Program, 1962.

(10) Using C. T. Prewitt's program for the IBM 7090 computer, 1962. This program uses a full matrix and minimizes the R defined in the text.

(11) This scheme is based on one suggested by D. W. J. Cruickshank, *et al.*, "Computing Methods and the Phase Problem in X-ray Crystal Analysis," R. Pepinsky, J. M. Robertson, and J. C. Speakman, Ed., Pergamon Press, New York, N. Y., 1961, p. 32.

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS

h	*k*	*l*	F_o	F_c	*h*	*k*	*l*	*F*	F_c	*h*	*k*		F_o	F_o
0	0	6	462	−448	1	1	0	371	284	2	1	1	190	−204
0	0	9	866	−927	1	1	6	131	−120	2	2	0	216	−156
0	0	12	112	−114	1	1	9	172	−210	2	2	3	27	−10
0	0	15	300	331	1	1	12	34	−18	2	3	2	39	52
0	0	18	423	441	1	1	15	94	104	2	4	1	89	100
0	1	5	320	−294	1	1	18	86	110	2	5	3	61	3
0	1	8	218	224	1	2	2	29	37	2	6	2	49	−66
0	1	11	390	420	1	2	5	23	34	2	7	1	51	−65
0	1	14	113	126	1	2	8	123	138	2	8	3	49	38
0	1	17	182	−189	1	2	11	61	−50	3	0	0	472	−400
0	2	1	219	177	1	2	14	35	−51	3	0	3	151	173
0	2	4	69	41	1	2	17	57	−62	3	1	2	307	382
0	2	7	23	−12	1	3	1	660	599	3	2	1	163	−213
0	2	10	140	−158	1	3	4	27	8	3	3	0	415	279
0	2	13	44	−53	1	3	7	362	−402	3	3	3	37	15
0	2	16	19	38	1	3	10	354	−368	3	4	2	310	−332
0	3	0	396	−400	1	3	13	62	55	3	5	1	35	−24
0	3	3	415	−339	1	3	16	223	273	3	6	3	143	120
0	3	6	124	−107	1	3	19	161	161	3	7	2	47	1
0	3	9	308	371	1	4	0	293	−282	4	0	1	527	−713
0	3	12	228	221	1	4	3	560	−464	4	1	0	370	−282
0	3	15	20	26	1	4	6	157	−178	4	1	3	224	271
0	4	2	185	183	1	4	9	290	296	4	2	2	38	5
0	4	5	517	508	1	4	12	316	305	4	3	1	44	−68
0	4	8	449	486	1	4	15	36	58	4	4	0	755	586
0	4	11	237	−213	1	4	18	204	−203	4	4	3	184	178
0	4	14	361	−335	1	5	2	64	76	4	5	2	334	−371
0	5	1	540	499	1	5	5	255	216	5	0	2	286	356
0	5	4	117	84	1	5	8	69	76	5	1	1	74	−127
0	5	7	396	−375	1	5	11	77	−92	5	2	0	190	164
0	5	10	308	−330	1	5	14	154	−152	5	2	3	50	56
0	5	13	21	10	1	5	17	23	−24	5	3	2	271	−325
0	6	0	211	−186	1	6	1	119	−122	5	4	1	66	−71
0	6	3	177	−165	1	6	4	36	13	5	5	3	80	83
0	6	6	82	−41	1	6	7	33	−5	6	0	0	203	−186
0	6	9	192	160	1	6	10	106	104	6	0	3	76	107
0	7	2	221	214	1	6	13	38	−8	6	1	2	36	29
0	7	5	68	−39	1	6	16	22	−13	6	2	1	28	73
0	8	1	470	−394	1	7	0	200	−179	6	3	3	36	7
0	9	3	212	183	1	7	3	168	160	6	4	2	76	−74
1	0	7	566	526	1	7	6	289	232	7	0	1	198	344
1	0	10	23	−13	1	7	9	91	90	7	1	3	164	−244
1	0	13	219	−269	1	7	12	170	−145	7	2	2	35	41
1	0	16	216	−265	1	8	2	304	222	8	0	2	46	113
1	0	19	48	57	1	8	5	87	−58	8	2	3	64	−86
										9	0	3	263	−310

