which formation of the binculear complex by the reaction

$$2CoL_5 + O_2 \longrightarrow L_5CoOOCoL_5$$

where L is one of a series of nitrogenous bases, was extremely rapid and difficult to reverse. One of the major differences may be the solvent (toluene in our studies, *vs.* water in Wilkins'). For that reason we are extending our investigations to aqueous solution, where we hope to find an answer to the seemingly great differences between the reactions of Co(II) complexes of various ligands in various solvents with molecular oxygen.

One additional reaction of cobalt(II) porphyrins must not be overlooked: the reaction of the four-coordinate cobalt(II) porphyrin directly with molecular oxygen in the absence of amines[2]

$$CoP + O_2 \rightleftarrows CoP\cdot O_2 \qquad (7)$$

This reaction is not favorable enough to study quantitatively at any accessible temperature in which the solvent is liquid (down to −95° in toluene), and thus it is quite unfavorable in comparison to reactions 3 and 4. A solution of Co(*p*-OCH$_3$)TPP in toluene containing 1 atm of air at −83.5° showed a detectable amount of its "base-off" O$_2$ adduct. This suggests that the equilibrium constant for reaction 7 is at least 100 times smaller than the "base on" O$_2$ adduct at that temperature. Glassy samples of Co(*p*-OCH$_3$)TPP in toluene which are not degassed show a unique epr spectrum at 77°K, which is present when the samples are not degassed and absent when they are degassed. Wayland[25] has reported the epr parameters of the species CoTPP·O$_2$ as $g_{\parallel} \sim 2.05$, $g_{\perp} = 1.993$, $|A_{\parallel}|$ not resolved, $|A_{\perp}| = 31$ G (0.0029 cm^{-1}). We observe a similar spectrum for Co(*p*-OCH$_3$)TPP; it is nonaxial, with $g_1 \sim 2.11$, $g_2 = 1.988$, $g_3 = 1.985$, $|A_1| \sim 0.0014$ cm^{-1} (not resolved), $|A_2| = 0.00251$ cm^{-1}, and $|A_3| = 0.00293$ cm^{-1}. The fact that this spectrum is nonaxial is a strong suggestion that in this "base off" Co–O$_2$ complex also, the oxygen moiety is unsymmetrically bound to the cobalt.

The fact that this "base off" Co-O$_2$ complex is significantly less stable than the CoP·B·O$_2$ species produced by reactions 3 and 4 suggests that the amine plays an important role of activating the cobalt for formation of the Co–O bond. It does appear, however, that the activation of Co(II) porphyrins by axial bases for the reaction with molecular oxygen is much less sensitive to the electronic and steric effects of the axial base than are the amine complexes of Schiff's bases and dimethylglyoxime with alkyl groups.[26]

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The Chemistry of Rhenium(IV) Chloride. II.[1] Structure of One of the Polymorphs (β) and Evidence for a New Polymorph (γ)[2]

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Abstract: The crystal structure of the form of rhenium(IV) chloride which is obtained by reaction of Re$_3$Cl$_9$ with ReCl$_5$ or SbCl$_3$ with ReCl$_5$ has been investigated. This substance proves to be identical with that first reported in 1967. The structure is here described in detail. The crystals belong to the monoclinic system, with unit cell parameters $a = 6.362$ (2) Å, $b = 6.273$ (2) Å, $c = 12.165$ (4) Å, $\beta = 93.15$ (5)°, $d_{\text{calcd}} = 4.49$ g cm^{-3} for $Z = 4$, and $d_{\text{measd}} = 4.50$ g cm^{-3}. Successful refinement was carried out in the space group *P*2/*c* using 1227 measured intensities, corrected for absorption. In the final cycle of full-matrix, anisotropic refinement the unit-weighted and weighted residuals were both 0.049. The structure consists of confacial bioctahedra, Re$_2$Cl$_9$, which are linked by shared terminal chlorine atoms. The Re–Re distance is 2.728 (2) Å which is indicative of metal-to-metal bonding. X-Ray powder diffraction patterns show that the form of ReCl$_4$ obtained by dechlorinating ReCl$_5$ with CCl$_2$=CCl$_2$ has a different structure.

