Solvent interactions and/or Jahn–Teller distortions would be expected to lift the orbital degeneracies of these configurations and reduce the orbital contributions to the *g* values. It should be pointed out that these configurations would be expected to lead to extremely short spin-lattice relaxation times *if* the e* orbitals were made up of a large contribution from metal d-orbitals. However, since the paramagnetic resonance results indicate that if these configurations are correct, these orbitals have very little admixture of metal orbitals, the situation might be analogous to the effect of orbital degeneracy in the benzene[20] and cyclooctatetraene[21] negative ions. In these cases the spin-lattice relaxation is only slightly enhanced in $C_6H_6^{\dot{-}}$ and not significantly in $C_8H_8^{\dot{-}}$. The principal objection to the $(e^*)^{1,3}$ configurations is that the monoanions are diamagnetic rather than having $S = 1$. However, if the e* orbitals are strongly delocalized on the ligands, electron repulsion terms may be relatively unimportant. Consequently, lower symmetry electrostatic fields from solvent interactions might remove the orbital degeneracy of e* sufficiently to yield a singlet ground state for the monoanions.

Finally, we have examined the e.p.r. spectrum of tris(dipyridyl)vanadium, $[V(dipy)_3]$.[13] This complex is known to have trigonal symmetry.[22] Its *g* value has been measured previously.[23] Tris(dipyridyl) complexes are generally considered to contain the metal in its lowest formal valence state consistent with the total charge on the complex; in this case the metal has been considered as V(0) ($d^5$).[13,14] Orgel[7] has discussed the electronic configurations of certain $[M(dipy)_3]^z$ complexes and has suggested the $(e_a{}^*)^4$ configuration (in our notation[2]) for $[Ti(dipy)_3]$. The $(e_a{}^*)^4(a_1{}^*)^1$ configuration for $[V(dipy)_3]$ is unlikely by the arguments already given.[2] The e.p.r. results for this complex are quite similar to those for the other vanadium complexes studied. We infer that the odd electron in $[V(dipy)_3]$ is likewise strongly delocalized on the ligand and suggest that the electronic structure may be analogous to that for $[VS_6C_6(C_6H_5)_6]$.

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# The Preparation and Characterization of Compounds Containing both Hexabromorhenate(IV) and the Trirhenium Nonabromide Group[1]

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From solutions of rhenium(III) bromide in concentrated aqueous HBr, compounds with the general formula $M_2Re_4Br_{15}$ (M = quinolinium, pyridinium, or tetraethylammonium ion) have been isolated. Evidently there is oxidation of some Re(III) to Re(IV), and, by using equimolar quantities of $Re_3Br_9$ and $[ReBr_6]^{2-}$, the quinolinium compound can be obtained more directly. A single crystal X-ray diffraction investigation shows the presence of $Re_3Br_3$ groups and $ReBr_6$ groups in the quinolinium compound. The visible spectra of the $M_2Re_4Br_{15}$ compounds indicate that $Re_3Br_9$ and $[ReBr_6]^{2-}$ are present. From the X-ray work, the dimensions of the $Re_3Br_9$ group have been established and it is clear that this group is structurally homologous to the $Re_3Cl_9$ group which is known to occur in numerous compounds derived directly from rhenium(III) chloride and in rhenium(III) chloride itself.

## Introduction

Recent studies in this[3–7] and other[8,9] laboratories have shown that compounds derived from the chloride and bromide of rhenium(III) have remarkable chemical and structural properties. The chloro compounds have been most extensively characterized, but the existence of the diverse species $Re_3Br_9L_3$, $Re_2Br_8{}^{2-}$, $ReBr_4{}^-$, and $[ReBr_4(H_2O)_2]^-$ has been briefly reported.[7,9a]

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[1] Supported by the U. S. Atomic Energy Commission.

[2] National Science Foundation Predoctoral Fellow (1962–present); Woodrow Wilson Honorary Fellow (1962–1963).

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[9a] NOTE ADDED IN PROOF.—In a preliminary communication [F. A. Cotton and S. J. Lippard, *J. Am. Chem. Soc.*, **86**, 4497 (1964)] the preparation of a number of derivatives of $Re_3Br_9$ has been described and spectroscopic evidence presented to justify their formulation as $Re_3Br_9$ derivatives. In another preliminary communication [J. E. Fergusson and B. R. Robinson, *Proc. Chem. Soc.*, 189 (1964)] the isolation of compounds which probably contain $[Re_3Br_{10}]^-$ and $[Re_3Br_{10}py_2]^-$ ions has been reported.

In this paper, we describe the preparation and characterization, principally by a single-crystal X-ray diffraction study, of a compound with the remarkable formula $(QnH)_2Re_4Br_{15}$, where QnH represents the quinolinium ion, $C_9H_7NH^+$, as well as analogous compounds containing pyridinium and tetraethylammonium ions. It is shown that these compounds contain $Re_3Br_9$ groups, which have the same sort of $Re_3$ cluster (Re–Re $\sim$ 2.47 Å.) as that previously found[3,5,6,8,9] in various rhenium(III) chloride derivatives and in $Re_3Br_9[(C_2H_5)_2C_6H_5P]_3$,[6] together with the well-known $[ReBr_6]^{2-}$ ion. Thus, the formulas of these substances might be more informatively written as $M_2[Re_3Br_9][ReBr_6]$, where M represents $C_9H_7NH^+$, $C_5H_5NH^+$, or $[(C_2H_5)_4N]^+$.

## Experimental

**Preparation of Compounds.**—The preparation of the $M_2Re_4Br_{15}$ compounds directly from rhenium(III) bromide poses certain difficulties. Since these compounds consist of both $Re_3Br_9$ units which contain Re(III), and $[ReBr_6]^{2-}$ ions which contain Re(IV), partial oxidation of the rhenium(III) bromide must occur. On the other hand, if oxidation does not occur, or occurs only to a slight extent, compounds such as $(QnH)_2Re_3Br_{11}$ precipitate from the reaction mixtures. Most of our study of preparative procedures has so far been carried out with the quinolinium compounds, but the preparative problem is being investigated further, with the intent of defining more precisely than is now possible the conditions for the deliberate preparation of the $M_2Re_3Br_{11}$ and $M_2Re_4Br_{15}$ compounds individually. We have found a reproducible method for obtaining $(QnH)_2Re_4Br_{15}$, however.

**$(QnH)_2Re_4Br_{15}$.**—Equimolar amounts (1.2 mmoles) of resublimed rhenium(III) bromide (taken to be $Re_3Br_9$) and $K_2ReBr_6$ were added to 150 ml. of 48% aqueous HBr on a steam bath and the mixture was allowed to stand overnight. The beaker was cooled and a small quantity of undissolved solid was removed by filtration. One ml. of redistilled quinoline was added with stirring to the filtrate, whereupon a golden yellow, crystalline solid (presumably $(QnH)_2ReBr_6$) immediately precipitated. After an hour of continued stirring, however, the yellow solid had entirely disappeared and a deep purple powder had begun to deposit slowly. After another hour, the purple solid was collected by filtration and dried under vacuum; yield 0.25 g. An X-ray powder photograph showed it to be identical with the $(QnH)_2Re_4Br_{15}$ which had previously been obtained (see below). While the $(QnH)_2Re_4Br_{15}$ made in this way is sufficiently crystalline to give rather grainy lines in the powder photograph, no crystals large enough for single crystal X-ray work have been obtained by this method.