this scheme, for $|F_o|/3.514 \leqq 30$, $K = -0.0171(|F_o|/3.514) + 0.685$, and, for $|F_o|/3.514 > 30$, $K = -0.00033\cdot(|F_o|/3.514) + 0.192$. This scheme attempts to make the product wK a constant, a necessary condition for meaningful refinement of the data. Subsequent refinement showed a strong interaction between the scale factor and the temperature factors and the temperature factor belonging to Cl_3 would not refine. Therefore, for the final refinement, both the scale factor, which was essentially constant by this time, and this one temperature factor were held fixed. Three cycles of refinement brought the residual finally to 0.159. A difference Fourier was then computed which showed no anomalies greater than one-sixth of an expected chlorine peak. Thus, while the precision is not as high as might be desirable for some purposes (but sufficient for our own, however), there seems no question about the correctness of the structure. We believe that failure to reach a small residual is primarily due to the inexactness of our absorption corrections. Neglect of anomalous dispersion corrections (mainly the imaginary part for Re, which is fairly large) may also be of some importance.

The final positional parameters and temperature factors are recorded in Table I, along with their standard deviations. Table II gives the final calculated structure factors (F_c), together with the square roots of the observed intensities which have been corrected for Lorentz and polarization factors (F_o).

Discussion

The Structure.—Figure 1 shows one Re_3Cl_9 unit, as it occurs in crystalline $ReCl_3$, together with part of one of its neighboring Re_3Cl_9 units. The other two, symmetrically related, neighbors occur so as to be linked to Re′ *via* Cl_1' and Cl_4' and to Re″ *via* Cl_1'' and Cl_4''. The chlorine

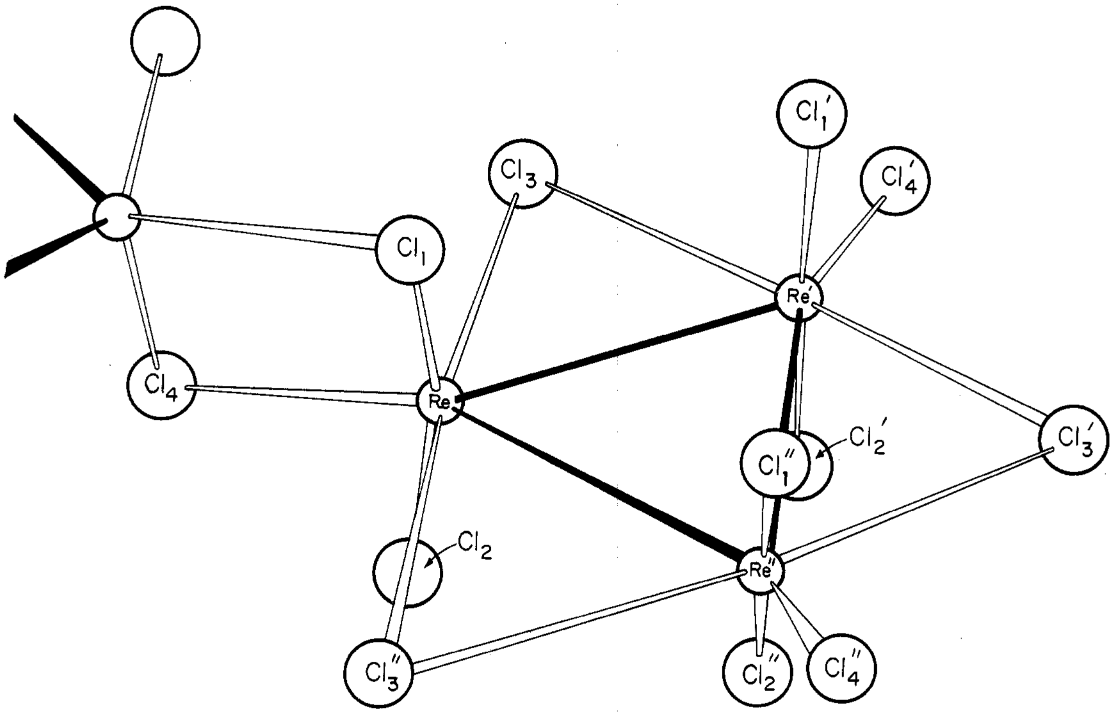

Fig. 1.—The Re_3Cl_9 cluster in rhenium(III) chloride. A portion of one of the nearest neighbors is shown to illustrate the manner in which the clusters are linked together through loose chlorine bridges.

