CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS

Chemical and Structural Studies of Rhenium(V) Oxyhalide Complexes. I. Complexes from Rhenium(III) Bromide[1]

BY F. A. COTTON AND S. J. LIPPARD[2]

Received July 12, 1965

The reactions of several cations (M) with rhenium(III) bromide in concentrated aqueous HBr under oxidative conditions have been investigated. When M is Cs^+, a compound containing the new oxotetrabromorhenate(V) anion is obtained. For the tetraphenylarsonium cation, the hexabromorhenate(IV) complex forms. Using tetraalkylammonium cations, the reaction is even more complex, yielding red, yellow, and black crystal mixtures which contain both Re(IV) and Re(V). For the case where M is tetraethylammonium ion, the red crystals are shown to be $[(C_2H_5)_4N][ReBr_4O(H_2O)]$, and the results of a complete single crystal X-ray study of this compound are presented. The anion consists of a square pyramidal $(ReBr_4O)$ unit with Re–Br bond lengths of 2.51 Å. and a short Re–O bond length of 1.71 Å. The water molecule is weakly coordinated to rhenium at the base of the pyramid, with a rather long Re–O distance of 2.32 Å. The tetraethylammonium cation in this compound is shown to have a disordered structure with two different orientations of the ion occurring in the lattice.

Introduction

Recent investigations in this laboratory have incated that rhenium(III) bromide is capable of forming a variety of derivatives including complexes of the type $Re_3Br_9L_3$,[3] $M_nRe_3Br_{9+n}$ (n = 1, 2, or 3),[3] and $M_2Re_4Br_{15}$.[4] The last of these was shown[4] to contain Re_3Br_9 groups and $[ReBr_6]^{2-}$ ions, where some of the rhenium had been oxidized to Re(IV). The isolation of red, yellow, and black crystal mixtures by the addition of alkylammonium bromides to solutions containing rhenium(III) bromide in 48% aqueous HBr has also been briefly reported.[5] The crystals were originally[5] thought to contain *trans*-$[ReBr_4(H_2O)_2]^-$ ions, but more extensive studies[6] have revealed that the anion is in fact $[ReBr_4O(H_2O)]^-$.

The susceptibility of solutions of rhenium(III) bromide in aqueous HBr to atmospheric oxidation, with the resultant formation of $[ReBr_6]^{2-}$, $[ReBr_4O(H_2O)]^-$, and $[ReBr_4O]^-$ complexes, will be the subject of this paper. The molecular structure of the $[ReBr_4O(H_2O)]^-$ molecule ion has been elucidated by a complete single crystal X-ray study, the results of which are presented and discussed herein.

Experimental

Preparation of Compounds.—The detailed preparations of all compounds are described below. Analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

Tetraethylammonium Oxotetrabromoaquorhenate(V), $[(C_2H_5)_4N][ReBr_4O(H_2O)]$.—This compound was prepared when a tenfold excess of tetraethylammonium bromide was added to a saturated solution of rhenium(III) bromide in 48% aqueous HBr.[7] Invariably, a mixture of red, yellow, and black crystals precipitated. In one instance the reaction mixture was heated on the steam bath for 10 days with free access of air. Slow evaporation of the solvent yielded large single crystals of the red compound along with the usual yellow and black products. The mixture was filtered on a glass frit, washed with three ice-cold portions of 48% HBr, and dried under vacuum over P_2O_5.

The ruby-red crystals were large (~5 mm. in diameter) polyhedra with well-developed faces and were readily separated from the mixture by hand with the aid of a microscope. Chemical analysis was consistent with the formula for tetraethylammonium oxotetrabromoaquorhenate(V); m.p. 127–129° dec.

Anal. Calcd. for $[(C_2H_5)_4N][ReBr_4O(H_2O)]$: C, 14.34; H, 3.32; N, 2.09; Br, 47.70. Found: C, 14.43; H, 3.72; N, 2.26; Br, 48.00.

Solubility.—The compound is soluble in acetone and acetonitrile to give red solutions and insoluble in ethers and cold 48% HBr. It hydrolyzes instantly in neutral water to form a black, insoluble residue.

Tetraethylammonium Dioxodibromorhenate(V), $[(C_2H_5)_4N][ReBr_2O_2]$.—Finely powdered $[(C_2H_5)_4N][ReBr_4O(H_2O)]$ (0.11648 g.) was heated to 125° in air in a Pyrex crucible to constant weight. The specimen was stored for a fixed time in a desiccator over silica gel during each of the cooling periods. The final weight of bright orange product was 0.08969 g., corresponding (within 3%) to a solid of composition $[(C_2H_5)_4N][ReBr_2O_2]$ remaining in the crucible. Chemical analysis confirmed the suggested formula.

Anal. Calcd. for $[(C_2H_5)_4N][ReBr_2O_2]$: C, 18.90; H, 3.94; N, 2.76. Found: C, 18.97; H, 3.90; N, 3.20.

Tetraethylammonium Hexabromorhenate(IV), $[(C_2H_5)_4N]_2[ReBr_6]$.—As described above, the preparation of $[(C_2H_5)_4N][ReBr_4O(H_2O)]$ from rhenium(III) bromide yields a product mixture containing yellow crystals. These could, with some difficulty, also be isolated manually and proved, upon chemical analysis, to be tetraethylammonium hexabromorhenate(IV).

Anal. Calcd. for $[(C_2H_5)_4N]_2[ReBr_6]$: C, 20.75; H, 4.32; N, 3.03. Found: C, 21.28; H, 4.91.

An independent preparation of this compound was accomplished by addition of an excess of tetraethylammonium bromide to a solution of $H_2[ReBr_6]$ prepared by dissolving 0.5 g. of $K_2[ReBr_6]$ in 50 ml. of dilute (3 N) nitric acid. Yellow crystals formed at once and were filtered and washed with cold, dilute nitric acid. After drying over P_2O_5 under vacuum, the product yield was 0.5 g.

---

[1] Supported by the United States Atomic Energy Commission.

[2] National Science Foundation Predoctoral Fellow, 1962–1965.

[3] F. A. Cotton, S. J. Lippard, and J. T. Mague, *Inorg. Chem.*, **4**, 508 (1965).

[4] F. A. Cotton and S. J. Lippard, *ibid.*, **4**, 59 (1965).

[5] 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*, **145**, 1305 (1964).

[6] F. A. Cotton and S. J. Lippard, *Chem. Commun.* (London), 245 (1965).

[7] The saturated solution was prepared by dissolving rhenium(III) bromide in a large excess of 48% aqueous HBr (*e.g.*, 2 g. of $(ReBr_3)_3$ in 300 ml. of acid), filtering off a small quantity of insoluble residue, and concentrating the resultant red filtrate at *ca.* 90° in air on a steam bath to the saturation point. The final concentration, estimated from an average of several preparations, was $\sim 5 \times 10^{-3}$ M in Re(III).

Anal. Found: C, 20.60; H, 4.37; N, 3.41.

The identity of these compounds was established by a comparison of their X-ray powder patterns using Cu Kα radiation with a nickel filter. The two patterns were indistinguishable.

Solubility.—The compound is soluble in acetonitrile and insoluble in 48% aqueous HBr.

Cesium Oxotetrabromorhenate(V), Cs[ReBr$_4$O].—To 100 ml. of an ice-cold saturated solution of rhenium(III) bromide in 48% HBr[7] was added a tenfold excess (~1.5 g.) of cesium bromide with rapid stirring. The bright orange precipitate which formed immediately was separated by filtration through a glass frit, washed with three portions of ice-cold 48% HBr, and dried under vacuum over P_2O_5; yield 0.16 g.

Anal. Calcd. for Cs[ReBr$_4$O]: Cs, 20.2; Br, 48.8. Found: Cs, 21.5; Br, 49.0.

Solubility.—The compound is soluble in 48% aqueous hydrobromic acid and insoluble in nonaqueous media. It hydrolyzes instantly in neutral water to form a black, insoluble residue.

Cesium Hexabromorhenate(IV), Cs$_2$[ReBr$_6$].—When orange Cs[ReBr$_4$O] was dissolved in hot aqueous 48% hydrobromic acid and the resultant solution volume reduced by evaporation on a steam bath, yellow single crystals of $Cs_2[ReBr_6]$ precipitated. In lieu of chemical analysis, these were characterized by their isomorphism with $Cs_2[PtBr_6]$ (*vide infra*). Alternatively, cesium hexabromorhenate could be prepared in a manner analogous to the preparation of $[(C_2H_5)_4N]_2[ReBr_6]$, by addition of 0.5 g. of CsBr to the solution of $H_2[ReBr_6]$. The yellow powder which formed was filtered and washed with dilute nitric acid. The dried product (yield 0.5 g.) gave an X-ray powder pattern identical with a powder pattern of $Cs_2[ReBr_6]$ obtained from Cs[ReBr$_4$O].

Tetraphenylarsonium Hexabromorhenate(IV), [(C$_6$H$_5$)$_4$As]$_2$[ReBr$_6$].—To 80 ml. of a saturated solution of rhenium(III) bromide in 48% aqueous HBr[7] was added a solution containing 5 g. of $[(C_6H_5)_4As]Cl$ in 80 ml. of methanol. After stirring for 10 min., a golden yellow solid was filtered. This was washed with three 10-ml. portions of methanol and dried under vacuum at 80°; yield 0.5 g.