**$(QnH)_2Re_3Br_{11}$ or $(QnH)_2Re_4Br_{15}$ from Rhenium(III) Bromide.**—To about 100 ml. of a saturated solution of rhenium(III) bromide in 48% aqueous HBr was added 1 ml. of redistilled quinoline, dropwise over a period of 15–20 min. at room temperature. In all cases save one, a red-brown microcrystalline solid began to form within a few minutes to 0.5 hr. This solid was separated by filtration, washed with several 2-ml. portions of cold 48% aqueous HBr, and dried under vacuum over $P_2O_5$; yield $\sim$0.3 g.

*Anal.* Calcd. for $C_{18}H_{16}N_2Re_3Br_{11}$: C, 12.71; H, 0.94; N, 1.65; Br, 51.77. Found: C, 12.7; H, 1.2; N, 1.77; Br, 52.4.

In one instance, the red-brown solid did not separate quickly and the beaker was left to stand for alternate half-day periods at 25° and on the steam bath, with free access of air. After several days a precipitate consisting of a few large yellow crystals (presumably $(QnH)_2ReBr_6$) and a much larger quantity of deep purple platelets had formed. This precipitate was separated by filtration and dried under vacuum over Drierite. The yellow crystals were easily removed manually, leaving 0.13 g. of the deep purple platelets.

*Anal.* Calcd. for $C_{18}H_{16}N_2Re_4Br_{15}$: C, 9.61; H, 0.72; N, 1.26. Found: C, 9.99; H, 1.1; N, 1.32.

It was from this material that the crystals used in the single crystal X-ray investigation were selected and it was with a powder pattern obtained on a ground sample of this material that the powder pattern of the $(QnH)_2Re_4Br_{15}$ obtained from $Re_3Br_9$ and $[ReBr_6]^{2-}$ in equimolar proportions was compared to identify the latter substance.

**Pyridinium and Tetraethylammonium Compounds of the $M_2Re_4Br_{15}$ Type.**—To a saturated solution of rhenium(III) bromide in 48% aqueous HBr was added a large excess of redistilled pyridine or tetraethylammonium bromide. After several hours of heating on a steam bath, the solution was cooled to 0° and the purple-black precipitate which had formed was separated by filtration, washed with a small quantity of cold 48% HBr, and dried under vacuum. The products were fine powders.

*Anal.* Calcd. for $C_{16}H_{32}N_2Re_4Br_{15}$: C, 8.80; H, 1.81; N, 1.27. Found: C, 8.76; H, 1.96; N, 1.15. Calcd. for $C_{10}H_{12}N_2Re_4Br_{15}$: C, 5.70; H, 0.56; N, 1.33. Found: C, 5.71; H, 0.89; N, 1.35.

**Visible and Ultraviolet Spectra.**—These were recorded either with a Beckman or a Cary Model 14 recording spectrophotometer using samples mulled in Nujol or dissolved in an appropriate solvent.

**Single Crystal X-Ray Work.**—Most of the crystals of $(QnH)_2Re_4Br_{15}$ were very thin plates, about 0.008 mm. thick; however, a platelet of dimensions 0.175 × 0.060 × 0.045 mm. was isolated and mounted on the end of a glass fiber with its *a* axis perpendicular to the X-ray beam. This crystal was used in the subsequent intensity measurements.

For the determination of the space group and lattice parameters, other crystals mounted along the *a* and *b* axes were examined using both the Weissenberg and precession cameras. A copper target was used in all the work reported here. Precision lattice parameters were obtained from measurements of the separation of the $K\alpha_1$–$K\alpha_2$ doublet for thirty reflections on zero level Weissenberg photographs according to the method of Main and Woolfson.[10] A least-squares program for the M.I.T. 7094 computer was written to analyze the data. The density was measured pycnometrically, both in bromoform and in *m*-xylene.

Intensity data were estimated visually from Weissenberg photographs for over 700 independent reflections. Levels $0kl$–$5kl$ were read. Intensity data were not taken for a mounting along the other axes because a suitable crystal could not be obtained. A multiple film technique was employed and the spots were compared to a scale prepared by timed exposures of one reflection. Approximately 100 reflections not systematically absent were recorded as zero. These were assigned one-half the value of the lowest visible intensity in later calculations.

Lorentz-polarization corrections were computed on the I.B.M. 7094 by means of the program DFSET-4.[11] In view of the large linear absorption coefficient ($\mu$ = 405 cm.$^{-1}$), it seemed advisable to correct for absorption. The crystal was assumed to be a square prism of dimensions 0.175 × 0.053 × 0.053 mm. (*vide supra*). To perform this calculation as well as to correct the raw data for LP effects, the DTRDB-GNABS data processing programs for the 7094 were used.[11] Both $|F_o|^2$ and $F_o|$ were generated in this manner.

In the subsequent treatment of the data, structure factor calculations and least-squares refinement cycles were carried out using the full-matrix program of Prewitt.[12] Equal weights were used. Scattering factors for rhenium were those of Thomas and Umeda[13] for Re(III), modified for anomalous dispersion by adding $-5.0$ electrons according to Templeton.[14] Atomic scattering factors for bromine were taken from the International

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(10) P. Main and M. M. Woolfson, *Acta Cryst.*, **16**, 731 (1963).

(11) The programs DFSET-4 and DTRDB-GNABS were kindly made available to us by M. J. Buerger's research group at M.I.T.

(12) C. Prewitt, M.I.T. (1962); SFLSQ-3, Full Matrix Least Squares Crystallographic Refinement Program for the I.B.M. 709/7090 Computer.

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

(14) D. H. Templeton in "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, England, 1962, Vol. III, p. 215.

Tables.[15] Carbon and nitrogen atoms were assigned identical form factors[16] based on atomic $Z = 6$ for $\sin \theta/\lambda = 0.0$, because it was impossible to identify unambiguously the nitrogen of the quinoline ring system on our Fourier maps. All Fourier syntheses were computed by ERFR-2.[17]

## Determination of Structure

$(QnH)_2Re_4Br_{15}$ crystallizes in the orthorhombic system with unit cell dimensions $a = 9.07 \pm 0.02$ Å., $b = 28.42 \pm 0.02$ Å., $c = 15.61 \pm 0.02$ Å. From the measured density ($\rho = 3.6 \pm 0.2$ g. cm.$^{-3}$), the number of formula weights per unit cell is 4 (calcd. $\rho = 3.5$ g. cm.$^{-3}$). Precession photographs for $hk0$, $hk1$, $hk2$, and $h0l$, together with Weissenberg photographs of $0kl$, $1kl$, and $2kl$, revealed the following systematic absences: $hkl$, for $h + k \neq n$; $h0l$, for $l \neq 2n$. These are consistent with any of three space groups,[18] Cmc$2_1$ (No. 36), C2cm (No. 40), or Cmcm (No. 63).