TABLE III

PRINCIPAL INTERATOMIC DISTANCES AND BOND ANGLES IN Re_3Cl_9

Bond distances, Å.	
Re–Re′	2.489 ± 0.006
Re–Cl_1	2.40 ± 0.05
Re–Cl_2	2.29 ± 0.06
Re–Cl_3	2.46 ± 0.04
Re–Cl_4	2.66 ± 0.05
Nonbonded distances, Å.	
Cl_1–Cl_4	3.21 ± 0.08
Cl_1–Cl_3	3.37 ± 0.08
Cl_1–Cl_1'	3.23 ± 0.03
Cl_2–Cl_2'	2.95 ± 0.03
Cl_2–Cl_3	3.43 ± 0.08
Cl_2–Cl_4	3.34 ± 0.05
Cl_3–Cl_4	3.64 ± 0.04
Re–Re_2[a]	3.93 ± 0.01
Interbond angles, deg.	
Cl_1–Re–Cl_2	162.9 ± 1.1
Cl_3–Re–Cl_4	90.3 ± 2.4
Cl_2–Re–Cl_4	84.5 ± 0.5
Cl_1–Re–Cl_4	78.4 ± 0.9
Cl_2–Re–Cl_3	92.3 ± 0.9
Re–Cl_4–Re_2[a]	101.6 ± 1.1
Re–Cl_3–Re′	60.7 ± 1.9

[a] Re_2 denotes rhenium atom in adjacent Re_3Cl_9.

atoms in the Cl_2 set are not involved in bridging to any other rhenium atoms. The Re_3Cl_9 units can be considered to be placed at the 6c special positions in the unit cell, which means that each Re_3Cl_9 unit has rigorous (crystallographic) symmetry, C_{3v}. The important interatomic distances and interbond angles are listed in Table III. The intervals listed are standard deviations as obtained in the least-squares refinement. In the following discussion, it should be remembered that the actual uncertainties for *ca.* 95% confidence are roughly twice these standard deviations.

The Re_3Cl_9 unit in rhenium(III) chloride has most of its dimensions identical with those in the Re_3Cl_9 units previously found[4–6] in the $[Re_3Cl_{12}]^{3-}$ and $[Re_3Cl_{11}]^{2-}$ ions and in $Re_3Cl_9[P(C_2H_5)_2C_6H_5]_3$. The Re–Re distances here, 2.489 (0.006) Å., are within the very narrow range of all those previously found, 2.47–2.49 Å. In previous cases the chlorine atoms lying above and below the plane of the rhenium atoms have not been chemically different (except in $[Re_3Cl_{11}]^{2-}$), and their distances from the rhenium atoms have been 2.30–2.39 Å. In rhenium(III) chloride, the two sets of out-of-plane chlorine atoms are in quite different chemical situations, those in the Cl_1 set being involved in intermolecular bridging and those in the Cl_2 set being terminal. While their bond distances, 2.40 (0.05) Å. and 2.29 (0.06) Å., respectively, differ by an amount which is just on the borderline of significance, the difference is probably real and is in the direction one might expect.

The Re–Cl intramolecular bridge bonds here, 2.46 (0.04) Å., appear to be slightly longer than those previously found, 2.37–2.41 Å., but again, the difference is just on the borderline of significance. It may also be noted that the plane of the three bridging chlorine atoms is shifted from the plane of the rhenium atoms by 0.10 (0.05) Å. This shift is reasonable, since it moves the bridging atoms toward the Cl_1 atoms which are farther from the plane of the rhenium atoms and away from the Cl_2 atoms, which are closer to the plane of the rhenium atoms; the net result is to make the Cl_1–Cl_3 and Cl_2–Cl_3 contacts about equal.