The earliest report[4] of the preparation of rhenium(IV) chloride has not been confirmed.[5,6] In 1966, an authentic sample of ReCl$_4$ was produced by accident in a commercial laboratory. Its identity has been confirmed[7] and some of its chemistry has been investi-

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gated.[8,9] Only recently have reproducible methods for the preparation of pure material of composition $ReCl_4$ been published.[10–13] Some fundamental questions still remain concerning rhenium(IV) chloride. This paper will attempt to answer some of them.

In our earlier report on the chemical properties of the "new" form of $ReCl_4$, we proposed that this form be designated β-$ReCl_4$, to distinguish it from the previously reported form, for which the designation α-$ReCl_4$ was proposed. In view of the now doubtful existence of the α material, the need for the distinguishing prefixes, α and β, might rightly be questioned. For several reasons, we consider it wise to continue using the prefix β. First, it has already acquired currency in secondary literature and it clearly identified the one substance of stoichiometry $ReCl_4$ whose existence, structure, and properties have previously been well documented and accepted. Its use will thus avoid ambiguity. Second, as will be shown later, there appears to be still another polymorph of $ReCl_4$, even though it is not produced by the previously described synthesis of "α-$ReCl_4$."

The previous structural characterization[7] of β-$ReCl_4$ was undertaken using the material obtained commercially. However, the investigation was not entirely satisfactory by contemporary standards of X-ray crystallography. The crystal fragments available were far from ideal for purposes of a single-crystal structural study and there were indications that disorder and/or twinning may have interfered. The structure failed to refine to an R value below 17%, although there seemed little doubt that its main features were correct. We considered it desirable to obtain a data set which would lead to a structure more secure in its details and accurate in its numerical parameters. It was also of interest to determine if all of the newly reported methods of preparation actually give the same polymorph of $ReCl_4$ and whether one or more of these are identical with the β form. Thus, a fresh single-crystal structural study was carried out using material prepared by the reaction of $ReCl_5$ with Re_3Cl_9 and powder diffraction patterns for various preparations of $ReCl_4$, including the original commercial one, were recorded and compared. These studies are reported here.

Experimental Section

Preparation. The method of Canterford and Colton[10] was used to obtain single crystals of β-$ReCl_4$. $ReCl_5$ and Re_3Cl_9 were heated in a sealed Vycor tube at 300° for 24 hr. $ReCl_5$ was used in slight stoichiometric excess. After 24 hr half of the sealed tube was pulled out of the furnace and the excess $ReCl_5$ was condensed in this cooler part. Most of the $ReCl_4$ remained in the hot end of the tube as a black mass, but some crystalline material adhered to the middle section of the tube. The tube was cooled and opened in an inert atmosphere box. The crystalline $ReCl_4$ from the middle of the tube was collected separately. Some crystals were placed in capillaries which were promptly sealed. Other portions were analyzed, giving chlorine contents of 43.0 and 42.9%. The theoretical value for $ReCl_4$ is 43.3%.

Samples of $ReCl_4$ were also prepared by reduction of $ReCl_5$ with $SbCl_3$ following the procedure of Frais, Guest, and Lock[11] and by dechlorination of $ReCl_5$ with $Cl_2C{=}CCl_2$ either in refluxing CCl_4, following the procedure of Brignole and Cotton,[12] or in neat $Cl_2C{=}CCl_2$ according to Muller and Waschinski.[13]

X-Ray Powder Patterns. These were recorded on samples of $ReCl_4$ prepared by each of the methods just mentioned and on a sample of the material originally supplied by Shattuck Chemical Co.[1,7–9] All samples were prepared in a dry nitrogen atmosphere and sealed in glass capillaries 0.5 mm in diameter. The patterns were recorded on film using conventional equipment supplied by the General Electric Co., with nickel-filtered Cu Kα radiation. Intensities were estimated visually on a scale of 1–10.

Single-Crystal Diffraction Data. A crystal of $ReCl_4$ approximately 0.2 × 0.1 × 0.1 mm was used throughout. Oscillation, Weissenberg, and precession photographs showed that the crystal belonged to the monoclinic system. The only systematic absence found was for $h0l$, $l = 2n + 1$. This suggests that the space group is either Pc or $P2/c$.