With 16 rhenium atoms and 60 bromine atoms in the unit cell, the three-dimensional Patterson function was somewhat formidable. Although the space group C2cm could be quickly ruled out by the vector set symmetry,[19] an unambiguous choice between the remaining two space groups proved to be impossible at this stage. If the acentric space group were the correct one, however, fortuitous positioning of several crystallographically independent rhenium atoms and bromine atoms at the same value of the $z$ coordinate would be required to fit any reasonable trial structure to the Patterson synthesis. Therefore, we choose the centric space group Cmcm, where all such $z$ coordinates are required to be the same. The successful refinement of the structure appears to justify our choice of space group.

Assuming the space group to be Cmcm, and with proper regard to packing and interatomic distances, we were able to arrive at a trial structure which accounted for many of the largest peaks. Of the 16 rhenium atoms, 8 were placed in 8-fold special positions: 8(g) with $x = 0.139$, $y = 0.210$; and 8 were placed in two sets of 4-fold special positions: 4(c) with $y = 0.133$ and $y = 0.899$. At this point, a molecular model was constructed which revealed a rather unusual structure. There were sets of three rhenium atoms forming equilateral triangles, a unit well known to us from previous investigations of Re–Cl systems.[3,5,6,8,9] In addition, isolated rhenium atoms were also present and the unit cell was thus found to consist of four trimers and four monomers for a total of 16 rhenium atoms.

Although it appeared that most of the remaining, heretofore unexplained, Patterson peaks would have readily been accounted for by the placement of bromine atoms in the obvious positions around the monomers and trimers, a structure factor calculation and Fourier synthesis were computed at once with signs based on the trial positions for the rhenium atoms only.

From the Fourier map, six bromine atoms were found to occupy octahedral apices about the isolated rhenium atom and eight (six axial and two bridging) about the rhenium trimer. In addition, a peak of slightly lower electron density, corresponding to a ninth bromine atom, was observed in the third bridging position of the trimer. However, this was omitted from the next structure factor calculation in view of the fact that its presence would necessarily require us to revise the molecular formula we were then assuming, *viz.*, $(QnH)Re_2Br_7$, as well as the valence state of one-fourth of the rhenium atoms. We had not, at this stage, recognized the true formula of the compound.

Two cycles of least-squares refinement of scale factors and atomic positional and isotropic thermal parameters for the Re and Br atoms brought the conventional $R$ (defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$) to 0.271. A difference Fourier was then computed and it revealed that the third bridging bromine, which had been ignored, had sharpened considerably and was evidently real. Thus, the molecular formula had to be revised to $(QnH)_2Re_4Br_{15}$.

Two more cycles of isotropic refinement, with signs based on all heavy atoms, dropped the residual to 0.22. Then, a second difference map was computed and the atoms of the quinolinium ion were located on the mirror plane at $x = 0$.

After the introduction of the light atoms into the structure and the correction of several errors in reading and processing the data, the residual fell to 0.18. Three more cycles in which scale factors, all atomic positional and isotropic thermal parameters, were refined reduced $R$ to 0.15. A difference Fourier map showed no anomalies.

The final $F_c$ values together with the $|F_o|$ values are given in Table I. The atomic positional parameters and isotropic temperature parameters, along with the standard deviations ($\sigma$) as computed in the last cycle of least-squares refinement, are given in Table II.

## Discussion

**Crystal Structure of $(QnH)_2Re_4Br_{15}$.**—The crystal structure reveals the presence of three chemical species, *viz.*, quinolinium ions, $Re_3Br_9$ groups, and $ReBr_6$ groups. For the quinolinium ions, the uncertainties in atomic coordinates are, not surprisingly, quite large, and it is also impossible to identify the nitrogen atom. Thus, in Table II all ten nonhydrogen atoms of the quinolinium ion have been labeled as carbon atoms. The structure and orientation of the quinolinium ion will be discussed later after the more important $Re_3Br_9$ and $ReBr_6$ groups have been considered.

**The $ReBr_6$ Group.**—The Re atom of this group lies at the intersection of two crystallographic mirror planes, one passing through $Br_{m3}$ and $Br'_{m3}$ and bisecting the $Br_{m1}$–$Re_m$–$Br'_{m1}$ and $Br_{m2}$–$Re_m$–$Br'_{m2}$ angles, the other containing the atoms $Br_{m1}$, $Br_{m1}$, $Br_{m2}$, $Br'_{m2}$, and $Re_m$. Thus there are only three independent Re–Br distances and only four independent Br–Re–Br angles. These are recorded in Table III and the numbering of the atoms is shown in Figure 1.

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(15) Reference 14, Vol. III, p. 220.

(16) Reference 14, Vol. III, p. 218.

(17) W. B. Sly, D. P. Shoemaker, and J. H. Van den Hende, ERFR-2, I.B.M. 709-7090 Fourier Program, 1962.

(18) Reference 14, Vol. I.

(19) M. S. Buerger, "Vector Space and its Applications in Crystal Structure Investigation," John Wiley and Sons, Inc., New York, N. Y., 1959, Chapter 9.