Anal. Calcd. for $[(C_6H_5)_4As]_2[ReBr_6]$: C, 40.25; H, 2.82; As, 10.45; Br, 33.50. Found: C, 39.11; H, 2.77; As, 9.91; Br, 33.04. This compound was also prepared by the method used for obtaining $[(C_2H_5)_4N]_2[ReBr_6]$. Addition of 0.62 g. of $[(C_6H_5)_4As]Br$ to the solution containing $H_2[ReBr_6]$ resulted in the formation of the desired yellow product, which was washed and dried as above; yield 0.83 g.

Anal. Found: C, 41.13; H, 2.86.

The molar conductivity, Λ_M, of this compound was measured on an approximately 10^{-3} *M* solution in nitromethane and found to be 146 ohm^{-1} cm.^{2}. This value is to be expected for a 2:1 electrolyte[8] and serves as an additional check on the chemical composition of $[(C_6H_5)_4As]_2[ReBr_6]$.

Infrared Spectra.—The infrared spectra of Nujol mulls of all complexes were recorded from 4000 to 600 cm.$^{-1}$ using a Perkin-Elmer Model 337 grating spectrometer. For each compound, the result was compared to the infrared spectrum of the free cation bromide, MBr, used to prepare it.

X-Ray Powder Photograph of Cs$_2$[ReBr$_6$].—The sample was packed into a 0.2-mm. Lindemann glass capillary and mounted in a 114.6-mm. Debye–Scherrer camera. The measurement was made using Cu Kα radiation with a nickel filter. No corrections were made for either film shrinkage or absorption.

Single Crystal X-Ray Investigation of [(C$_2$H$_5$)$_4$N][ReBr$_4$O(H$_2$O)].—Using nickel-filtered copper radiation, single crystals were examined on the Weissenberg camera in order to determine the space group and unit cell parameters. The density was measured by flotation in a mixture of CH_3I and $CHBr_3$. Intensity data were then taken on a crystal of approximate dimensions 0.15 × 0.15 × 0.10 mm., mounted along the *c* axis. A General Electric XRD-5 spectrogoniometer equipped with a counter detector was used to record the intensities of ~700 independent reflections in the levels *hk*0–*hk*5, for which sin θ <0.93. Since only a few reflections (*e.g.*, 714) were too weak to be measured, these were assigned the value 0.0 in the structure determination. The 709/7090 program, GONIO-MIXG2, written by Professor D. P. Shoemaker, was used to calculate the settings of the XRD-5 as well as the LP corrections for each reflection. Since at the time we did not have access to a computer program to assist in the calculation of absorption corrections for the diffractometer geometry (Eulerian cradle), none was made, despite the fact that for the crystal being investigated μt was twice the optimum[9] value of 2.0.

The three-dimensional Patterson synthesis and all Fourier summations were performed with the aid of MIFR-2.[10] Structure factor calculations and least-squares refinement cycles were carried out using the full-matrix program of Prewitt,[11] with equal weights being assigned to the intensities. Scattering factors for rhenium were those of Thomas and Umeda[12] for Re(0) modified for the real part of anomalous dispersion by adding −5.0 electrons, according to Templeton.[13] The imaginary part of the dispersion correction is small and was ignored. Atomic scattering factors for bromine were taken from the International Tables[14] and were similarly corrected for anomalous dispersion.[13] Carbon and nitrogen form factors were also taken from the Tables[15] and used without further correction.

Results

Preparations.—The products of the reactions between MBr (where M is tetraethylammonium, cesium, or tetraphenylarsonium ion) and saturated solutions of rhenium(III) bromide have been described above. In addition, we have investigated similar reactions of other cation bromides, in particular, the tetraalkylammonium bromides. When an excess of R_4NBr, R = CH_3, *n*-C_3H_7, or *n*-C_4H_9, was added to a solution of $(ReBr_3)_3$ in 48% aqueous HBr prepared by prolonged heating in air,[7] mixtures of red, yellow, and black solids precipitated. The presence of all three colored products was easily detected on the microscope stage, but the small size of the particles precluded manual separation. In analogy to the tetraethylammonium salts, it seems likely that the red components of the mixtures are of the type $(R_4N)[ReBr_4O]$ or $(R_4N)[ReBr_4O(H_2O)]$, and the yellow components, $(R_4N)_2[ReBr_6]$. Even for the case where R = C_2H_5, it was impossible to isolate enough of the black components for chemical analysis. It was possible, however, to isolate a small amount of black material for an infrared spectrum, the results of which are presented below.

The thermal decomposition of $[(C_2H_5)_4N][ReBr_4O(H_2O)]$ in air to form $[(C_2H_5)_4N][ReBr_2O_2]$ has been examined by a weight loss experiment. Although there is no direct information concerning the nature of the gaseous products of this decomposition, it is still

---

[8] See, for example, F. A. Cotton, B. F. G. Johnson, and R. M. Wing, *Inorg. Chem.*, **4**, 502 (1965), and references contained therein.

[9] M. J. Buerger, "X-Ray Crystallography," John Wiley and Sons, Inc., New York, N. Y., 1942, p. 178 ff.

[10] MIFR-2 is an updated version of the Sly–Shoemaker–Van den Hende Fourier program, ERFR-2. [W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, "A Two and Three Dimensional Fourier Program for the IBM 709/7090," ERFR-2 (1962)].

[11] C. T. Prewitt, SFLSQ-3, "A Full-Matrix Crystallographic Least-Squares Refinement Program for the IBM 709/7090 Computer, Massachusetts Institute of Technology, 1962.

[12] L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957).

[13] D. H. Templeton in "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, England, 1962, Vol. III, p. 215.

[14] Reference 13, Vol. III, p. 220.

[15] Reference 13, Vol. III, p. 218.

TABLE I

INFRARED DATA FOR VARIOUS COMPOUNDS PREPARED FROM RHENIUM(III) BROMIDE AND CONTAINING ONE OR MORE ReO GROUPS

Compound	Absorption maximum, cm.$^{-1\,a}$	Assignment
$Cs[ReBr_4O]$	955 vs	ReO str. freq.[b]
$[(C_2H_5)_4N][ReBr_4O(H_2O)]$	3360 m, br	Water str. mode[c]
	1605 s	Water bend. mode[c]
	1005 vs	ReO str. freq.[b]
	625 m, vbr	Water mode[c]
$[(C_2H_5)_4N][ReBr_2O_2]$	935 vs	Nonlinear ReO_2 grouping
	875 s, br	
Black product of $[(C_2H_5)_4N]Br-(ReBr_3)_3$ reaction	3350 w, br	*d*
	1600 m	*d*
	1005 vs	*d*
	934 s	Nonlinear ReO_2 grouping
	875 s, br	

[a] s, strong; m, medium; w, weak; br, broad; v, very. [b] See, for example, J. Chatt and G. A. Rowe, *J. Chem. Soc.*, 4019 (1962). [c] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 155 ff. [d] $[(C_2H_5)_4N][ReBr_4O(H_2O)]$ impurity; see text.

possible to calculate an "expected weight loss" since $[(C_2H_5)_4N][ReBr_2O_2]$ is the sole product remaining in the crucible. The loss of 26.8 mg. from 116.5 mg. of starting material agrees very well with the expected value of 27.6 mg. One possible reaction scheme might be

$$[(C_2H_5)_4N][ReBr_4O(H_2O)](s) + {}^1/_2O_2(g) \xrightarrow{125°} [(C_2H_5)_4N][ReBr_2O_2](s) + Br_2(g) + H_2O(g)$$

Several attempts were also made to dehydrate tetraethylammonium oxotetrabromoaquorhenate(V) at 125° under vacuum, but the presence of water bands in the infrared spectrum of the products indicated that dehydration did not occur to any great extent. In accord with this observation, we found that the X-ray powder patterns of the products were indistinguishable from that of the starting material.

Infrared Spectra.—Table I contains a summary of compounds whose infrared bands could not be attributed to cation absorptions. In each case, the new bands are listed and a most probable assignment is made. Included in the table is the result for the black product of the reaction between rhenium(III) bromide and tetraethylammonium bromide. Since it was impossible to separate this compound completely from those which precipitated with it (*vide supra*), its spectrum is contaminated with bands due to $[(C_2H_5)_4N][ReBr_4O(H_2O)]$ and $[(C_2H_5)_4N]_2[ReBr_6]$. Noteworthy, however, is the presence of two strong bands at 875 (broad) and 935 cm.$^{-1}$ which do not occur in the spectra of either possible contaminant. The actual spectra of $[(C_2H_5)_4N][ReBr_4O(H_2O)]$ and $[(C_2H_5)_4N]Br$ in the 700–1200 cm.$^{-1}$ region, which will be discussed in detail later, are shown in Figure 1.