The crystal was then mounted on a General Electric manual diffractometer and aligned with the a^* axis parallel to the ϕ axis of the eucentric goniometer. Using Mo Kα radiation filtered with Nb foil (0.04 mm), preliminary measurements revealed strong reflections out to 2θ values as high as 100°. Unit cell parameters were therefore evaluated not only by measuring the settings for the Mo Kα maxima of about 30 reflections but also by measurements of the Kα_1–Kα_2 separations for about 20 high-angle (35–100°) reflections. A takeoff angle of 1° was used. These data give the following unit cell dimensions: $a = 6.362\,(2)$ Å, $b = 6.273\,(2)$ Å, $c = 12.165\,(4)$ Å, $\beta = 93.15\,(5)°$. With these unit cell dimensions, the density calculated for $Z = 4$ is 4.49 g cm^{-3}. The density measured pycnometrically is 4.50 g cm^{-3}.

The intensities of 1227 independent reflections, including 109 which should be systematically absent in $P2/c$, with $2\theta \leqslant 55°$ were measured on the diffractometer. A moving crystal–moving counter technique was used, with a constant scan range of 2.67°. Peak intensity was measured for 40 sec and background was measured for 20 sec each at 1.33° above and below the peak. A takeoff angle of 3° was used, and the pulse-height discriminator was set to accept 95% of the Mo Kα peak. During the data collection process the intensities of the 200, 020, and 006 peaks were checked regularly. They showed only random fluctuations which were within ±3%.

The intensities, I, were taken as $I = P - B_1 - B_2$, where P, B_1, and B_2 are the peak counts and the two background counts, respectively. The observed structure factors were calculated from the equation $|F_o| = (I/\mathrm{Lp})^{1/2}$ where Lp is the Lorentz and polarization correction. The estimated standard deviation of $|F_o|$, $\sigma(F_o)$, was set equal to $[\sigma_I{}^2 + (0.02I)^2]^{1/2}(\mathrm{Lp})^{-1/2}$.

Solution and Refinement. The atomic positional parameters previously obtained[7] were used as input for a cycle of isotropic full-matrix least-squares refinement in the space group $P2/c$. The result strongly implied that the input parameters were correct. Four more cycles were run, leading to the following discrepancy indices: $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o| = 0.086$, $R_2 = (\Sigma w||F_o| - |F_c||^2)/\Sigma w|F_o|^2 = 0.107$. The weighting factors, w, were set equal to $[\sigma(F_o)]^{-2}$.

The data were now corrected for absorption using the linear absorption coefficient $\mu = 286.3$ cm^{-1}. The shape of the crystal was measured as carefully as possible under a microscope. It was approximated by a solid of eight faces. As a partial check on the adequacy of this approximation, the transmission coefficient as a function of ϕ at $\chi = 90°$ was calculated and found to be in acceptable agreement with the observed variations in intensities.

Refinement was continued using absorption-corrected data and anisotropic temperature factors, leading to $R_1 = 0.051$ and $R_2 = 0.056$. Nine reflections for which $||F_o| - |F_c||/\sigma \geqslant 10$ were then omitted and refinement converged with $R_1 = R_2 = 0.049$. A difference electron density map showed no significant peaks. There was considerable random noise in the vicinity of the rhenium atom.

The following computer programs were used: PDATA (B. G. DeBoer) for calculating diffractometer settings, REDUCE (B. G. DeBoer and J. G. Norman, Jr.) for data reduction, SFIX (a local version of C. T. Prewitt's SFLS-5) for least-squares refinement, based on minimization of the function $w||F_o| - |F_c||^2$, FORDAP (A. Zalkin) for Fourier synthesis, STAN1 (B. G. DeBoer) for molecular geometry, ABSCOR (N. W. Alcock, B. Lee, and V. W. Day) for absorption corrections, ORTEP (C. K. Johnson) for preparing illustrations, SPADEX (Z. Mester) for calculating indices for powder patterns. A list of the observed and calculated structure factors is available.[14]

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(14) This list will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from

Table I. Atomic Positional Parameters and Anisotropic Temperature Parameters[a,b]