Table I: Observed and Calculated Structure Factors

| H | K | L | FOBS | FCAL |
|---|---|---|---|---|
| 0 | 6 | 0 | 96.82 | -96.63 |
| 0 | 8 | 0 | 118.14 | 115.01 |
| 0 | 10 | 0 | 147.31 | 143.14 |
| 0 | 12 | 0 | 323.26 | -304.34 |
| 0 | 14 | 0 | 77.42 | 83.74 |
| 0 | 16 | 0 | 159.57 | -157.43 |
| 0 | 18 | 0 | 132.10 | 142.08 |
| 0 | 20 | 0 | 11.63 | -7.57 |
| 0 | 24 | 0 | 51.23 | 57.58 |
| 0 | 4 | 1 | 225.38 | 243.73 |
| 0 | 6 | 1 | 52.55 | -52.98 |
| 0 | 8 | 1 | 85.36 | 88.84 |
| 0 | 10 | 1 | 222.85 | -225.96 |
| 0 | 12 | 1 | 211.18 | 193.46 |
| 0 | 14 | 1 | 158.23 | 139.36 |
| 0 | 16 | 1 | 214.83 | -213.81 |
| 0 | 18 | 1 | 57.66 | -73.78 |
| 0 | 20 | 1 | 5.27 | 5.66 |
| 0 | 22 | 1 | 105.52 | 113.30 |
| 0 | 24 | 1 | 43.69 | -62.73 |
| 0 | 4 | 2 | 159.97 | 161.03 |
| 0 | 6 | 2 | 32.90 | 23.99 |
| 0 | 8 | 2 | 77.20 | -81.63 |
| 0 | 10 | 2 | 152.14 | -140.96 |
| 0 | 12 | 2 | 181.54 | 170.51 |
| 0 | 14 | 2 | 68.21 | -57.58 |
| 0 | 16 | 2 | 56.36 | 55.97 |
| 0 | 18 | 2 | 13.83 | 19.00 |
| 0 | 20 | 2 | 71.25 | -75.46 |
| 0 | 22 | 2 | 5.55 | 4.54 |
| 0 | 24 | 2 | 26.59 | -29.85 |
| 0 | 2 | 3 | 2.70 | -4.16 |
| 0 | 6 | 3 | 38.74 | 50.32 |
| 0 | 8 | 3 | 251.52 | 260.69 |
| 0 | 10 | 3 | 40.55 | -30.68 |
| 0 | 12 | 3 | 147.23 | -126.19 |
| 0 | 14 | 3 | 134.19 | -126.01 |
| 0 | 16 | 3 | 185.29 | 187.48 |
| 0 | 18 | 3 | 5.27 | -2.44 |
| 0 | 20 | 3 | 71.71 | -77.48 |
| 0 | 22 | 3 | 64.41 | -76.40 |
| 0 | 24 | 3 | 28.18 | 33.02 |
| 0 | 8 | 4 | 97.38 | 99.38 |
| 0 | 10 | 4 | 189.26 | 173.03 |
| 0 | 12 | 4 | 126.71 | -120.44 |
| 0 | 14 | 4 | 96.00 | 110.69 |
| 0 | 16 | 4 | 5.29 | 8.42 |
| 0 | 18 | 4 | 78.10 | -89.85 |
| 0 | 20 | 4 | 73.02 | 81.81 |
| 0 | 22 | 4 | 18.27 | -6.71 |
| 0 | 24 | 4 | 20.25 | -17.49 |
| 0 | 4 | 5 | 178.80 | 168.17 |
| 0 | 6 | 5 | 100.00 | -104.52 |
| 0 | 8 | 5 | 122.11 | -127.63 |
| 0 | 10 | 5 | 102.44 | -102.65 |
| 0 | 12 | 5 | 165.88 | 159.57 |
| 0 | 14 | 5 | 106.43 | 94.05 |
| 0 | 16 | 5 | 115.19 | -114.04 |
| 0 | 18 | 5 | 13.94 | 1.41 |
| 0 | 20 | 5 | 20.55 | 19.59 |
| 0 | 22 | 5 | 111.10 | 123.60 |
| 0 | 4 | 6 | 101.30 | 112.56 |
| 0 | 8 | 6 | 144.48 | -139.87 |
| 0 | 10 | 6 | 169.57 | -194.46 |
| 0 | 12 | 6 | 235.13 | 231.11 |
| 0 | 14 | 6 | 123.48 | -110.47 |
| 0 | 16 | 6 | 66.41 | 69.49 |
| 0 | 18 | 6 | 53.41 | -61.23 |
| 0 | 20 | 6 | 6.83 | 3.97 |
| 0 | 22 | 6 | 5.89 | 1.32 |
| 0 | 2 | 7 | 97.57 | 89.94 |
| 0 | 4 | 7 | 193.77 | -187.71 |
| 0 | 6 | 7 | 82.29 | 67.94 |
| 0 | 8 | 7 | 64.20 | -64.06 |
| 0 | 10 | 7 | 224.50 | 194.64 |
| 0 | 12 | 7 | 152.28 | -154.60 |
| 0 | 14 | 7 | 89.53 | -101.37 |
| 0 | 16 | 7 | 120.64 | 135.23 |
| 0 | 18 | 7 | 35.95 | 48.67 |
| 0 | 20 | 7 | 13.69 | 11.93 |
| 0 | 22 | 7 | 127.65 | -109.40 |
| 0 | 2 | 8 | 63.79 | -83.19 |
| 0 | 4 | 8 | 86.20 | -99.98 |
| 0 | 6 | 8 | 15.31 | -12.50 |
| 0 | 8 | 8 | 45.99 | 47.72 |
| 0 | 10 | 8 | 78.44 | 75.00 |
| 0 | 12 | 8 | 154.88 | -150.91 |
| 0 | 14 | 8 | 35.19 | 27.87 |
| 0 | 16 | 8 | 72.82 | -81.32 |
| 0 | 18 | 8 | 52.54 | 40.02 |
| 0 | 20 | 8 | 44.10 | 37.40 |
| 0 | 2 | 9 | 56.20 | 64.12 |
| 0 | 4 | 9 | 88.62 | 86.38 |
| 0 | 6 | 9 | 5.16 | 3.48 |
| 0 | 8 | 9 | 32.52 | -36.95 |
| 0 | 10 | 9 | 16.34 | -26.50 |
| 0 | 12 | 9 | 79.05 | 86.46 |
| 0 | 14 | 9 | 88.87 | 99.14 |
| 0 | 16 | 9 | 168.37 | -185.08 |
| 0 | 18 | 9 | 36.14 | -42.06 |
| 0 | 0 | 10 | 207.77 | -187.62 |
| 0 | 2 | 10 | 5.80 | 9.97 |
| 0 | 4 | 10 | 94.21 | 92.31 |
| 0 | 6 | 10 | 29.07 | -14.78 |
| 0 | 8 | 10 | 5.56 | -6.91 |
| 0 | 10 | 10 | 37.53 | -33.11 |
| 0 | 12 | 10 | 55.72 | 63.06 |
| 0 | 14 | 10 | 28.10 | -25.06 |
| 0 | 16 | 10 | 29.38 | 33.34 |
| 0 | 18 | 10 | 42.86 | 33.90 |
| 0 | 2 | 11 | 28.23 | 15.92 |