The Re–Cl_4 bonds (where Cl_4 is a "Cl_2" of an adjacent Re_3Cl_9 unit; see Fig. 1.) are here appreciably longer, 2.66 (0.01) Å., than those previously found,[4b] ~2.52 Å. This difference is real and is reasonable in view of the fact that these chlorine atoms are in this case bridg-

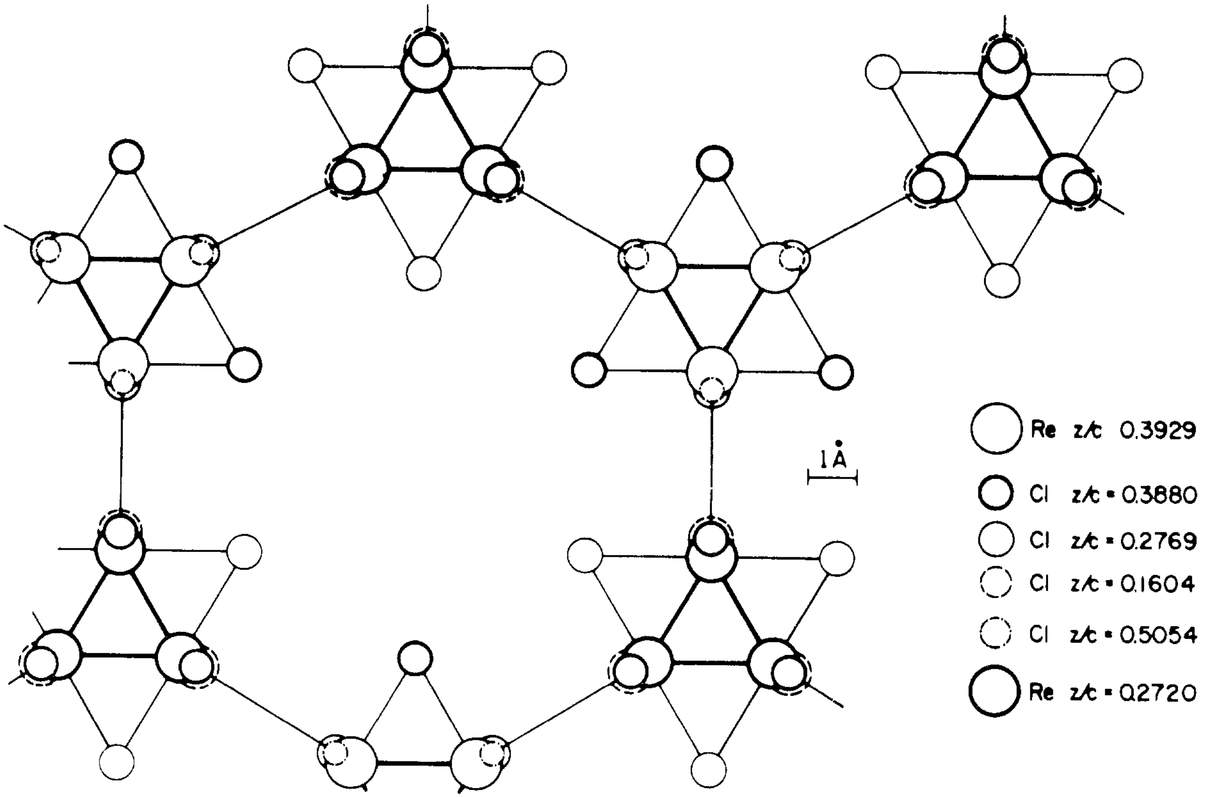

Fig. 2.—A view of a portion of one of the four-layer lamina, projected down the crystallographic *c* axis.

Table IV

Spectra of Rhenium(III) Chloride in Various Solvents and of Several Compounds Known to Contain the Re_3Cl_9 Group

Solvent (concn.)	Positions of absorption maxima, cm.$^{-1}$ (ϵ_{max})			
Acetone (7.77 × 10^{-5} *M*)	8,580 (43)	13,300 (410)	19,400 (1610)	22,200 (790), 25,000 (850)
Sulfolane[a] (2.74 × 10^{-4} *M*)		13,200 (510)	19,400 (1700)	22,000 (1130)
Glacial acetic acid (saturated)		12,750 (1*x*)[b]	19,000 (3*x*)[b]	23,000 (2*x*)[b]
Mulled in Nujol	10,200	12,850	16,300	
$Cs_3Re_3Cl_{12}$ mulled in Nujol		12,400	18,000	
$Re_3Cl_9[P(C_2H_5)_2C_6H_5]_3$ mulled in Nujol		12,100	18,200	
$Re_3Cl_9[P(C_2H_5)_2C_6H_5]_3$ in $CHCl_3$		12,300 (420)	18,600 (1490)	22,700 (1400)[c]
$Cs_3Re_3Cl_{12}$ in 12 *M* HCl		12,800 (470)	19,200 (1770)	25,000 (1020)
12 *M* HCl	8,400 (116)	13,000 (400)	19,200 (1460)	
60% $HClO_4$	10,300 (53)	13,000 (1*x*)[b]	20,000 (5*x*)[b]	