Atom	x	y	z	Equiv isotropic B	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Re	0.18466 (6)	0.26727 (6)	0.31251 (3)	1.00	0.77 (2)	1.13 (2)	1.12 (2)	0.00 (1)	0.17 (1)	0.00 (1)
Cl(1)	0.2520 (5)	0.1129 (5)	0.4787 (3)	2.12	2.2 (1)	2.5 (1)	1.7 (1)	0.0 (1)	0.0 (1)	0.5 (1)
Cl(2)	0.1337 (4)	0.4071 (6)	0.1272 (2)	1.79	1.1 (1)	2.7 (1)	1.6 (1)	−0.5 (1)	0.4 (1)	0.6 (1)
Cl(3)	0.3569 (5)	0.5683 (5)	0.3653 (3)	1.90	1.8 (1)	1.6 (1)	2.3 (1)	−0.3 (1)	0.2 (1)	−0.5 (1)
Cl(4)	0.0	−0.0503 (6)	0.25	1.80	1.4 (2)	1.3 (2)	2.7 (2)	0.0 (0)	−0.2 (1)	0.0 (0)
Cl(5)	0.50	0.0930 (7)	0.25	1.79	0.9 (1)	1.5 (2)	3.1 (2)	0.0 (0)	0.9 (1)	0.0 (0)

[a] Numbers in parentheses are estimated standard deviations, occurring in the least significant figure listed. [b] The form of the temperature parameter expression is: $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

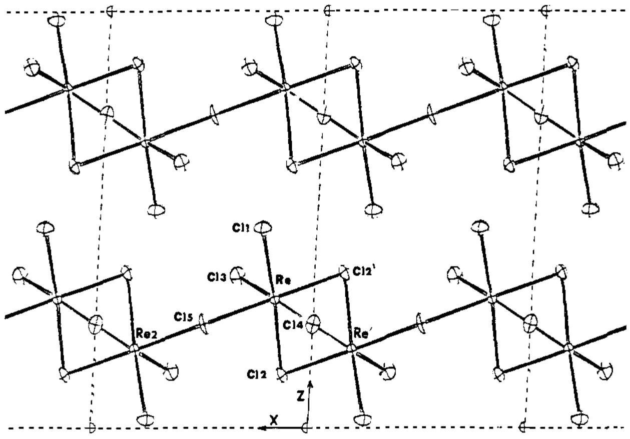

Figure 1. A projection of the structure in the y direction. The y axis is directed away from the reader. The crystallographic two-fold axes pass through Cl(4) and Cl(5).

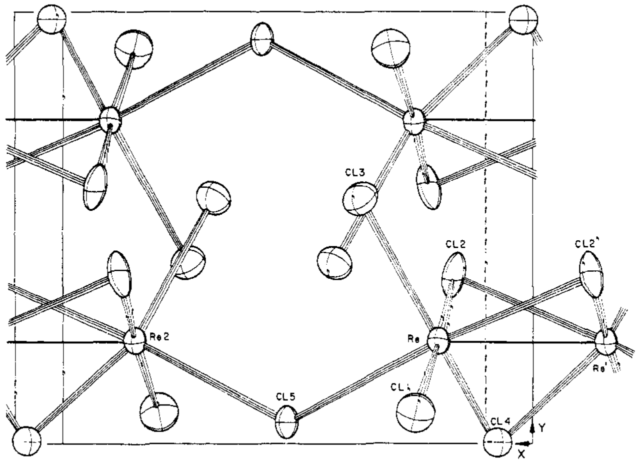

Figure 2. A projection of the structure in the c^* direction.

Results

Structure of β-Rhenium(IV) Chloride. The final atomic positional and temperature parameters are recorded in Table I. Figure 1 shows the structure in projection on the ac plane. It defines the atom numbering scheme followed in the tables and emphasizes the arrangement of chains of linked Re_2Cl_9 bioctahedra parallel to the a direction. The crystallographic two-fold axes pass through Cl(4) and Cl(5). Figure 2 shows the contents of one unit cell projected in the c^* direction and indicates clearly the angle at the bridging atom, Cl(5). Tables II and III present various interatomic distances and angles.

Table II. Bond Distances, Ångströms[a]

Re–Re	2.728 (2)	Cl(1)–Cl(4)	3.297 (4)
Re–Cl(1)	2.261 (3)	Cl(1)–Cl(5)	3.275 (4)
Re–Cl(2)	2.424 (3)	Cl(2)–Cl(3)	3.314 (5)
Re–Cl(2′)	2.361 (3)	Cl(2)–Cl(2′)	3.519 (6)
Re–Cl(3)	2.259 (3)	Cl(2)–Cl(4)	3.366 (5)
Re–Cl(4)	2.414 (3)	Cl(2)–Cl(5)	3.341 (4)
Re–Cl(5)	2.442 (2)	Cl(3)–Cl(2′)	3.287 (4)
Cl(1)–Cl(3)	3.257 (5)	Cl(3)–Cl(5)	3.439 (5)
Cl(1)–Cl(2′)	3.277 (5)	Cl(4)–Cl(5)	3.306 (2)

[a] Numbers in parentheses are estimated standard deviations, occurring in the least significant figure listed.