| 0 | 4 | 11 | 76.80 | -82.21 |
| 0 | 6 | 11 | 27.43 | 33.36 |
| 0 | 8 | 11 | 63.46 | 64.28 |
| 0 | 10 | 11 | 26.48 | 35.09 |
| 0 | 12 | 11 | 62.57 | -81.80 |
| 0 | 14 | 11 | 67.42 | -68.06 |
| 0 | 16 | 11 | 97.92 | 107.89 |
| 0 | 0 | 12 | 189.96 | 184.53 |
| 0 | 2 | 12 | 99.62 | -83.31 |
| 0 | 4 | 12 | 49.12 | -61.13 |
| 0 | 6 | 12 | 54.89 | -59.18 |
| 0 | 8 | 12 | 58.72 | 77.21 |
| 0 | 10 | 12 | 117.68 | 111.86 |
| 0 | 12 | 12 | 109.23 | -114.76 |
| 0 | 2 | 13 | 98.77 | -95.36 |
| 0 | 4 | 13 | 99.77 | 97.39 |
| 0 | 6 | 13 | 54.46 | -59.76 |
| 0 | 8 | 13 | 5.72 | -13.60 |
| 0 | 10 | 13 | 71.96 | -93.41 |
| 0 | 0 | 14 | 157.14 | -155.35 |
| 0 | 2 | 14 | 61.06 | 66.18 |
| 1 | 5 | 0 | 3.34 | 5.62 |
| 1 | 7 | 0 | 12.44 | 4.90 |
| 1 | 9 | 0 | 96.47 | 99.21 |
| 1 | 11 | 0 | 124.48 | -112.02 |
| 1 | 13 | 0 | 65.46 | -83.91 |
| 1 | 15 | 0 | 73.70 | -54.76 |
| 1 | 17 | 0 | 6.44 | -12.57 |
| 1 | 19 | 0 | 91.03 | 92.08 |
| 1 | 21 | 0 | 41.05 | -42.22 |
| 1 | 23 | 0 | 45.21 | 53.16 |
| 1 | 25 | 0 | 7.57 | 5.10 |
| 1 | 5 | 1 | 12.02 | 7.89 |
| 1 | 7 | 1 | 81.29 | 73.15 |
| 1 | 9 | 1 | 14.00 | 19.21 |
| 1 | 11 | 1 | 132.14 | -132.50 |
| 1 | 13 | 1 | 263.31 | 222.43 |
| 1 | 15 | 1 | 104.20 | -100.05 |
| 1 | 17 | 1 | 62.03 | -82.14 |
| 1 | 19 | 1 | 30.60 | -34.26 |
| 1 | 21 | 1 | 24.73 | 29.81 |
| 1 | 23 | 1 | 15.02 | 29.37 |
| 1 | 25 | 1 | 35.95 | -54.77 |
| 1 | 3 | 2 | 125.43 | 122.87 |
| 1 | 5 | 2 | 25.79 | 17.73 |
| 1 | 7 | 2 | 11.59 | 17.21 |
| 1 | 9 | 2 | 46.08 | -54.22 |
| 1 | 11 | 2 | 31.70 | 26.36 |
| 1 | 13 | 2 | 16.97 | 16.39 |
| 1 | 15 | 2 | 29.98 | -30.20 |
| 1 | 17 | 2 | 55.47 | 60.77 |
| 1 | 19 | 2 | 28.61 | -32.30 |
| 1 | 21 | 2 | 17.46 | -22.64 |
| 1 | 23 | 2 | 8.66 | -16.07 |
| 1 | 25 | 2 | 32.63 | 40.30 |
| 1 | 3 | 3 | 111.39 | -100.20 |
| 1 | 5 | 3 | 6.72 | -0.32 |
| 1 | 7 | 3 | 174.82 | 184.25 |
| 1 | 9 | 3 | 14.60 | 24.74 |
| 1 | 11 | 3 | 38.74 | -33.12 |
| 1 | 13 | 3 | 163.37 | -132.39 |
| 1 | 15 | 3 | 91.31 | 90.51 |
| 1 | 17 | 3 | 21.24 | 33.37 |
| 1 | 19 | 3 | 42.70 | -60.78 |
| 1 | 21 | 3 | 29.85 | -35.04 |
| 1 | 23 | 3 | 34.81 | -44.59 |
| 1 | 1 | 4 | 40.73 | -30.91 |
| 1 | 3 | 4 | 53.96 | -52.70 |
| 1 | 5 | 4 | 63.11 | -62.53 |
| 1 | 7 | 4 | 14.27 | -9.09 |
| 1 | 9 | 4 | 130.21 | 116.64 |
| 1 | 11 | 4 | 23.28 | 44.86 |
| 1 | 13 | 4 | 8.28 | -15.92 |
| 1 | 15 | 4 | 109.17 | 100.65 |
| 1 | 17 | 4 | 61.65 | -74.55 |
| 1 | 19 | 4 | 7.49 | -8.20 |
| 1 | 21 | 4 | 39.08 | 49.33 |
| 1 | 23 | 4 | 7.74 | -15.03 |
| 1 | 3 | 5 | 69.34 | 64.14 |
| 1 | 5 | 5 | 12.34 | 4.78 |
| 1 | 7 | 5 | 133.82 | -131.19 |
| 1 | 9 | 5 | 64.32 | -50.49 |
| 1 | 11 | 5 | 35.36 | -28.63 |
| 1 | 13 | 5 | 159.27 | 149.14 |
| 1 | 15 | 5 | 63.82 | -60.76 |
| 1 | 17 | 5 | 24.60 | 19.02 |
| 1 | 19 | 5 | 9.78 | 4.04 |
| 1 | 21 | 5 | 33.14 | 39.29 |
| 1 | 23 | 5 | 41.37 | 65.17 |
| 1 | 3 | 6 | 126.57 | 121.92 |
| 1 | 5 | 6 | 46.64 | 49.39 |
| 1 | 7 | 6 | 33.28 | 26.77 |
| 1 | 9 | 6 | 213.37 | -184.25 |
| 1 | 11 | 6 | 50.73 | 55.94 |
| 1 | 13 | 6 | 31.94 | 43.81 |
| 1 | 15 | 6 | 29.05 | -40.46 |
| 1 | 17 | 6 | 8.31 | 17.11 |
| 1 | 19 | 6 | 26.46 | -33.04 |
| 1 | 21 | 6 | 8.10 | 19.96 |
| 1 | 23 | 6 | 7.95 | -10.37 |
| 1 | 1 | 7 | 148.32 | 146.49 |
| 1 | 3 | 7 | 111.61 | -93.26 |
| 1 | 5 | 7 | 5.75 | -9.95 |
| 1 | 7 | 7 | 45.19 | -35.87 |
| 1 | 9 | 7 | 6.24 | 9.12 |
| 1 | 11 | 7 | 87.37 | 98.94 |
| 1 | 13 | 7 | 155.32 | -170.31 |
| 1 | 15 | 7 | 52.07 | 67.03 |
| 1 | 17 | 7 | 30.57 | 39.85 |
| 1 | 19 | 7 | 34.36 | 37.97 |
| 1 | 21 | 7 | 26.15 | -32.02 |
| 1 | 1 | 8 | 158.46 | 154.72 |
| 1 | 3 | 8 | 138.87 | -111.18 |
| 1 | 5 | 8 | 6.24 | 3.12 |
| 1 | 7 | 8 | 6.42 | -1.47 |
| 1 | 9 | 8 | 6.68 | 22.56 |
| 1 | 11 | 8 | 52.48 | -54.86 |