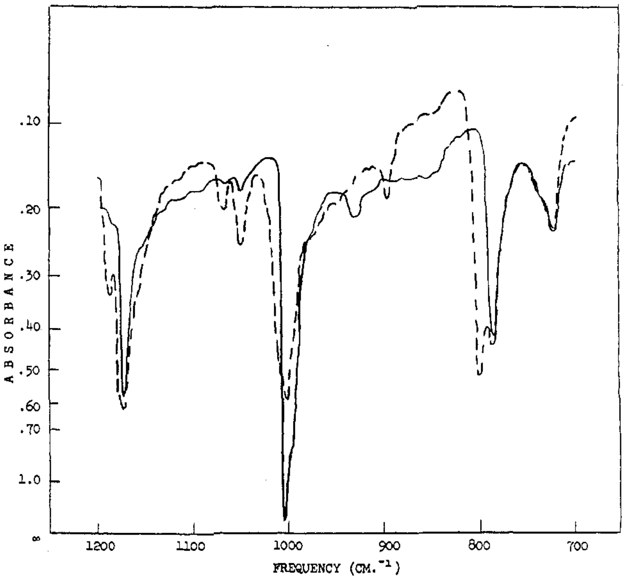

Figure 1.—Infrared spectra of $[(C_2H_5)_4N][ReBr_4O(H_2O)]$ (———) and $[(C_2H_5)_4N]Br$ (---------) in the 700–1200 cm.$^{-1}$ region.

TABLE II

X-RAY POWDER DIFFRACTION DATA FOR $Cs_2[ReBr_6]$ AND $Cs_2[PtBr_6]$—INTERPLANAR SPACINGS AND RELATIVE LINE INTENSITIES

$Cs_2[ReBr_6]$		$Cs_2[PtBr_6]^a$	
d, Å.	I/I_0	*d*, Å.	I/I_0
6.05	50	6.16	70
5.25	5	5.32	9
3.73	30	3.76	55
3.19	70	3.21	30
3.06	90	3.07	75
2.65	100	2.66	100
2.43	7	2.44	5
2.37	7	2.38	3
2.17	20	2.17	25
2.04	20	2.05	25
1.98	2		
1.88	90	1.88	65
1.80	20	1.80	20
		1.77	5
1.68	20	1.68	13
		1.62	5
1.60	40	1.60	20
1.54	35	1.54	20
1.49	20	1.49	13
1.42	25	1.42	11
1.39	10	1.39	1
1.33	25	1.33	9
1.26	20	1.25	7
1.23	20	1.23	7
1.22	20	1.22	7
1.19	20	1.19	15

[a] Data from ref. 16.

X-Ray Powder Photographs.—The observed *d* spacings and relative intensities of the diffraction lines for $Cs_2[ReBr_6]$ are summarized in Table II. Included for comparison are the published[16] spacings for $Cs_2[PtBr_6]$. From the table it is evident that these two compounds are isomorphous.

Unit Cell and Space Group.—From oscillation and Weissenberg photographs it was evident that $[(C_2H_5)_4N][ReBr_4O(H_2O)]$ crystallizes in the orthorhombic system. The dimensions of the unit cell were estab-

---

[16] J. V. Smith, Ed., "Powder Diffraction File," American Society of Testing Materials, Philadelphia, Pa., 1963, No. 9-400.

lished on the diffractometer as a, 11.14 Å.; b, 11.54 Å.; c, 12.90 Å., all ±0.02 Å. An analysis of the Weissenberg data revealed the following systematic absences: $0kl$, $k + l \neq 2n$, and $h0l$, $h \neq 2n$, from which it may be inferred[17] that the space group is either the centric Pnam (No. 62 with the b and c axes interchanged) or the acentric $Pna2_1$ (No. 33). Using the measured density, $\rho = 2.7 \pm 0.1$ g./cc., it follows that the number of formula weights in the unit cell is four; the calculated density is then 2.67 g./cc.

Determination of the Structure.—The set of intensities, corrected for Lorentz and polarization effects, was used to compute a three-dimensional Patterson map, from which no clear basis for choice between the two possible space groups was available. The acentric one, $Pna2_1$, was tentatively assumed, in which all atoms occupy the fourfold general set of positions (4a)[17]: x, y, z; $\bar{x}, \bar{y}, {}^1/_2 + z$; ${}^1/_2 - x, {}^1/_2 + y, {}^1/_2 + z$; ${}^1/_2 + x, {}^1/_2 - y, z$. From the Patterson map, the approximate coordinates of the rhenium atoms were easily determined as: $x = 0.25$, $y = 0.103$, z arbitrary, which gave a value for the closest Re–Re approach of 6.5 Å.; clearly we were dealing with a monomeric rhenium complex. A complication immediately arose, however, in that the x coordinate of ${}^1/_4$ for rhenium introduced higher symmetry into the unit cell than that required by either space group. In particular, with $x = {}^1/_4$, the rhenium atoms were also related to each other by a centering condition on the A face. When the above rhenium coordinates were used to phase the observed structure amplitudes, values for hkl, $k + l \neq 2n$, were calculated as zero.

With phases based on rhenium, then, a three-dimensional Fourier synthesis was computed which revealed several peaks, some of which no doubt resulted from the false symmetry. Four large peaks in an approximately square array about the rhenium atom predominated. These were taken to be bromine atoms and a new Fourier map was computed using these as well as the rhenium atom to determine phases. Because of the bromine contributions, there was considerably better resolution of peaks on this map than on the first one, but it was impossible to locate all the light atoms unambiguously. Two peaks did appear near the rhenium atom, however, on an axis perpendicular to the plane of bromine atoms. These peaks were assigned to oxygen atoms. From the difference in the approximate rhenium–oxygen bond distances for these two atoms, 1.7 *vs.* 2.3 Å., it appeared that the anion was oxotetrabromoaquorhenate(V) rather than *trans*-diaquotetrabromorhenate(III) as we were then assuming (*cf.* Discussion).

Subsequently, three cycles of least-squares refinement of the scale factor and the positional and isotropic thermal parameters reduced the R value (defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$) to 0.19 (all reflections), but two problems arose. First, electron density maps computed at the various stages of refinement gave no clear picture of the tetraethylammonium ion. In addition, since the correlation matrix showed large (>0.70) interactions[18] between the coordinates of bromine atoms which would have been related by the mirror planes at $z = {}^1/_4, {}^3/_4$ in Pnam (see below), it seemed possible that our initial choice of the space groups $Pna2_1$ was incorrect.

At this point, the rhenium and oxygen atoms were reassigned to sets of fourfold special positions (4c) and the bromine atoms to two sets of eightfold general positions (8d) in Pnam,[17] using values for the x, y, and z coordinates obtained from the last cycle of refinement in $Pna2_1$, with one exception: as required by the symmetry of the centric space group, the z coordinates of the rhenium and oxygen atoms were fixed at 0.25. From these assignments, a single cycle of least-squares refinement of all parameters was run and, from the resulting structure factors, a Fourier map was prepared. As expected, the correlation matrix no longer showed any pronounced interactions (coefficients < 0.10) and the R value dropped to 0.17. In interpreting the Fourier map, we realized from symmetry that in Pnam, the nitrogen atoms of the four $[(C_2H_5)_4N]^+$ ions must occupy the fourfold special positions (4c) and, consequently, a close inspection of the electron density along the mirror planes at $z = {}^1/_4, {}^3/_4$ was undertaken. Success was met when a peak of height 700 (using the MIFR-2 arbitrary scale[10] for which the values for the peak heights of the oxygen atoms on our Fourier maps were 825 ± 20) was located on the mirror at $z = {}^3/_4$. Now under these circumstances, two of the four ethyl groups attached to each nitrogen atom would also be expected to lie on this mirror plane, whereas the other two groups would be crystallographically related by it. Careful contouring of the Fourier map did not reveal these features. Instead, two peaks of heights 500 and 550 were found in general positions (8d), each at a distance of ~2.5 Å. from the nitrogen atom. Since from the known dimensions of the tetraethylammonium ion, the calculated distance from the nitrogen atom to each of the four terminal carbon atoms of the ethyl groups is 2.5 Å., we assigned the new peaks to these atoms. Having done so, we were then forced to conclude that, in order to preserve the plane of symmetry through the $[(C_2H_5)_4N]^+$ group in the crystal, the inner, methylene, carbon atoms had to be disordered.

To test our hypothesis, a cycle of least-squares refinement of the positional and isotropic thermal parameters of the terminal carbon atoms, along with the corresponding parameters of the oxygen, bromine, and rhenium atoms, was carried out, and another Fourier synthesis was computed. All parameters refined to reasonable values and R was reduced to 0.15. From the Fourier map, the missing, disordered carbon atoms were located, each at a distance of about 1.5 Å. from the nitrogen atom and having peak heights of 250 ± 50. Thus, the indicated disorder is such that the four methylene-bridge carbon atoms of the tetraethylammonium ion (and, incidentally, all of the hy-

---

(17) Reference 13, Vol. I.

(18) S. Geller, *Acta Cryst.*, **14**, 1026 (1961).

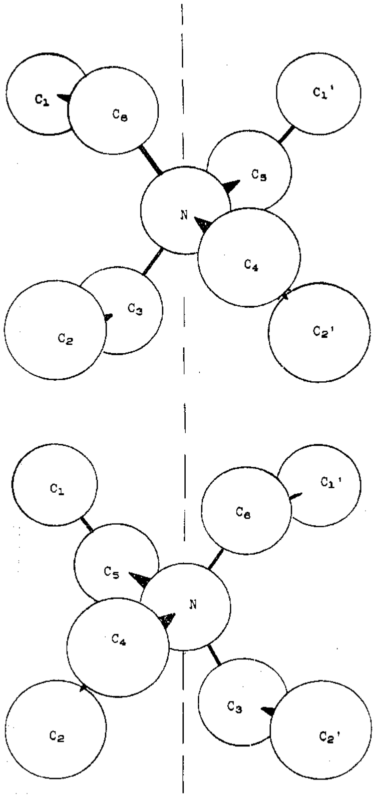

Figure 2.—Molecular structure and atom labeling scheme of the disordered tetraethylammonium ion in tetraethylammonium oxotetrabromoaquorhenate(V). The crystallographically required mirror plane is indicated by a dashed line through the nitrogen atoms. The two stereochemical orientations shown reveal the nature of the disorder.

drogen atoms bonded to *both* $-CH_2$ and $-CH_3$ types of carbon atoms) have two different spatial orientations (Figure 2). As a result, throughout the entire crystal lattice, the symmetry required by the space group Pnam is preserved.