Table III. Bond Angles, Degrees[a]

Cl(1)–Re–Cl(2)	174.6 (1)	Cl(3)–Re–Cl(2′)	90.7 (1)
Cl(1)–Re–Cl(2′)	90.3 (1)	Cl(3)–Re–Cl(5)	93.9 (1)
Cl(1)–Re–Cl(3)	92.2 (1)	Cl(3)–Re–Cl(4)	178.1 (1)
Cl(1)–Re–Cl(4)	89.6 (1)	Cl(5)–Re–Cl(4)	85.8 (1)
Cl(1)–Re–Cl(5)	88.2 (1)	Cl(4)–Re–Cl(2′)	89.7 (1)
Cl(2)–Re–Cl(2′)	94.7 (1)	Cl(5)–Re–Cl(2′)	175.2 (1)
Cl(2)–Re–Cl(3)	90.0 (1)	Re–Cl(2)–Re′	69.5 (1)
Cl(2)–Re–Cl(4)	88.2 (1)	Re–Cl(4)–Re′	68.8 (1)
Cl(2)–Re–Cl(5)	86.7 (1)	Re–Cl(5)–Re(2)	126.8 (2)

[a] Numbers in parentheses are estimated standard deviations, occurring in the least significant figure listed.

Comparison of Different Preparations. Table IV lists the d spacings obtained by powder diffractometry for four different samples. The column headed "commercial sample" is for the material, originally purchased from Shattuck Chemical Co., on which all of the work reported in ref 1, 7–9 was conducted. The columns headed preparation 1, 2, and 3 refer to the following. Preparation 1, the same batch of material from which the specimen for the single-crystal study was obtained, was prepared by the reaction of Re_3Cl_9 with $ReCl_5$. Preparation 2, material was prepared by the method of Brignole and Cotton.[12] Preparation 3, material was prepared using neat tetrachloroethylene, as described by Muller and Waschinski.[13]

The films for the commercial sample and preparation 1 are essentially indistinguishable to the eye. As shown in Table IV, the former contains a few more lines than the latter, but all are very weak. A set of indices is given for these two powder patterns. These indices were computed from the single-crystal data for preparation 1. It is clear that all of the observed powder lines in the commercial sample, with the exception of a few weak ones, match lines of similar relative intensity in

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Table IV. Powder Patterns for Four Samples of Rhenium(IV) Chloride with Different Origins[a]