| 1 | 13 | 8 | 24.64 | -28.92 |
| 1 | 15 | 8 | 23.91 | -19.11 |
| 1 | 17 | 8 | 27.18 | -31.41 |
| 1 | 19 | 8 | 36.07 | 49.46 |
| 1 | 1 | 9 | 6.31 | 1.86 |
| 1 | 3 | 9 | 118.89 | 109.03 |
| 1 | 5 | 9 | 6.70 | 7.44 |
| 1 | 7 | 9 | 12.20 | -3.13 |
| 1 | 9 | 9 | 17.87 | 19.93 |
| 1 | 11 | 9 | 19.88 | -28.86 |
| 1 | 13 | 9 | 108.89 | 126.05 |
| 1 | 15 | 9 | 63.13 | -80.31 |
| 1 | 17 | 9 | 91.89 | -97.36 |
| 1 | 19 | 9 | 23.56 | 26.66 |
| 1 | 1 | 10 | 52.57 | -61.75 |
| 1 | 3 | 10 | 44.71 | 47.05 |
| 1 | 5 | 10 | 11.03 | -3.45 |
| 1 | 7 | 10 | 12.52 | -14.65 |
| 1 | 9 | 10 | 7.53 | 16.62 |
| 1 | 11 | 10 | 7.76 | 0.45 |
| 1 | 13 | 10 | 8.00 | 18.42 |
| 1 | 15 | 10 | 8.19 | -2.40 |
| 1 | 17 | 10 | 43.13 | 53.56 |
| 1 | 1 | 11 | 59.79 | 52.84 |
| 1 | 3 | 11 | 50.85 | -56.23 |
| 1 | 5 | 11 | 7.32 | -7.91 |
| 1 | 7 | 11 | 51.39 | 52.67 |
| 1 | 9 | 11 | 7.83 | 15.49 |
| 1 | 11 | 11 | 12.41 | 9.96 |
| 1 | 13 | 11 | 86.56 | -97.15 |
| 1 | 15 | 11 | 48.16 | 50.87 |
| 1 | 1 | 12 | 43.08 | 40.09 |
| 1 | 3 | 12 | 59.28 | -67.28 |
| 1 | 5 | 12 | 29.00 | -39.62 |
| 1 | 7 | 12 | 15.67 | -15.07 |
| 1 | 9 | 12 | 83.35 | 109.93 |
| 1 | 11 | 12 | 18.47 | -21.84 |
| 1 | 13 | 12 | 12.41 | -19.31 |
| 1 | 1 | 13 | 99.40 | -116.77 |
| 1 | 3 | 13 | 17.92 | 21.64 |
| 1 | 5 | 13 | 7.53 | 12.62 |
| 1 | 7 | 13 | 22.53 | -38.31 |
| 1 | 9 | 13 | 20.13 | -37.70 |
| 1 | 1 | 14 | 24.88 | -35.72 |
| 2 | 4 | 0 | 169.73 | -172.67 |
| 2 | 6 | 0 | 69.29 | 72.07 |
| 2 | 8 | 0 | 4.69 | -3.02 |
| 2 | 10 | 0 | 76.34 | -72.23 |
| 2 | 12 | 0 | 3.98 | -13.01 |
| 2 | 14 | 0 | 114.02 | -113.90 |
| 2 | 16 | 0 | 14.33 | 20.17 |
| 2 | 18 | 0 | 20.33 | 20.57 |
| 2 | 20 | 0 | 5.14 | 29.64 |
| 2 | 22 | 0 | 5.35 | -22.42 |
| 2 | 24 | 0 | 34.36 | 42.10 |
| 2 | 4 | 1 | 74.38 | -74.96 |
| 2 | 6 | 1 | 136.61 | 180.35 |
| 2 | 8 | 1 | 16.12 | -14.83 |
| 2 | 10 | 1 | 19.98 | 18.92 |
| 2 | 12 | 1 | 27.68 | -36.98 |
| 2 | 14 | 1 | 57.73 | 58.32 |
| 2 | 16 | 1 | 46.68 | -47.41 |
| 2 | 18 | 1 | 93.68 | -90.53 |
| 2 | 20 | 1 | 37.12 | 47.91 |
| 2 | 22 | 1 | 21.40 | -35.36 |
| 2 | 24 | 1 | 5.45 | 15.39 |
| 2 | 2 | 2 | 21.14 | 32.92 |
| 2 | 0 | 2 | 12.52 | 2.98 |
| 2 | 4 | 2 | 41.96 | -47.09 |
| 2 | 6 | 2 | 8.12 | -7.28 |
| 2 | 8 | 2 | 3.33 | 6.53 |
| 2 | 10 | 2 | 3.84 | 4.50 |
| 2 | 12 | 2 | 11.24 | 14.14 |
| 2 | 14 | 2 | 31.07 | -27.89 |
| 2 | 16 | 2 | 48.44 | 44.48 |
| 2 | 18 | 2 | 9.92 | -0.57 |
| 2 | 20 | 2 | 5.24 | -7.58 |
| 2 | 22 | 2 | 43.60 | -37.12 |
| 2 | 24 | 2 | 5.44 | 12.65 |
| 2 | 2 | 3 | 8.00 | -1.07 |
| 2 | 4 | 3 | 43.06 | -37.35 |
| 2 | 6 | 3 | 106.69 | 108.65 |
| 2 | 8 | 3 | 82.55 | 73.05 |
| 2 | 10 | 3 | 15.63 | -9.60 |
| 2 | 12 | 3 | 117.49 | -99.71 |
| 2 | 14 | 3 | 50.66 | 63.99 |
| 2 | 16 | 3 | 4.99 | -6.28 |
| 2 | 18 | 3 | 19.62 | -15.69 |
| 2 | 20 | 3 | 43.12 | -49.86 |
| 2 | 24 | 3 | 62.62 | 51.70 |
| 2 | 22 | 3 | 28.46 | -26.42 |
| 2 | 0 | 4 | 104.54 | -83.35 |
| 2 | 2 | 4 | 118.03 | -99.94 |
| 2 | 4 | 4 | 79.33 | 96.97 |
| 2 | 6 | 4 | 87.18 | -77.67 |
| 2 | 8 | 4 | 21.33 | 30.32 |
| 2 | 10 | 4 | 55.16 | 60.54 |
| 2 | 12 | 4 | 27.93 | -13.07 |
| 2 | 14 | 4 | 127.71 | 128.21 |
| 2 | 16 | 4 | 28.17 | -25.13 |
| 2 | 18 | 4 | 24.67 | -33.50 |
| 2 | 20 | 4 | 10.99 | -11.92 |
| 2 | 22 | 4 | 51.52 | 52.04 |
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| 2 | 4 | 5 | 41.44 | -28.65 |
| 2 | 6 | 5 | 5.34 | 15.30 |
| 2 | 8 | 5 | 114.83 | -141.29 |
| 2 | 10 | 5 | 14.14 | 30.59 |
| 2 | 12 | 5 | 25.88 | 22.37 |
| 2 | 14 | 5 | 4.97 | -6.73 |
| 2 | 16 | 5 | 52.12 | 40.31 |
| 2 | 18 | 5 | 10.79 | -6.20 |
| 2 | 20 | 5 | 34.62 | 38.62 |
| 2 | 22 | 5 | 19.08 | 22.57 |
| 2 | 0 | 6 | 3.79 | -15.35 |
| 2 | 2 | 6 | 58.96 | -40.79 |