Next, the four methylene carbon atoms were introduced in general positions (8d) of the space group and, along with the other atoms, refined by the least-squares technique. To account for the disorder mathematically, the form factor table for each new carbon atom was reduced by a factor of two in the calculation. After two cycles of isotropic refinement, the changes in the parameters of all atoms were less than half their standard deviations. The final value of R, 0.135, was calculated including all reflections in the summation except approximately ten of the strongest, having $|F_o| < |F_c|$; these were assumed to have been affected by extinction and were removed from the calculation. A difference Fourier map, based on the structure factors calculated in the last cycle of refinement, showed no peaks greater than would be expected for hydrogen atoms anywhere in the unit cell, except within 0.75 Å. of the rhenium and bromine atoms, indicating the anisotropic character of their thermal motions. In view of the fact that absorption corrections were not made, however, we did not attempt to refine anisotropically, despite the fact that the residual would probably have been lowered somewhat had we done so.

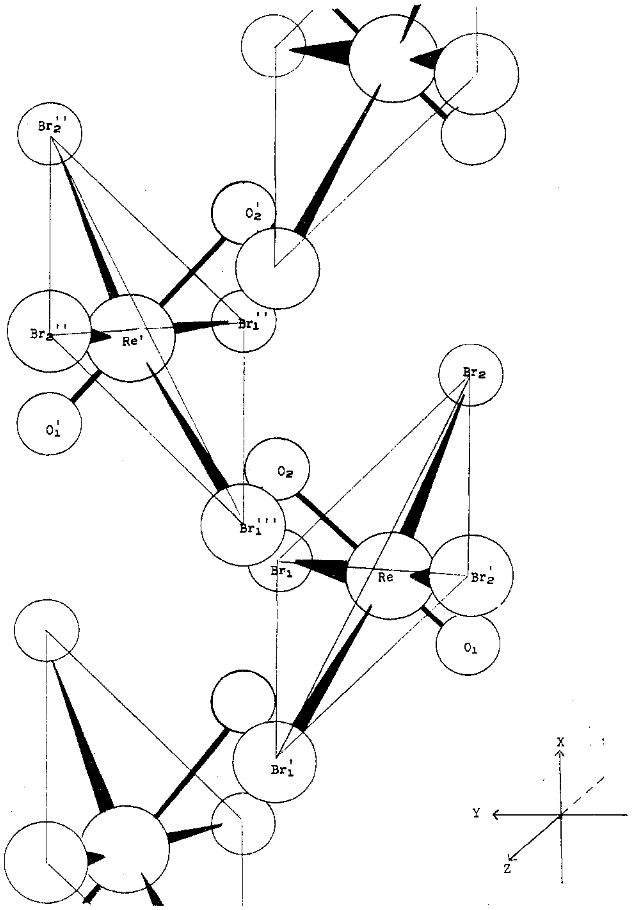

Figure 3.—Molecular structure, packing, and atom labeling scheme of the network of $[ReBr_4O(H_2O)]^-$ ions in the tetraethylammonium oxotetrabromoaquorhenate(V) lattice. Atoms actually labeled are in the same unit cell. All rhenium and oxygen atoms line on the mirror plane at $Z = {}^1/_4$. Chemical bonds are indicated by heavy lines.

The final F_c and $|F_o|$ values may be found in Table III. The atomic positional and isotropic temperature parameters for all atoms, along with their standard deviations, are given in Table IV. All important bond angles and bond lengths were calculated with the aid of MGEOM[19] and are summarized in Tables V and VI for the $[ReBr_4O(H_2O)]^-$ anion and $[(C_2H_5)_4N]^+$ cation, respectively. Also included in Table V are the closest nonbonded contact distances between neighboring $[ReBr_4O(H_2O)]^-$ units in the lattice. For a description of the numbering scheme used in the tables as well as the packing arrangement of the $[ReBr_4O(H_2O)]^-$ ions in the crystal, the reader is referred to Figures 2 and 3.

Discussion

Nature of the Oxidative Decomposition of Re_3Br_9.—We have seen that the reaction between monopositive cations and rhenium(III) bromide in concentrated aqueous HBr is extremely complex. Under mild, nonoxidative conditions, derivatives of the Re_3Br_9 trimer crystallize.[3] In a preceding paper,[4] we have shown

---

[19] J. S. Wood, "MGEOM—Molecular Geometry Program for the IBM 709/7090/7094 Computer," Massachusetts Institute of Technology, 1964.

TABLE III

LIST OF OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $[(C_2H_5)_4N][ReBr_4O(H_2O)]$