hkl indices	Commercial sample	Preparation 1	Preparation 2	Preparation 3
	6.535 (2)			
010	6.215 (3)		8.867 (4)	8.934 (5)
002	5.926 (6)	6.046 (7)	7.167 (4)	7.182 (3)
	5.698 (2)			6.537 (1)
011	5.588 (10)	5.574 (10)	6.057 (1)	6.088 (1)
10$\bar{2}$	4.450 (5)	4.506 (7)	5.513 (10)	5.455 (10)
11$\bar{1}$	4.201 (5)	4.220 (7)	5.082 (2)	5.040 (1)
013 (?)	3.357 (1)		4.695 (2)	4.733 (1)
200, 020	3.126 (2)	3.159 (3)	4.379 (7)	4.369 (8)
11$\bar{3}$, 021, 004	3.022 (2)	3.068 (3)	4.018 (1)	3.978 (1)
113	2.921 (2)	2.965 (2)	3.579 (1)	
022, 21$\bar{1}$	2.776 (8)	2.793 (5)	3.408 (1)	
211	2.714 (8)	2.718 (7)	3.215 (2)	3.198 (2)
104	2.663 (1)	2.661 (1)	3.132 (2)	3.115 (1)
21$\bar{2}$	2.603 (2)	2.611 (2)	2.945 (2)	2.931 (2)
11$\bar{4}$	2.557 (2)	2.553 (2)	2.867 (2)	2.858 (1)
21$\bar{3}$, 12$\bar{3}$	2.414 (1)		2.734 (7)	2.718 (7)
	2.359 (2)		2.622 (3)	2.600 (2)
20$\bar{4}$	2.257 (3)	2.257 (2)	2.558 (2)	
22$\bar{1}$, 220	2.217 (1)	2.225 (2)	2.472 (3)	2.485 (1)
204	2.156 (3)	2.154 (2)	2.369 (6)	2.359 (7)
115, 12$\bar{4}$	208.5 (7)	2.087 (5)	2.261 (4)	2.248 (3)
031, 222	2.053 (7)	2.060 (5)	2.181 (1)	
006, 310, 214	2.019 (6)	2.029 (4)	2.138 (1)	
31$\bar{1}$	1.985 (8)	1.987 (6)	2.082 (4)	2.075 (5)
302, 13$\bar{1}$, 311	1.953 (3)	1.945 (3)	2.026 (4)	2.023 (5)
025, 223, 016	1.922 (1)		1.976 (2)	
21$\bar{5}$	1.884 (4)	1.893 (2)	1.950 (1)	1.942 (1)
033, 12$\bar{5}$	1.852 (1)		1.905 (1)	1.900 (2)
22$\bar{4}$	1.824 (1)	1.826 (2)	1.853 (1)	1.841 (2)
13$\bar{3}$	1.788 (6)	1.786 (5)	1.826 (4)	1.816 (3)
20$\bar{6}$	1.749 (2)	1.751 (4)	1.764 (4)	1.751 (3)
31$\bar{4}$	1.719 (1)	1.720 (1)	1.693 (2)	1.699 (1)
026	1.698 (2)	1.697 (1)		1.671 (1)
017	1.670 (4)	1.665 (2)	1.613 (2)	1.608 (1)
126	1.618 (1)	1.617 (2)		1.553 (2)
323	1.588 (1)	1.581 (1)	1.529 (2)	1.523 (2)
13$\bar{5}$	1.546 (1)	1.541 (1)	1.487 (2)	1.476 (1)
402	1.513 (4)	1.509 (2)	1.438 (2)	1.433 (1)
14$\bar{2}$	1.481 (1)	1.481 (1)	1.390 (3)	1.384 (3)
31$\bar{6}$, 043	1.462 (1)	1.460 (1)	1.371 (3)	1.368 (3)
40$\bar{4}$	1.449 (1)			
14$\bar{3}$, 332	1.433 (1)	1.432 (1)		
33$\bar{3}$	1.412 (1)	1.411 (1)		
325	1.391 (2)	1.392 (1)		
422	1.364 (4)	1.365 (3)		
24$\bar{3}$	1.339 (1)	1.333 (1)		
243	1.319 (2)	1.317 (1)		
42$\bar{4}$	1.305 (4)	1.305 (1)		

[a] *d* spacings are in ångströms; numbers in parentheses are relative intensities, visually estimated. The origin of the specimens is explained in the text.

preparation 1 and can be indexed satisfactorily for β-$ReCl_4$. Frais, Guest, and Lock[11] previously made a similar comparison of powder data for their preparations with *d* spacings calculated from the preliminary single-crystal data.[15] The present work is conclusive as to the identity of the original commercial sample and the β-$ReCl_4$ prepared by the reaction of Re_3Cl_9 with $ReCl_5$, since it involves not only successful indexing of the powder pattern for the latter, but direct comparison of the two powder patterns.

Finally, in Table IV are listed the powder lines for preparations in which $ReCl_5$ was dechlorinated by $Cl_2C{=}CCl_2$ under different experimental conditions. It is evident that the two products are identical with each other but different from β-$ReCl_4$.

Discussion

Structure of β-$ReCl_4$. The present study confirms the previously reported[7] structure of β-$ReCl_4$. With the present data set, refinement proceeded satisfactorily in the space group *P*2/*c* to unit-weighted and weighted residuals of 0.049, thus removing all uncertainty about the correctness of the structure.

The structure can be described as zig-zag chains of Re_2Cl_9 confacial bioctahedra, in which one terminal chlorine atom at each end is shared between two bioctahedra. The chains run parallel to the crystallographic *a* axis. The angle at the bridging chlorine atom (Cl(5)) that is shared by two bioctahedra is 127°. Single chlorine bridges (as opposed to sets of two or three) of this type are not very common, although a few have been observed previously, as, for example, connecting the clusters in Nb_6Cl_{14} and $(Mo_6Cl_8)Cl_4$.