| 2 | 4 | 6 | 138.86 | 115.51 |
| 2 | 6 | 6 | 14.49 | 8.38 |
| 2 | 8 | 6 | 63.59 | -62.47 |
| 2 | 10 | 6 | 23.82 | -34.20 |
| 2 | 12 | 6 | 21.78 | 16.90 |
| 2 | 14 | 6 | 22.50 | 30.83 |
| 2 | 16 | 6 | 44.78 | -60.89 |
| 2 | 18 | 6 | 5.77 | 25.85 |
| 2 | 20 | 6 | 5.76 | -15.23 |
| 2 | 2 | 7 | 7.09 | -15.56 |
| 2 | 4 | 7 | 72.98 | 61.09 |
| 2 | 6 | 7 | 163.73 | -144.40 |
| 2 | 8 | 7 | 59.66 | 59.75 |
| 2 | 10 | 7 | 4.77 | -14.93 |
| 2 | 12 | 7 | 36.98 | 36.07 |
| 2 | 14 | 7 | 57.34 | -61.70 |
| 2 | 16 | 7 | 16.02 | 18.17 |
| 2 | 18 | 7 | 75.29 | 67.41 |
| 2 | 20 | 7 | 33.98 | -35.85 |
| 2 | 0 | 8 | 128.50 | 102.67 |
| 2 | 2 | 8 | 17.01 | 19.60 |
| 2 | 4 | 8 | 39.46 | -38.61 |
| 2 | 6 | 8 | 44.24 | 39.08 |
| 2 | 8 | 8 | 4.98 | -5.93 |
| 2 | 10 | 8 | 55.30 | -41.25 |
| 2 | 12 | 8 | 5.33 | -13.56 |
| 2 | 14 | 8 | 36.35 | -38.41 |
| 2 | 16 | 8 | 32.74 | -27.94 |
| 2 | 18 | 8 | 29.12 | 15.79 |
| 2 | 20 | 8 | 5.99 | 16.40 |
| 2 | 2 | 9 | 96.90 | 80.16 |
| 2 | 4 | 9 | 4.85 | 15.98 |
| 2 | 6 | 9 | 5.07 | 11.84 |
| 2 | 8 | 9 | 39.91 | 33.13 |
| 2 | 10 | 9 | 5.46 | -11.57 |
| 2 | 12 | 9 | 65.99 | 52.67 |
| 2 | 14 | 9 | 5.84 | -4.83 |
| 2 | 16 | 9 | 61.84 | -68.11 |
| 2 | 18 | 9 | 42.21 | -46.07 |
| 2 | 0 | 10 | 95.19 | -88.91 |
| 2 | 2 | 10 | 51.13 | 41.99 |
| 2 | 4 | 10 | 48.37 | -41.51 |
| 2 | 6 | 10 | 5.22 | -3.75 |
| 2 | 8 | 10 | 18.47 | 22.27 |
| 2 | 10 | 10 | 22.83 | 34.01 |
| 2 | 12 | 10 | 16.59 | 6.87 |
| 2 | 14 | 10 | 51.16 | -41.88 |
| 2 | 16 | 10 | 65.08 | 62.70 |
| 2 | 2 | 11 | 5.17 | -4.96 |
| 2 | 4 | 11 | 5.25 | -8.10 |
| 2 | 6 | 11 | 5.35 | -0.14 |
| 2 | 8 | 11 | 34.42 | 40.40 |
| 2 | 10 | 11 | 5.70 | 1.04 |
| 2 | 12 | 11 | 60.22 | -40.25 |
| 2 | 14 | 11 | 5.98 | 3.44 |
| 2 | 0 | 12 | 5.33 | -11.83 |
| 2 | 2 | 12 | 5.35 | 6.79 |
| 2 | 4 | 12 | 44.46 | -51.84 |
| 2 | 6 | 12 | 36.36 | -19.17 |
| 2 | 8 | 12 | 61.31 | 50.92 |
| 2 | 10 | 12 | 25.97 | 33.65 |
| 2 | 12 | 12 | 5.69 | -17.16 |
| 2 | 2 | 13 | 43.91 | -46.97 |
| 2 | 4 | 13 | 28.18 | -23.44 |
| 2 | 6 | 13 | 53.34 | 51.79 |
| 3 | 3 | 0 | 8.94 | 7.42 |
| 3 | 9 | 0 | 55.61 | -62.16 |
| 3 | 5 | 0 | 157.59 | -167.29 |
| 3 | 7 | 0 | 153.12 | 162.59 |
| 3 | 11 | 0 | 3.69 | 25.83 |
| 3 | 13 | 0 | 66.45 | -69.78 |
| 3 | 15 | 0 | 34.78 | -38.68 |
| 3 | 17 | 0 | 36.59 | 44.60 |
| 3 | 19 | 0 | 4.84 | -23.95 |
| 3 | 21 | 0 | 41.76 | 43.56 |
| 3 | 23 | 0 | 5.14 | -16.65 |
| 3 | 3 | 1 | 33.70 | -36.00 |
| 3 | 5 | 1 | 73.41 | 71.29 |
| 3 | 7 | 1 | 27.10 | 25.19 |
| 3 | 9 | 1 | 72.49 | -68.58 |
| 3 | 11 | 1 | 32.31 | 34.18 |
| 3 | 13 | 1 | 37.65 | 27.68 |
| 3 | 15 | 1 | 20.82 | 29.61 |
| 3 | 17 | 1 | 84.33 | -101.00 |
| 3 | 19 | 1 | 10.88 | 1.10 |
| 3 | 21 | 1 | 34.00 | 37.18 |
| 3 | 23 | 1 | 5.15 | -12.68 |
| 3 | 1 | 2 | 60.99 | -61.58 |
| 3 | 3 | 2 | 20.53 | 23.02 |
| 3 | 5 | 2 | 94.03 | 95.91 |
| 3 | 7 | 2 | 63.42 | -66.63 |
| 3 | 9 | 2 | 11.52 | -3.40 |
| 3 | 11 | 2 | 14.08 | 7.42 |
| 3 | 13 | 2 | 9.56 | -2.71 |
| 3 | 15 | 2 | 26.77 | 25.44 |
| 3 | 17 | 2 | 19.41 | -23.40 |
| 3 | 19 | 2 | 19.94 | 31.58 |
| 3 | 21 | 2 | 33.34 | -44.08 |
| 3 | 23 | 2 | 5.12 | 2.34 |
| 3 | 1 | 3 | 14.07 | 22.38 |
| 3 | 3 | 3 | 36.70 | -38.68 |
| 3 | 5 | 3 | 2.81 | -1.64 |
| 3 | 7 | 3 | 45.67 | 49.28 |
| 3 | 9 | 3 | 95.22 | 73.58 |
| 3 | 11 | 3 | 74.22 | -61.10 |
| 3 | 13 | 3 | 40.99 | -48.13 |
| 3 | 15 | 3 | 26.36 | 31.23 |
| 3 | 17 | 3 | 20.77 | 19.94 |
| 3 | 19 | 3 | 5.00 | 6.86 |
| 3 | 21 | 3 | 58.72 | -70.20 |
| 3 | 23 | 3 | 16.47 | 21.93 |
| 3 | 1 | 4 | 10.13 | 3.03 |
| 3 | 3 | 4 | 14.90 | -12.55 |
| 3 | 5 | 4 | 109.94 | -84.78 |
| 3 | 7 | 4 | 41.21 | 38.60 |
| 3 | 9 | 4 | 64.04 | 52.49 |
| 3 | 11 | 4 | 4.03 | 0.44 |
| 3 | 13 | 4 | 22.98 | 17.06 |