H	K	L	FOBS	FCAL
0	0	4	151.	-170.
0	1	5	52.	-70.
0	2	2	79.	-97.
0	2	4	78.	87.
0	3	1	77.	-80.
0	3	5	227.	-244.
0	4	0	244.	285.
0	4	2	191.	208.
0	4	4	400.	-497.
0	5	1	162.	-163.
0	5	3	79.	-75.
0	5	5	18.	18.
0	6	0	146.	-136.
0	6	2	208.	193.
0	6	4	231.	-218.
0	7	1	201.	186.
0	7	3	145.	-136.
0	7	5	140.	149.
0	8	0	271.	266.
0	8	4	161.	-137.
0	9	1	112.	97.
0	9	3	216.	-199.
0	9	5	162.	160.
0	10	0	266.	259.
0	10	2	179.	-164.
0	10	4	99.	93.
0	11	1	41.	-44.
0	11	3	22.	-1.
0	11	5	45.	-25.
0	12	0	147.	147.
0	12	2	86.	-75.
0	13	5	118.	-122.
1	1	2	50.	-59.
1	1	3	52.	49.
1	1	4	119.	137.
1	1	5	119.	-140.
1	2	1	40.	-46.
1	2	2	189.	274.
1	2	3	7.	-1.
1	2	4	151.	-174.
1	2	5	3.	-10.
1	3	1	21.	-29.
1	3	2	33.	-39.
1	3	3	76.	-95.
1	3	4	129.	164.
1	3	5	55.	60.
1	4	0	61.	-79.
1	4	1	29.	35.
1	4	2	121.	153.
1	4	3	95.	102.
1	4	4	161.	-197.
1	4	5	43.	-55.
1	5	0	51.	-56.
1	5	1	49.	49.
1	5	2	20.	13.
1	5	4	12.	8.
1	5	5	209.	244.
1	6	0	33.	-39.
1	6	1	17.	-14.
1	6	2	124.	-118.
1	6	3	66.	-68.
1	6	4	202.	215.
1	6	5	48.	45.
1	7	0	145.	-147.
1	7	1	103.	102.
1	7	2	32.	-30.
1	7	3	111.	-107.
1	7	4	150.	144.
1	7	5	95.	91.
1	8	0	273.	275.
1	8	1	97.	95.
1	8	2	204.	-192.
1	8	3	85.	68.
1	8	4	128.	125.
1	8	5	20.	-25.
1	9	0	23.	14.
1	9	1	210.	-203.
1	9	2	16.	-12.
1	9	3	30.	-27.
1	9	4	10.	8.
1	9	5	54.	-53.
1	10	0	102.	-99.
1	10	1	6.	-9.
1	10	2	47.	-42.
1	10	3	50.	-50.
1	10	4	148.	145.
1	10	5	40.	31.
1	11	0	77.	-81.
1	11	1	148.	-144.
1	11	2	42.	-41.
1	11	3	165.	158.
1	11	4	125.	126.
1	11	5	144.	-147.
1	12	0	70.	-69.
1	12	1	31.	32.
1	12	2	115.	114.
1	12	3	84.	83.
1	12	5	43.	-46.
2	0	1	51.	-71.
2	0	3	51.	68.
2	0	4	125.	-156.
2	1	2	17.	-14.
2	1	3	59.	-69.
2	1	4	130.	154.
2	1	5	84.	96.
2	2	0	72.	-84.
2	2	2	81.	92.
2	2	4	85.	-95.
2	2	5	199.	-222.
2	3	1	154.	196.
2	3	2	87.	94.
2	3	3	198.	-237.
2	3	4	197.	-232.
2	3	5	183.	202.
2	4	0	67.	89.
2	4	1	50.	55.
2	4	2	147.	-178.
2	4	3	12.	-14.
2	4	4	198.	234.
2	4	5	31.	34.
2	5	0	57.	-68.
2	5	1	43.	54.
2	5	2	22.	-24.
2	5	3	6.	-5.
2	5	4	76.	86.
2	5	5	25.	23.
2	6	0	153.	175.
2	6	1	175.	213.
2	6	2	156.	-176.
2	6	3	175.	207.
2	6	4	152.	172.
2	6	5	94.	-84.
2	7	0	131.	146.
2	7	1	155.	-158.
2	7	2	31.	-21.
2	7	3	122.	137.
2	7	4	60.	-63.
2	7	5	123.	-136.
2	8	0	77.	-64.
2	8	1	33.	35.
2	8	2	26.	22.
2	8	3	61.	62.
2	8	4	29.	9.
2	8	5	30.	-31.
2	9	0	44.	43.
2	9	1	132.	-125.
2	9	2	31.	-36.
2	9	3	144.	144.
2	9	4	36.	36.
2	9	5	122.	-134.
2	10	0	169.	-175.
2	10	1	22.	19.
2	10	2	156.	158.
2	10	3	137.	145.
2	10	4	144.	-140.
2	10	5	98.	-86.
2	11	0	29.	30.
2	11	1	24.	35.
2	11	2	20.	12.
2	11	3	39.	-30.
2	11	4	38.	-40.
2	11	5	44.	37.
2	12	0	99.	-88.
2	12	1	13.	18.
2	12	2	78.	77.
2	12	3	85.	92.
2	12	5	52.	-53.
3	1	0	41.	56.
3	1	1	63.	75.
3	1	2	80.	102.
3	1	4	153.	-195.
3	1	5	142.	174.
3	2	1	91.	108.
3	2	2	171.	-218.
3	2	3	39.	-45.
3	2	4	198.	238.
3	2	5	47.	57.
3	3	1	87.	-98.
3	3	2	34.	26.
3	3	3	12.	4.
3	3	4	170.	-189.
3	3	5	24.	-20.
3	4	0	150.	176.
3	4	1	10.	-19.
3	4	2	127.	-141.
3	4	3	134.	-156.
3	4	4	105.	118.
3	4	5	76.	97.
3	5	0	95.	105.
3	5	1	244.	-309.
3	5	2	60.	-63.
3	5	3	104.	111.
3	5	4	33.	38.
3	5	5	109.	-130.
3	6	0	154.	-155.
3	6	1	14.	11.
3	6	2	69.	74.
3	6	3	93.	102.
3	6	4	22.	-29.
3	6	5	75.	-72.
3	7	0	191.	226.
3	7	1	89.	-98.
3	7	2	28.	9.
3	7	3	79.	77.
3	7	4	157.	-163.
3	7	5	82.	-88.
3	8	0	127.	-127.
3	8	1	139.	-164.
3	8	2	152.	161.
3	8	3	49.	-53.
3	8	4	171.	-179.
3	8	5	25.	-2.
3	9	0	44.	-49.
3	9	1	23.	10.
3	9	2	37.	36.
3	9	3	141.	-148.
3	9	4	31.	-24.
3	9	5	119.	111.
3	10	0	114.	-105.
3	10	1	22.	14.
3	10	2	30.	29.
3	10	3	73.	73.
3	10	4	34.	21.
3	10	5	57.	-46.
3	11	0	72.	87.
3	11	1	133.	138.
3	11	2	73.	77.
3	11	3	123.	-136.
3	11	4	173.	-191.
3	11	5	121.	129.
3	12	0	109.	132.
3	12	1	17.	-23.
3	12	4	93.	98.
3	12	5	64.	82.
4	0	1	134.	137.
4	0	3	108.	-101.
4	0	4	431.	524.
4	0	5	95.	95.
4	1	0	124.	151.
4	1	1	19.	23.
4	1	2	54.	-54.
4	1	4	23.	-11.
4	1	5	125.	-141.
4	2	0	50.	57.
4	2	1	57.	-68.
4	2	2	68.	-75.
4	2	3	140.	-155.
4	2	4	71.	79.
4	2	5	75.	85.
4	3	0	8.	16.
4	3	1	230.	-299.
4	3	2	97.	-106.
4	3	3	109.	106.
4	3	4	149.	161.
4	3	5	104.	-117.
4	4	1	56.	-67.
4	4	2	115.	111.
4	4	3	71.	78.
4	4	4	108.	106.
4	4	5	75.	-77.
4	5	0	67.	62.
4	5	1	70.	75.
4	5	2	16.	-12.
4	5	3	110.	121.
4	5	4	39.	-20.
4	5	5	74.	-81.
4	6	0	175.	-197.
4	6	1	136.	-151.
4	6	2	133.	144.
4	6	3	14.	11.
4	6	4	105.	-112.
4	6	5	34.	-48.
4	7	0	112.	-122.
4	7	1	107.	111.
4	7	2	68.	70.
4	7	3	129.	-143.
4	7	3	129.	-143.
4	7	4	37.	-33.
4	7	5	125.	121.
4	8	0	145.	-168.
4	8	1	14.	-0.
4	8	2	16.	-24.
4	8	3	71.	-20.
4	8	4	149.	152.
4	8	5	13.	12.
4	9	0	42.	-58.
4	9	1	150.	153.
4	9	2	65.	61.
4	9	3	65.	-66.
4	9	4	86.	-63.
4	9	5	88.	90.
4	10	0	59.	66.
4	10	1	33.	50.
4	10	2	140.	-142.
4	10	3	117.	-101.
4	10	4	185.	185.
4	10	5	87.	81.
4	11	0	11.	7.
4	11	1	18.	-19.
4	11	2	25.	-21.
4	11	3	73.	63.
4	11	4	29.	30.
4	11	5	30.	-45.
4	12	2	64.	-76.
4	12	5	31.	47.
5	1	0	136.	140.
5	1	1	13.	-9.
5	1	2	85.	-78.
5	1	3	241.	258.
5	1	4	47.	38.
5	1	5	171.	-173.
5	2	0	87.	-95.
5	2	1	103.	-124.
5	2	2	150.	172.
5	2	3	114.	129.
5	2	4	195.	-222.
5	2	5	111.	-118.
5	3	0	17.	18.
5	3	1	95.	98.
5	3	2	49.	54.
5	3	3	19.	22.
5	3	4	94.	-99.
5	3	5	6.	5.
5	4	0	157.	-174.
5	4	1	101.	-95.
5	4	2	101.	104.
5	4	3	24.	49.
5	4	4	51.	-57.
5	4	5	47.	-61.
5	5	0	91.	-89.
5	5	1	264.	322.
5	5	2	109.	121.
5	5	3	24.	9.
5	5	4	115.	-135.
5	5	5	48.	55.
5	6	0	164.	196.
5	6	1	40.	47.
5	6	2	44.	-44.
5	6	3	35.	-28.
5	6	4	40.	-46.
5	6	5	29.	33.
5	7	0	20.	-16.
5	7	1	74.	71.
5	7	2	66.	80.
5	7	3	67.	-71.
5	7	3	67.	-71.
5	7	4	109.	-119.
5	7	5	65.	82.
5	8	0	59.	63.
5	8	1	58.	78.
5	8	2	132.	-142.
5	8	3	151.	-134.
5	8	4	190.	193.
5	8	5	121.	116.
5	9	0	60.	70.
5	9	1	50.	49.
5	9	2	59.	-55.
5	9	3	198.	205.
5	9	4	52.	46.
5	9	5	131.	-132.
5	10	0	141.	159.
5	10	1	11.	16.
5	10	2	21.	-13.
5	10	3	22.	-5.
5	10	4	73.	-85.
5	10	5	20.	11.
5	11	0	98.	114.
5	11	1	118.	-125.
5	11	2	65.	-67.
5	11	3	91.	97.
5	11	5	93.	-98.
5	12	5	32.	-50.
6	0	0	23.	7.
6	0	1	180.	-160.
6	0	2	236.	206.
6	0	3	157.	132.
6	0	4	358.	-331.
6	0	5	153.	-131.
6	1	0	11.	17.
6	1	1	18.	5.
6	1	2	109.	102.
6	1	3	167.	-160.
6	1	4	193.	-184.
6	1	5	124.	119.
6	2	0	71.	-71.
6	2	1	206.	-208.
6	2	2	56.	50.
6	2	3	207.	-204.
6	2	4	37.	-32.
6	2	5	104.	78.
6	3	0	201.	-234.
6	3	1	179.	187.
6	3	2	103.	104.
6	3	3	59.	-61.
6	3	4	16.	-11.
6	3	5	70.	80.
6	4	0	212.	244.
6	4	1	71.	84.
6	4	2	76.	-73.
6	4	3	116.	-122.
6	4	4	38.	-33.
6	4	5	98.	102.
6	5	0	10.	14.
6	5	1	25.	-30.
6	5	2	29.	40.
6	5	3	79.	-88.
6	5	4	60.	-78.
6	5	5	57.	60.
6	6	0	106.	121.
6	6	1	13.	2.
6	6	2	108.	-114.
6	6	3	224.	-273.
6	6	4	110.	111.
6	6	5	176.	191.
6	7	0	37.	31.
6	7	1	68.	-89.
6	7	2	104.	-112.
6	7	3	125.	124.
6	7	3	175.	124.
6	7	4	147.	164.
6	7	5	108.	-110.
6	8	0	73.	57.
6	8	1	42.	-44.
6	8	2	31.	32.
6	8	3	38.	-30.
6	8	4	103.	-90.
6	8	5	18.	11.
6	9	0	54.	78.
6	9	1	108.	-112.
6	9	2	86.	-84.
6	9	3	62.	62.
6	9	4	96.	81.
6	9	5	72.	-74.
6	10	0	89.	-84.
6	10	1	125.	-141.
6	10	2	109.	114.
6	10	3	40.	21.
6	10	4	114.	-128.
6	10	5	49.	-57.
6	11	5	12.	28.
6	12	2	27.	60.
7	1	0	238.	-219.
7	1	1	130.	110.
7	1	2	113.	92.
7	1	3	89.	-79.
7	1	4	0.	-11.
7	1	5	99.	94.
7	2	0	169.	141.
7	2	1	134.	127.
7	2	2	144.	-131.
7	2	3	182.	-165.
7	2	4	115.	115.
7	2	5	166.	144.
7	3	0	146.	-141.
7	3	1	0.	6.
7	3	2	73.	-61.
7	3	3	35.	36.
7	3	4	219.	193.
7	3	5	27.	-26.
7	4	0	81.	72.
7	4	1	151.	156.
7	4	2	75.	-69.
7	4	3	21.	-15.
7	4	4	72.	66.
7	4	5	63.	54.
7	5	0	103.	110.
7	5	1	75.	-80.
7	5	2	135.	-143.
7	5	3	106.	102.
7	5	4	152.	155.
7	6	0	0.	-42.
7	6	1	90.	-100.
7	6	2	48.	50.
7	6	3	10.	6.
7	6	4	83.	-56.
7	6	5	13.	-28.
7	7	0	93.	-98.
7	7	1	44.	-41.
7	7	2	86.	-100.
7	7	3	56.	73.
7	7	4	204.	229.
7	7	5	57.	-62.
7	8	0	84.	-114.
7	8	1	41.	-40.
7	8	2	108.	117.
7	8	3	196.	220.
7	8	4	113.	-112.
7	8	5	139.	-167.
7	9	0	55.	-55.
7	9	1	61.	62.
7	9	2	66.	66.
7	9	3	50.	-52.
7	9	4	74.	-79.
7	9	5	53.	64.
7	10	0	31.	-0.
7	10	1	62.	-55.
7	10	2	12.	11.
7	10	4	54.	-23.
7	10	5	16.	-4.
8	0	1	180.	146.
8	0	2	161.	-118.
8	0	3	206.	-174.
8	0	4	86.	-54.
8	0	5	191.	157.
8	1	0	31.	-26.
8	1	1	115.	-92.
8	1	2	107.	-87.
8	1	3	19.	-8.
8	1	4	204.	164.
8	1	5	38.	-31.
8	2	0	71.	57.
8	2	1	205.	187.
8	2	2	45.	-32.
8	2	3	109.	82.
8	2	4	20.	19.
8	2	5	19.	-7.
8	3	0	266.	247.
8	3	1	55.	-34.
8	3	2	161.	-133.
8	3	3	124.	111.
8	3	4	70.	53.
8	3	5	116.	-95.
8	4	0	111.	104.
8	4	1	133.	-117.
8	4	2	85.	81.
8	4	3	120.	104.
8	4	4	225.	-200.
8	4	5	105.	-102.
8	5	0	51.	-36.
8	5	1	72.	-66.
8	5	2	33.	-25.
8	5	3	39.	-28.
8	5	4	96.	68.
8	5	5	7.	5.
8	6	0	38.	-45.
8	6	1	36.	-39.
8	6	2	88.	83.
8	6	3	229.	214.
8	6	4	118.	-103.
8	6	5	174.	-161.
8	7	0	54.	-53.
8	7	1	58.	73.
8	7	2	116.	118.
8	7	3	86.	-62.
8	7	4	150.	-160.
8	7	5	69.	68.
8	8	0	106.	128.
8	8	1	24.	29.
8	8	2	30.	-18.
8	8	3	11.	1.
8	8	4	48.	-61.
8	8	5	15.	5.
8	9	0	125.	-106.
8	9	1	46.	44.
8	9	2	103.	100.
8	9	3	92.	-91.
8	9	5	67.	72.
8	10	2	79.	-75.
8	10	5	75.	93.
9	1	0	147.	121.
9	1	1	152.	-123.
9	1	2	154.	-130.
9	1	3	56.	-44.
9	1	4	157.	136.
9	1	5	25.	-18.
9	2	0	158.	-132.
9	2	1	168.	-141.
9	2	2	95.	79.
9	2	3	178.	149.
9	2	4	36.	-33.
9	2	5	157.	-141.
9	3	0	21.	-12.
9	3	1	43.	-35.
9	3	2	31.	21.
9	3	3	63.	-51.
9	3	4	28.	-27.
9	3	5	36.	30.
9	4	0	14.	-3.
9	4	1	106.	-114.
9	4	2	57.	49.
9	4	3	143.	94.
9	4	4	101.	-82.
9	4	5	132.	-94.
9	5	0	164.	-163.
9	5	1	58.	-41.
9	5	2	159.	137.
9	5	3	203.	-176.
9	5	4	146.	-115.
9	5	5	131.	111.
9	6	0	65.	-56.
9	6	1	90.	83.
9	6	2	65.	-49.
9	6	3	53.	-57.
9	6	4	135.	119.
9	6	5	61.	63.
9	7	0	53.	-39.
9	7	1	34.	32.
9	7	2	70.	58.
9	7	3	36.	-38.
9	7	4	72.	-71.
9	7	5	31.	29.
9	8	0	129.	122.
9	8	1	150.	119.
9	8	2	72.	-62.
9	8	3	111.	-139.
9	8	5	108.	128.
9	9	4	87.	93.
9	9	5	17.	10.
10	0	1	191.	-152.
10	0	2	63.	34.
10	0	3	221.	178.
10	0	4	141.	110.
10	0	5	193.	-158.
10	1	0	124.	-111.
10	1	1	87.	71.
10	1	2	89.	72.
10	1	3	74.	61.
10	1	4	57.	-42.
10	1	5	21.	-16.
10	2	0	17.	-1.
10	2	1	18.	-0.
10	2	2	18.	20.
10	2	3	194.	163.
10	2	4	42.	-37.
10	2	5	142.	-108.
10	3	0	128.	-110.
10	3	1	22.	-1.
10	3	2	182.	154.
10	3	3	127.	-105.
10	3	4	218.	-181.
10	3	5	95.	73.
10	4	0	122.	-97.
10	4	1	153.	122.
10	4	2	79.	-66.
10	4	3	101.	-86.
10	4	4	214.	176.
10	4	5	100.	100.
10	5	0	11.	-26.
10	5	1	61.	56.
10	5	2	25.	11.
10	5	3	60.	53.
10	5	4	26.	-3.
10	5	5	21.	-23.
10	6	0	44.	35.
10	6	1	179.	170.
10	6	2	53.	-42.
10	6	3	72.	-48.
10	6	4	48.	43.
10	6	5	79.	80.
10	7	0	146.	143.
10	7	1	57.	-42.
10	7	5	17.	-18.
10	8	5	34.	-27.
11	1	0	66.	-52.
11	1	1	22.	19.
11	1	2	160.	131.
11	1	3	13.	4.
11	1	4	221.	-181.
11	1	5	20.	3.
11	2	0	38.	41.
11	2	1	181.	151.
11	2	2	41.	-28.
11	2	3	151.	-126.
11	2	4	38.	17.
11	2	5	144.	130.
11	3	0	169.	140.
11	3	1	14.	-12.
11	3	2	24.	-15.
11	3	3	15.	1.
11	3	4	90.	-71.
11	3	5	21.	-3.
11	4	0	9.	1.
11	4	1	71.	63.
11	4	2	31.	-23.
11	4	3	164.	-141.
11	4	4	45.	41.
11	5	0	164.	161.
11	5	1	23.	-13.
11	5	2	141.	-131.
11	5	4	121.	109.
11	5	5	31.	-39.
11	6	2	24.	17.
11	6	5	88.	-80.
12	0	0	75.	-61.
12	0	1	194.	163.
12	0	2	17.	-9.
12	1	0	196.	159.
12	1	1	25.	12.
12	1	2	95.	-72.
12	1	4	20.	11.
12	2	0	26.	-25.
12	2	1	64.	-46.
12	2	5	119.	97.
12	3	5	21.	0.
12	4	2	19.	4.
12	4	5	112.	-108.