A check of Wyckoff's compilation[16] indicates that the β-$ReCl_4$ structure is unique among metal tetrahalides. Presumably one reason why this unique structure is adopted here is that it allows for direct Re–Re interaction, across the shared octahedral face. The Re–Re distance of 2.728 Å is indicative of a metal–metal bond. It may be compared with the Re–Re distances of 2.74 and 2.76 Å in the hexagonally close packed metal,[17] and with Re–Re distances in various other bi- and trinuclear compounds in which Re–Re bonds of various strengths exist.[18] Thus, in compounds based on the Re_3 trinuclear cluster, where double bonds occur, the distances are about 2.48 Å, and in the various binuclear species containing quadrupole bonds, the Re–Re distances are about 2.24 Å. In the molecules $Re_2Cl_3O(PPh_3)_2(C_2H_5COO)_2$ and $Re_2Cl_5O(PPh_3)_2(C_2H_5COO)$, where octahedrally coordinated rhenium atoms share an edge, the Re–Re distance are 2.51 and 2.52 Å, respectively. Thus the distance of 2.728 Å found here is relatively long, but still short enough to be consistent with the occurrence of an attractive Re–Re interaction. It will be shown below that the overall dimensions of the Re_2Cl_9 bioctahedron imply that there is such an attractive interaction, though not an especially strong one, as compared with that in the isoelectronic $W_2Cl_9{}^{3-}$ ion.

Comparison with Other M_2X_9 Structures. In a recent paper the structural criteria for determining the nature (*i.e.*, attractive or repulsive) and strength of the M–M interaction in confacial bioctahedra have been discussed and applied to a number of known structures.[19] The important parameters for β-$ReCl_4$ in this connection are summarized in Table V and contrasted with those for the $M_2Cl_9{}^{3-}$ systems, containing Cr, Mo, and W, in which the M–M interaction ranges from repulsive to moderately attractive to strongly attractive. These $M_2Cl_9{}^{3-}$ ions are isoelectronic (*i.e.*, contain d^3 M ions) with β-$ReCl_4$. It should be noted though that in β-$ReCl_4$ the bioctahedron is significantly distorted from

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[15] The strongest powder line, at 5.58 Å, was indexed in ref 11 as 001. This is inconsistent with the systematic extinctions for the space group, *P*2/*c*. However, this line can be satisfactorily indexed as 011.

[16] R. W. G. Wyckoff, "Crystal Structures," Vol. 2, 2nd ed, Interscience, New York, N. Y., 1964, pp 127–148.

[17] C. T. Sims, C. M. Craighead, and R. I. Jaffee, *J. Metals*, 7, 168 (1955).

[18] (a) *Cf.* F. A. Cotton, *Accounts Chem. Res.*, 2, 240 (1969), for original literature sources. (b) More recent references may be found in F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N. Y., 1972, pp 977–988.

[19] F. A. Cotton and D. A. Ucko, *Inorg. Chim. Acta*, **6**, 161 (1972).

Table V. Comparison of the Bioctahedron in β-$ReCl_4$ with Some Others

Structure parameter[a]	β-$ReCl_4$	$Cr_2Cl_9^{3-}$	$Mo_2Cl_9^{3-}$	$W_2Cl_9^{3-}$
M–M, Å	2.73	3.12	2.66	2.41
d'/d	1.05[b]	1.23	0.98	0.90
$90° - \alpha'$, deg	−0.9	4.2	−4.2	−8.0
$\beta - 70.53°$, deg	−1.2	5.9	−6.0	−12.5

[a] *Cf.* ref 19 for definitions of the parameters. [b] $d = 1.30$ A; $d' = 1.36$ Å.

D_{3h} symmetry, particularly by the participation of one terminal chlorine atom in bridging between two bioctahedra. Thus some of the individual distances and angles of a given type deviate appreciably from the mean values for that type.