[a] Sulfolane is tetrahydrothiophene sulfone. [b] These figures give relative ϵ_{max} values as multiples of some constant, *x*. [c] This band, and to some extent those at similar energies in other compounds and solutions, owes part of its extinction to lying on the low-energy wings of ultraviolet absorption bands.

ing intermolecularly. As noted previously,[4-6] the bonding to rhenium atoms in these centrifugal positions does not appear to be either strong or important for the stability of the cluster itself, so this lengthening of the Re–Cl_4 type bond seems quite credible.

The intermolecular Re–Re distance, 3.93 Å., is so long as to preclude any significant direct interaction.

The packing of the molecules in the unit cell can be described as follows. There are infinite lamina, four atoms thick, running perpendicular to the *c* axis. The outer layers of each laminum contain Cl_2 atoms, while the inner layers are made up of the Re, Cl_1, Cl_3, and Cl_4 atoms. A projection down the *c* axis of one of the four-layered lamina is shown in Fig. 2.

In summary, hexagonal rhenium(III) chloride contains well-defined Re_3Cl_9 units, having almost exactly the same dimensions as they have in other compounds, which are loosely joined into a laminar structure by chlorine atom bridges.

Spectra of Solutions.—The existence of the Re_3Cl_9 group in rhenium(III) chloride and its occurrence in many, and perhaps all, compounds prepared directly (*i.e.*, without change in oxidation state or severe reaction conditions) from $ReCl_3$, would naturally lead one to suspect that Re_3Cl_9 units are present in solutions of rhenium(III) chloride in various solvents. As we have suggested earlier,[3] this would account for the much earlier observation[12] that "the freshly made aqueous solution gives no precipitate with silver nitrate, and so can contain no chloride ions." Slow hydrolysis does evidently occur, however. The fact[11] that after

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[12] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, 1950, Vol. II, p. 1312. References to original literature are given here.

the solid has taken up water from a moist atmosphere and then been dehydrated in a desiccator it is "in a very fine state of division, which is unusually reactive" can easily be explained as the result of H_2O splitting the intermolecular bridges when it enters, thus reducing $ReCl_3$ to hydrated Re_3Cl_9 units or small assemblies thereof, from which the complete crystal structure is not regenerated when the water molecules are removed.

However, another of the older observations appears to be inconsistent with the results and views outlined above, namely, that a solution of rhenium(III) chloride in glacial acetic acid contains dimers,[13] Re_2Cl_6. Molecular weight measurements, using solute and solvent which are both hygroscopic, require great caution, since even slight decomposition (*i.e.*, an average of only one Cl^- ion produced per six $ReCl_3$ simplest formula units) could lead to an apparent molecular weight corresponding to Re_2Cl_6. Moreover, the solutions used were extremely dilute ($\sim 10^{-3}$ *M*) and were allowed to stand for 2.5–24 hr. (average 12.5 hr.) until steady freezing points were established. Since rhenium(III) chloride slowly dissociates and/or hydrolyzes in water to give free Cl^- ions, it may behave similarly in glacial acetic acid, even if water has been excluded completely, over periods of many hours. We believe that despite the care with which Wrigge and Biltz' measurements appear to have been made, their result could be incorrect.

Using sulfolane (tetrahydrothiophene sulfone) we find a cryoscopically measured molecular weight of 885 ± 60, while that for Re_3Cl_9 would be 887.

The visible spectra of various solutions provide definite evidence that the major species present in fresh solutions of rhenium(III) chloride in a variety of solvents are $Re_3Cl_9X_n$, where X may be Cl, H_2O, or other solvent molecules and *n* may be 1, 2, or 3. In Table IV and Fig. 3, spectral data for rhenium(III) chloride in various solvents are presented, along with data for solids or solutions containing $[Re_3Cl_{12}]^{3-}$ or $[Re_3Cl_9[P(C_2H_5)_2C_6H_5]_3$. The great similarity of all these spectra is clearly evident and it seems scarcely credible that the different solutions could contain markedly different species, such as Re_2Cl_6, as against Re_3Cl_9.