that atmospheric oxidation of rhenium(III), with accompanying destruction of the trirhenium cluster, can occur in air at steam bath temperature (*ca.* 90°) to form mixed complexes containing both rhenium(III) and rhenium(IV). Here, the oxidation of rhenium(III) bromide to form products containing the $[ReBr_4O]^-$, $[ReBr_4O(H_2O)]^-$, and $[ReBr_6]^{-2}$ ions has been investigated. In particular, the reactions of three different types of cations with the Re_3Br_9 trimer under oxidative conditions have been elucidated and will be discussed below.

Cesium ion precipitates the $[ReBr_4O]^-$ group to form cesium oxotetrabromorhenate(V). This compound has been characterized by the strong ReO band at 955 cm.$^{-1}$ in its infrared spectrum (Table I) and by its chemical analysis. We may conclude, therefore, that rhenium(V) is a major product of the oxidative degradation of the Re_3Br_9 trimer in 48% HBr. This result is somewhat surprising in view of the facts (1) that solutions of $KReO_4$ in hot, 48% aqueous HBr produce $K_2[ReBr_6]$ in good yields[20] and (2) that $Cs[ReBr_4O]$ itself may be reduced in hot aqueous HBr to form $Cs_2[ReBr_6]$. One possible explanation is that the formation of $Cs[ReBr_4O]$ from an ice-cold solution containing the decomposition products of the oxidation

---

[20] F. Kraus and H. Steinfeld, *Ber.*, **64**, 2552 (1931).