The bioctahedron in β-$ReCl_4$ is most similar to $Mo_2Cl_9^{3-}$. Clearly, the M–M interaction is not repulsive, as it is in $Cr_2Cl_9^{3-}$, but it is not nearly so strongly attractive as that in $W_2Cl_9^{3-}$. A "diagonal relationship" in which the Mo^{3+} and Re^{4+} species have similar structures is not particularly surprising. The two are isoelectronic, but each, for different reasons, will tend to form less strong M–M bonds than that in $W_2Cl_9^{3-}$. For molybdenum the interaction is weaker in accord with the general trend toward weaker bonding as a group is ascended. For β-$ReCl_4$ the increased positive charge of the 4+ ion presumably has the effect of contracting the 5d orbitals, as compared with those in W^{3+}, and thus reducing the effectiveness of metal–metal overlap.

Even though the M–M bonding is weaker in $Mo_2Cl_9^{3-}$ than it is in $W_2Cl_9^{3-}$, it is still sufficient to give a spin-singlet ground state[20] in $Mo_2Cl_9^{3-}$. The Re–Re bond in β-$ReCl_4$ is slightly longer than that in $Mo_2Cl_9^{3-}$, and Table V suggests that the Re–Re interaction may be correspondingly a little weaker than that in $Mo_2Cl_9^{3-}$. Nevertheless, it is apparently strong enough to stabilize a spin-singlet ground state, since β-$ReCl_4$ is reported to have a small (580×10^{-6} cgs units) temperature-independent paramagnetism from 90 to 300 K.

Polymorphs of $ReCl_4$. As noted in the introductory section, the actual existence of α-$ReCl_4$ is doubtful at best. The existence of the β form is now fully established. Its structure is accurately known, and its powder diffraction pattern (Table IV) can serve as a convenient means of identification. Several methods for its preparation are also available and have been reproduced in two or more laboratories. Recently, the region of stability of β-$ReCl_4$ in the phase diagram of the Re–Cl system has been defined.[21]

In their report of the preparation of $ReCl_4$ by dechlorination of $ReCl_5$ with $Cl_2C{=}CCl_2$ in refluxing CCl_4, Brignole and Cotton[12] (B and C) noted that while their product gave several reactions which were qualitatively the same as those reported for β-$ReCl_4$, it had several solubility differences. The possibility that the substance obtained by B and C's method was a different polymorph of $ReCl_4$ was, of course, considered and work was undertaken to check on this. It was soon found by the present authors that B and C's material has a different powder pattern from that of β-$ReCl_4$. We delayed publishing this result in order to complete an accurate redetermination of the structure of β-$ReCl_4$. In the meantime, Muller and Waschinski[13] (M and W) reported their results using unsaturated chlorocarbons to dechlorinate $ReCl_5$. They concluded that both $Cl_2C{=}CClCCl_3$ and neat $Cl_2C{=}CCl_2$ afforded a product which was not β-$ReCl_4$. They proposed calling this γ-$ReCl_4$ and, most appropriately, put the question of whether the B and C material would not also be γ-$ReCl_4$.

Our results and conclusions are in good agreement with those of M and W. As Table IV shows, the substances obtained by B and C's method ($CCl_2{=}CCl_2$ in CCl_4) and M and W's method (neat $CCl_2{=}CCl_2$) are identical with each other but different from β-$ReCl_4$.

Our experience with γ-$ReCl_4$ indicates that it will be extremely difficult, if not impossible, to obtain single crystals of this substance large enough to use for structure determination. M and W report a set of unit cell dimensions which they derived from a powder pattern for γ-$ReCl_4$. We have found that this unit cell is capable of providing indices for all of the powder lines we observe for γ-$ReCl_4$. This does not, of course, prove it to be correct.

Comparison with Technetium(IV) Chloride. The structures of β-$ReCl_4$ and the only known polymorph[22] of $TcCl_4$ are quite different. While in each case the metal atom is surrounded by a distorted octahedron of chlorine atoms, the linking of these octahedra by means of shared chlorine atoms follows quite different patterns. In $TcCl_4$ the octahedra share edges in such a way as to leave the unshared chlorine atoms of each octahedron in cis positions. The Tc–Tc distances are 3.62 Å and the angles in the rhombus formed by the two metal atoms and the bridging chlorine atoms imply that the metal atoms are repelling each other.

Comparison of the $TcCl_4$ and β-$ReCl_4$ structures affords a good example of the normal trend[18a] toward increased metal–metal bonding as a group is descended, provided other factors remain constant.

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