The least "typical" of the spectra is that of crystalline rhenium(III) chloride, for which the strongest band is displaced some 2000 cm.$^{-1}$ lower than the average position at which it occurs in the other cases. This may be due to the fact that the Re_3Cl_9 group is much more distorted from D_{3h} symmetry in this case than in the others. This strongest band is generally somewhat more variable in position and shape than the one at 12,000–13,000 cm.$^{-1}$. It is also possible that in the mull of rhenium(III) chloride some preferential orientation of the crystal fragments occurs so that, if the strong band is complex, a lower energy component is absorbing preferentially to a higher energy one.

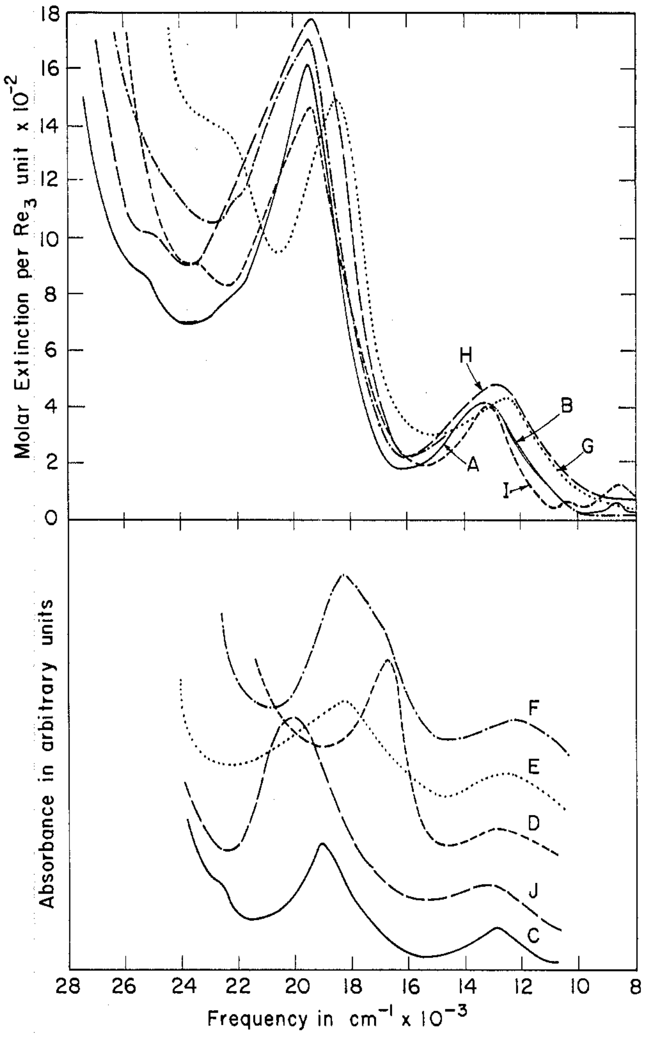

Fig. 3.—Visible spectra of various species known or presumed to contain Re_3Cl_9 groups. Upper part gives solution spectra for which extinction coefficients were measured: $ReCl_3$ in acetone (———); $Cs_3Re_3Cl_{12}$ in 12 *M* HCl (– – – –); $ReCl_3$ in 12 *M* HCl (---------); $Re_3Cl_9[P(C_2H_5)_2C_6H_5]_3$ in $CHCl_3$ (· · · · · ·); $ReCl_3$ in sulfolane (—·—·). Lower part gives mull spectra and those for solutions where extinction coefficients were not measured: $ReCl_3$ in glacial acetic acid (———); $ReCl_3$ in 60% $HClO_4$ (– – – –); $ReCl_3$ mulled in Nujol (---------); $Cs_2Re_3Cl_{12}$ mulled in Nujol (· · · · · ·); $Re_3Cl_9[P(C_2H_5)_2C_6H_5]_3$ mulled in Nujol (—·—·).

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[13] F. W. Wrigge and W. Biltz, *Z. anorg. allgem. Chem.*, **228**, 372 (1936).