TABLE IV

FINAL ATOM POSITIONAL AND ISOTROPIC THERMAL PARAMETERS FOR $[(C_2H_5)_4N][ReBr_4O(H_2O)]^a$

Atom[b,c]	x/a	y/b	z/c	B
Re (4c)	0.2299 (2)	0.0953 (2)	0.250	0.0012 (400)
Br_1 (8d)	0.1433 (4)	0.2277 (4)	0.1148 (7)	1.4 (1)
Br_2 (8d)	0.3617 (5)	0.0065 (4)	0.1134 (8)	1.8 (1)
O_1 (4c)	0.119 (3)	−0.008 (3)	0.250	0.5 (8)
O_2 (4c)	0.385 (3)	0.229 (3)	0.250	0.5 (8)
N (4c)	0.260 (4)	0.119 (3)	0.750	0.003 (845)
C_1 (8d)	0.370 (6)	0.234 (6)	0.608 (9)	5.4 (19)
C_2 (8d)	0.138 (7)	0.006 (6)	0.610 (9)	5.4 (18)
C_3 (8d)	0.134 (7)	0.125 (6)	0.683 (8)	0.04 (155)
C_4 (8d)	0.262 (9)	0.007 (8)	0.692 (9)	2.0 (23)
C_5 (8d)	0.253 (7)	0.218 (7)	0.678 (9)	0.6 (17)
C_6 (8d)	0.370 (9)	0.110 (8)	0.683 (10)	1.7 (21)

[a] Intervals given are standard deviations. [b] See Figures 2 and 3 for atom labeling scheme. [c] Space group classification of atomic position, as given in ref. 17, is in parentheses beside each atom.

TABLE V

DIMENSIONS OF THE $[ReBr_4O(H_2O)]^-$ GROUP IN $[(C_2H_5)_4N][ReBr_4O(H_2O)]^{a,b}$

Bond Distance, Å.

Re–Br_1	2.51 ± 0.01
Re–Br_2	2.51 ± 0.01
Re–O_1	1.71 ± 0.04
Re–O_2	2.32 ± 0.04

Distance of the rhenium atom from the crystallographically required plane of bromine atoms = 0.32 Å.

Angles, Deg.

Br_1–Re–Br_2	89.2 ± 0.2
Br_1–Re–Br_1'	88.0 ± 0.2
Br_2–Re–Br_2'	89.1 ± 0.2
Br_1–Re–Br_2'	163.7 ± 0.2
Br_1–Re–O_1	98.4 ± 0.7
Br_2–Re–O_1	97.9 ± 0.8
Br_1–Re–O_2	83.2 ± 0.9
Br_2–Re–O_2	80.6 ± 0.9
O_1–Re–O_2	177 ± 1

Dimensions of Closest Interanionic Contacts, Å.

O_1–Br_1''	3.40 ± 0.03
Br_1''–O_2–Br_1'''	61.6 ± 0.6°

[a] Intervals given are standard deviations. [b] See Figure 3 for atom labeling scheme.

TABLE VI

DIMENSIONS OF THE $[(C_2H_5)_4N]^+$ ION IN $[(C_2H_5)_4N][ReBr_4O(H_2O)]^{a,b}$

Bond Distances, Å.

N–C_3	1.64 ± 0.11
N–C_4	1.50 ± 0.12
N–C_5	1.46 ± 0.11
N–C_6	1.50 ± 0.11
C_3–C_2 (= C_3–C_2')[c]	1.68 ± 0.12
C_4–C_2 (= C_4–C_2')[c]	1.70 ± 0.14
C_5–C_1 (= C_5–C_1')[c]	1.59 ± 0.12
C_6–C_1 (= C_6–C_1')[c]	1.74 ± 0.13

Angles, Deg.

C_3–N–C_4	109 ± 6
C_3–N–C_5	104 ± 6
C_3–N–C_6	114 ± 6
C_4–N–C_5	111 ± 6
C_4–N–C_6	102 ± 6
C_5–N–C_6	117 ± 6
N–C_3–C_2 (= N–C_3–C_2')[c]	102 ± 7
N–C_4–C_2 (= N–C_4–C_2')[c]	108 ± 7
N–C_5–C_1 (= N–C_5–C_1')[c]	114 ± 7
N–C_6–C_1 (= N–C_6–C_1')[c]	104 ± 6

[a] Intervals given are standard deviations. [b] See Figure 2 for atom labeling scheme. [c] Alternate labeling results from the molecular disorder of the ion in the crystal (*cf.* Figure 2 and text).

of the Re_3Br_9 trimer is kinetically favored over the formation of $Cs_2[ReBr_6]$, but that the latter forms as the thermodynamically stable product when $Cs[ReBr_4O]$ is heated to *ca.* 95° in concentrated aqueous HBr. In accord with this hypothesis is the fact that, when $Cs[ReBr_4O]$ was dissolved in concentrated HBr at room temperature and the resulting solution evaporated at 11 mm. over P_2O_5, essentially all of the starting material was recovered, as shown by the ReO band at 955 $cm.^{-1}$ in the infrared spectrum of the product. The faster rate of formation of $Cs[ReBr_4O]$ *vs.* $Cs_2[ReBr_6]$ might result from extensive ion-pair formation between Cs^+ and the oxygen atom of the $[ReBr_4O]^-$ ion in solution.

The second type of cation investigated was $[(C_6H_5)_4As]^+$, which produced only tetraphenylarsonium hexabromorhenate(IV) when added to a solution of rhenium(III) bromide in HBr prepared under oxidative conditions. For this cation, we consider it likely that the reaction is thermodynamically, rather than kinetically, controlled in order to account for the formation of $[(C_6H_5)_4As]_2[ReBr_6]$ as the only product. Because of its smaller charge density and greater steric requirements, the $[(C_6H_5)_4As]^+$ ion probably does not form a very strong ion pair with $[ReBr_4O]^-$ in solution as does the Cs^+ ion.

With tetraalkylammonium cations, there is close competition between the various thermodynamic and kinetic effects. Mixtures of red, yellow, and black crystals are usually obtained, but in the case of the tetraethylammonium ion, deep purple $[(C_2H_5)_4N]_2Re_4Br_{15}$ can be generated as well.[4] The reason why this latter compound forms in some instances, but tricolored mixtures form in others, is not well understood. From a limited investigation of these phenomena, we found that rapid cooling (to 0°) of the solution tended to precipitate $[(C_2H_5)_4N]_2Re_4Br_{15}$, whereas slow evaporation produced crystal mixtures.

Let us consider now the nature of the three colored products produced with the tetraethylammonium cation. Of these, the yellow compound is the easiest to discuss. From its chemical composition and from a comparison of its X-ray powder pattern with an independently prepared sample, it is clear that the hexabromorhenate(IV) anion is precipitated from the reaction mixture as the yellow tetraethylammonium salt. Next we have the black material, which is the least well-characterized. Infrared evidence (Table I) strongly suggests the occurrence of ReO groups in this compound, the bands at 875 and 935 $cm.^{-1}$ being consistent with the presence of a nonlinear ReO_2 grouping.[21] Finally, there is the red compound, $[(C_2H_5)_4N][ReBr_4O(H_2O)]$, which de-

---

(21) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 103 ff.

composes in air to form $[(C_2H_5)_4N][ReBr_2O_2]$, as shown by a weight loss experiment and by the infrared spectrum of the product (Table I). It was originally thought that the red compound contained either *cis*- or *trans*-diaquotetrabromorhenate(III) anions, with pseudo-octahedral symmetry about the metal atom.[5] In particular, the absence of an infrared band in the 900–1000 cm.$^{-1}$ range (Figure 1) was taken as strong evidence against the presence of an ReO group. As mentioned earlier, however, the short (1.71 Å.) Re–O bond distance found in the X-ray crystal structure requires that this compound be formulated as tetraethylammonium oxotetrabromoaquorhenate(V). In the light of this discovery, we re-examined its infrared spectrum and, indeed, were able to assign a band at 1005 cm.$^{-1}$ to the ReO stretching frequency. For, as depicted in Figure 1, the band which occurs at about 1000 cm.$^{-1}$ in the free $[(C_2H_5)_4N]^+$ cation has been augmented in the complex, presumably by the superposition of the ReO band. A more detailed study of the infrared spectra of this and other $[ReBr_4O]^-$-containing compounds has recently been undertaken and will be published shortly.[22]

Crystal Structure of $[(C_2H_5)_4N][ReBr_4O(H_2O)]$.— The crystal structure of tetraethylammonium oxotetrabromoaquorhenate(V) is composed of monomeric $[ReBr_4O(H_2O)]^-$ units and $[(C_2H_5)_4N]^+$ ions. Figure 3 illustrates part of the infinite network of anions in the lattice, symmetric about the mirror plane at $z = {}^1/_4$ (for $0 < y < {}^1/_2$) and extending along the x axis in both directions. A similar network of anions (not shown in the figure) extends in the x direction along the mirror plane at $z = {}^3/_4$ (for ${}^1/_2 < y < 1$). The tetraethylammonium cations form a complementary network throughout the crystal, being symmetrically disposed about the mirror planes at $z = {}^1/_4$ (for ${}^1/_2 < y < 1$) and ${}^3/_4$ (for $0 < y < {}^1/_2$). As a result, the unit cell volume is rather effectively filled, and no large empty spaces remain in the lattice.

Despite the relative positioning of anions in the crystal (Figure 3), a calculation of closest interanionic contact distances (Table V) revealed that no appreciable chemical interaction between them exists. Thus, the nearest nonbonded approach occurs between the oxygen (O_2) and bromine (Br_1'' and Br_1''') atoms of two neighboring anions at a distance of 3.40 Å., which is in good agreement with the value to be expected from taking the sum of the van der Waals radii for these two atoms (3.35 Å.).[23a]

Although the crystallographically required point symmetry of the $[ReBr_4O(H_2O)]^-$ ion is only m or C_s, an examination of Table V will reveal that its virtual point symmetry is 4mm, or C_{4v}. A noteworthy feature of this anion is that, instead of the rhenium atom being coplanar with the surrounding bromine atoms, it lies 0.32 Å. above their plane, being 2.51 Å. away from each. This distortion is no doubt related to the rhenium–(oxo)-oxygen bond distance of 1.71 Å., which is rather short compared to the value of 1.80 Å. found[24] in other rhenium oxo complexes Furthermore, the value of 2.32 Å. for the rhenium–(aquo)-oxygen bond distance is rather long for coordinated water[25] and suggests that this bond is a rather weak one. Perhaps the best way of describing the complex, then, would be to consider the square-pyramidal ($ReBr_4O$) grouping as the basic structural unit with another, weakly coordinated ligand (H_2O) attached to its base. Alternatively, one could call the complex a distorted octahedron, but for reasons to be discussed in a later paper[22] this latter description is less satisfactory.

The molecular disorder of the tetraethylammonium ion in the crystal structure of $[(C_2H_5)_4N][ReBr_4O(H_2O)]$, as manifest in Figure 2, is of considerable interest. In a qualitative sense, we may think of the disorder as a means of reducing the large negative entropy contribution to the free energy of crystallization which would occur if, in the crystal, the ion actually were restricted to the full C_s point symmetry required by the space group. More explicitly, by removing the restriction that $[(C_2H_5)_4N]^+$ possess a plane of symmetry, the disorder increases the number of degrees of freedom of the ion in the crystal and, consequently, the entropy of crystallization. Since $\Delta F = \Delta H - T\Delta S$, the free energy of crystallization then increases, favoring the precipitation of complex.

The actual dimensions of the $[(C_2H_5)_4N]^+$ ion are in good agreement with the values to be expected. From Table VI we find the average carbon–nitrogen and carbon–carbon bond distances to be 1.52 ± 0.11 and 1.68 ± 0.13 Å., respectively, comparable within the error limits to the values of 1.47 and 1.54 Å. which may be calculated from the covalent radii of the atoms.[23b] Similarly, the bond angles range from a low value of 102° to a high one of 117° with a mean value of 108°, which is near the expected tetrahedral bond angle.

The standard deviations in the bond angles and bond lengths of the atoms comprising the tetraethylammonium ion are quite large (Table V). This is not unreasonable, however, in view of their relatively small contribution to the scattering power of the crystal.

Several comments are in order concerning the final values for the isotropic temperature factors. From the large standard deviations for the light atom temperature factors, we may conclude that they are of limited significance. More important is the fact that, since no corrections for absorption were made, the temperature factors, which have a mathematical form similar to that of the transmission coefficient, undoubtedly refined to adjust for uncorrected absorption. Thus the absolute values of B reported in Table IV are probably meaningless. Relative to each other, however, there may be some physical significance to the

---

[22] F. A. Cotton and S. J. Lippard, to be published.

[23] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y. (1960): (a) Table 7-20, p. 260; (b) Table 7-2, p. 224.

[24] L. E. Sutton, Ed., "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958, p. M89.

[25] A. F. Wells, "Structural Inorganic Chemistry," 3rd Ed., Clarendon Press, Oxford, 1962, pp. 588–593.

temperature factors. For example, the terminal carbon atoms of the ethyl groups (C_1 and C_2) have B values of about 5.4, whereas the methylene bridging carbon atoms, whose thermal motions are more restricted, have smaller values of B ($\sim$0–2). Similar trends may be noted among the atoms comprising the $[ReBr_4O(H_2O)]^-$ ion.

Acknowledgments.—We wish to thank Professor D. P. Shoemaker for allowing us to use his XRD-5 diffractometer and D. C. Richardson for obtaining and reading the powder photograph of $Cs_2[ReBr_6]$. We also thank the M.I.T. Computation Center for access to the I.B.M. 7094 computer, and Dr. John Wood for helpful discussions.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PURDUE UNIVERSITY, WEST LAFAYETTE, INDIANA

The Infrared and Raman Spectra of a Triphenylphosphine Derivative of $Ni(CO)_4$[1]

BY WALTER F. EDGELL AND MICHAEL P. DUNKLE

Received February 1, 1965

The infrared and Raman spectra of $Ni(CO)_3P(C_6H_5)_3$ and $P(C_6H_5)_3$ in cyclohexane were obtained for the identification of the modes of vibration localized in the $PNi(CO)_3$ group of $Ni(CO)_3P(C_6H_5)_3$. The Raman spectra were obtained by means of an electrodeless mercury arc powered by high-frequency radiation. The principal Raman exciting line was the 4358 Å. Hg line. The spectra are interpreted in terms of C_{3v} symmetry for the $PNi(CO)_3$ group and frequencies are assigned to the fundamentals. The nature of the bonding is discussed from a molecular orbital point of view and compared with that in $Ni(CO)_4$. The C–O stretching frequencies permit one to estimate the π^*_{CO} participation index as 0.28 compared with a PI value 0.19 for a CO in $Ni(CO)_4$. Thus, there is an increase of about 0.5 electron in the π^*_{CO} orbitals of the $Ni(CO)_3$ moiety on passing from $Ni(CO)_4$ to $Ni(CO)_3P(C_6H_5)_3$, much of which results from a substantial reduction in the charge back-transferred into the π acceptor orbitals of the $P(C_6H_5)_3$ ligand from the value for CO in $Ni(CO)_4$.

Introduction

Bonding in metal carbonyls is currently of interest. A molecular orbital description has been used in this laboratory to interpret the vibrational spectra of a number of metal carbonyls.[2–5] An important factor in this description is the extent of the presence of the carbon monoxide π^* orbitals in the electron-filled molecular orbitals of the metal carbonyl moiety or species. The π^* participation increases substantially in the isoelectronic series—$Ni(CO)_4$, $Co(CO)_4^-$, $Fe(CO)_4^{2-}$—as the atomic number of the metal atom decreases. A consideration of the Hartree–Fock terms in the molecular orbital secular equation suggests that this will also happen in a given metal carbonyl moiety as negative charge on it is increased.

The purpose of this work was to study the complete infrared and Raman spectra of a metal carbonyl derivative in which a basic ligand is present to donate charge to the metal carbonyl group and to apply these spectra to a consideration of the bonding. A phosphine derivative, mono(triphenylphosphine)tricarbonylnickel, was chosen for this study. The primary interest lies in the nature of the bonding and the vibrations localized in the $PNi(CO)_3$ group.

The interest in substituted metal carbonyls is shown by several recent studies.[6–12] For the most part, the spectroscopic studies have been restricted to the C–O stretching vibrations, and most of the fundamental vibrations have been unobserved. While this study was in progress Bouquet and Bigorgne[11] reported a rather complete Raman spectrum of a nickel carbonyl–arsine derivative and interpreted their results in terms of valence bond theory.

Experimental

Chemicals.—Nickel tetracarbonyl (International Nickel), diethyl ether (Mallinckrodt, anhydrous), and nitrogen (Linde, high purity) were used as received. Triphenylphosphine (Eastman, White Label) was sublimed. Cyclohexane (Matheson, reagent grade) was distilled under nitrogen from lithium aluminum hydride.

Preparation of Mono(triphenylphosphine)tricarbonylnickel, $Ni(CO)_3P(C_6H_5)_3$.—The compound was prepared by a modification of the procedure given by Reppe and Schweckendiek.[13] Attention should be directed to the extreme toxicity of $Ni(CO)_4$, and the following reaction should be carried out in an efficient

---

[1] Based upon the Ph.D. Thesis of M. P. Dunkle, Purdue University, Jan. 1964.

[2] W. F. Edgell, Abstracts, 134th National Meeting of the American Chemical Society, Sept. 1958; various papers presented before American Chemical Society local sections, 1958–1960; Abstracts, 139th National Meeting of the American Chemical Society, March 1961.

[3] W. F. Edgell, J. Huff, J. Thomas, H. Lehman, C. Angell, and G. Asato, *J. Am. Chem. Soc.*, **82**, 1254 (1960).

[4] W. F. Edgell, W. E. Wilson, and R. Summitt, *Spectrochim. Acta*, **19**, 863 (1963).

[5] Theses, Purdue University. J. R. Huff, M.S. (1956); Ph.D. (1962); R. Summitt, Ph.D. (1961); J. J. Rosaz, M.S. (1962); J. P. Thomas, Ph.D. (1962).

[6] M. Bigorgne and A. Zelwer, *Bull. soc. chim. France*, 1986 (1960).

[7] L. S. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.*, **81**, 4200 (1959).

[8] J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

[9] A. F. Clifford and A. K. Mukerjee, *Inorg. Chem.*, **2**, 151 (1963).

[10] L. S. Meriwether and J. R. Leto, *J. Am. Chem. Soc.*, **83**, 3192 (1961).

[11] G. Bouquet and M. Bigorgne, *Bull. soc. chim. France*, 433 (1962).

[12] F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

[13] W. Reppe and W. J. Schweckendiek, *Ann.*, **560**, 104 (1948).