| 3 | 15 | 4 | 4.86 | 0.25 |
| 3 | 17 | 4 | 16.90 | 14.58 |
| 3 | 19 | 4 | 34.31 | -41.49 |
| 3 | 21 | 4 | 35.75 | 46.08 |
| 3 | 1 | 5 | 3.43 | 3.05 |
| 3 | 3 | 5 | 36.04 | -31.59 |
| 3 | 5 | 5 | 42.16 | 41.69 |
| 3 | 7 | 5 | 47.50 | -47.38 |
| 3 | 9 | 5 | 106.51 | -82.83 |
| 3 | 11 | 5 | 57.29 | 54.21 |
| 3 | 13 | 5 | 24.04 | 20.91 |
| 3 | 15 | 5 | 17.18 | 18.81 |
| 3 | 17 | 5 | 29.67 | -33.43 |
| 3 | 19 | 5 | 5.25 | 1.29 |
| 3 | 21 | 5 | 47.16 | 47.47 |
| 3 | 3 | 6 | 10.61 | -5.34 |
| 3 | 5 | 6 | 169.42 | 144.78 |
| 3 | 7 | 6 | 103.78 | -108.64 |
| 3 | 9 | 6 | 16.66 | -0.71 |
| 3 | 11 | 6 | 10.84 | -28.11 |
| 3 | 13 | 6 | 36.38 | 42.58 |
| 3 | 15 | 6 | 7.21 | -0.75 |
| 3 | 17 | 6 | 30.65 | -34.15 |
| 3 | 19 | 6 | 17.57 | -36.38 |
| 3 | 21 | 6 | 29.44 | -40.21 |
| 3 | 1 | 7 | 46.21 | -48.69 |
| 3 | 3 | 7 | 49.85 | 47.43 |
| 3 | 5 | 7 | 68.10 | -61.88 |
| 3 | 7 | 7 | 18.27 | -9.14 |
| 3 | 9 | 7 | 66.21 | 60.75 |
| 3 | 11 | 7 | 23.11 | -30.60 |
| 3 | 13 | 7 | 21.63 | -13.23 |
| 3 | 15 | 7 | 25.44 | -36.00 |
| 3 | 17 | 7 | 57.83 | 76.41 |
| 3 | 19 | 7 | 5.52 | -2.89 |
| 3 | 1 | 8 | 83.13 | 63.85 |
| 3 | 3 | 8 | 26.75 | -14.13 |
| 3 | 5 | 8 | 94.89 | -78.52 |
| 3 | 7 | 8 | 68.77 | 71.99 |
| 3 | 9 | 8 | 13.20 | -26.75 |
| 3 | 11 | 8 | 5.02 | -1.82 |
| 3 | 13 | 8 | 15.23 | -16.65 |
| 3 | 15 | 8 | 34.80 | -30.34 |
| 3 | 17 | 8 | 18.20 | 22.95 |
| 3 | 1 | 9 | 36.76 | 24.55 |
| 3 | 3 | 9 | 40.54 | 30.96 |
| 3 | 5 | 9 | 11.58 | 11.36 |
| 3 | 7 | 9 | 15.98 | 11.26 |
| 3 | 9 | 9 | 42.56 | -34.04 |
| 3 | 11 | 9 | 34.37 | 25.30 |
| 3 | 13 | 9 | 40.80 | 38.68 |
| 3 | 15 | 9 | 20.33 | -19.92 |
| 3 | 17 | 9 | 45.76 | -52.59 |
| 3 | 1 | 10 | 36.02 | -33.47 |
| 3 | 3 | 10 | 14.14 | 14.91 |
| 3 | 5 | 10 | 34.69 | 31.31 |
| 3 | 7 | 10 | 31.00 | -28.36 |
| 3 | 9 | 10 | 5.23 | 1.70 |
| 3 | 11 | 10 | 17.25 | 13.34 |
| 3 | 13 | 10 | 16.72 | -10.30 |
| 3 | 15 | 10 | 28.24 | 27.83 |
| 3 | 1 | 11 | 12.11 | -7.49 |
| 3 | 3 | 11 | 5.00 | -3.39 |
| 3 | 5 | 11 | 14.85 | -15.82 |
| 3 | 7 | 11 | 10.66 | 14.22 |
| 3 | 9 | 11 | 46.96 | 41.34 |
| 3 | 1 | 12 | 16.90 | 14.52 |
| 3 | 3 | 12 | 5.11 | -1.77 |
| 3 | 5 | 12 | 76.07 | -74.85 |
| 3 | 7 | 12 | 43.44 | 48.65 |
| 3 | 9 | 12 | 17.51 | 13.66 |
| 3 | 1 | 13 | 11.52 | 7.97 |
| 4 | 4 | 0 | 101.73 | -105.61 |
| 4 | 6 | 0 | 2.90 | -2.00 |
| 4 | 8 | 0 | 50.95 | 54.71 |
| 4 | 10 | 0 | 14.63 | -23.85 |
| 4 | 12 | 0 | 15.63 | -4.22 |
| 4 | 14 | 0 | 57.72 | -52.49 |
| 4 | 16 | 0 | 4.52 | 9.42 |
| 4 | 18 | 0 | 9.87 | 13.22 |
| 4 | 20 | 0 | 15.32 | 0.53 |
| 4 | 22 | 0 | 5.00 | 17.44 |
| 4 | 2 | 1 | 28.26 | 33.39 |
| 4 | 4 | 1 | 2.28 | -17.20 |
| 4 | 6 | 1 | 70.78 | 76.30 |
| 4 | 8 | 1 | 55.02 | -56.96 |
| 4 | 10 | 1 | 11.12 | -3.86 |
| 4 | 12 | 1 | 36.03 | 30.53 |
| 4 | 14 | 1 | 33.71 | 25.74 |
| 4 | 16 | 1 | 36.27 | -23.40 |
| 4 | 18 | 1 | 59.57 | -67.65 |
| 4 | 20 | 1 | 40.95 | 45.58 |
| 4 | 22 | 1 | 5.02 | 0.24 |
| 4 | 2 | 2 | 33.40 | -33.38 |
| 4 | 4 | 2 | 75.32 | 69.53 |
| 4 | 6 | 2 | 11.68 | 7.51 |
| 4 | 8 | 2 | 45.50 | -48.77 |
| 4 | 10 | 2 | 9.48 | 11.87 |
| 4 | 12 | 2 | 4.27 | -8.70 |
| 4 | 14 | 2 | 23.40 | 27.28 |
| 4 | 16 | 2 | 10.38 | -7.77 |
| 4 | 18 | 2 | 10.84 | 7.67 |
| 4 | 20 | 2 | 3.70 | -5.33 |
| 4 | 22 | 2 | 25.93 | -27.88 |
| 4 | 2 | 3 | 22.42 | -25.31 |
| 4 | 4 | 3 | 2.80 | 8.78 |
| 4 | 6 | 3 | 3.06 | -24.21 |
| 4 | 8 | 3 | 98.56 | 99.28 |
| 4 | 10 | 3 | 16.41 | -20.34 |
| 4 | 12 | 3 | 59.87 | -47.61 |
| 4 | 14 | 3 | 4.70 | -1.16 |
| 4 | 16 | 3 | 14.95 | 10.99 |
| 4 | 18 | 3 | 33.08 | 38.06 |
| 4 | 20 | 3 | 47.51 | -52.27 |
| 4 | 0 | 4 | 3.15 | -10.75 |
| 4 | 2 | 4 | 31.74 | -21.05 |
| 4 | 4 | 4 | 64.28 | -54.45 |
| 4 | 6 | 4 | 23.14 | -25.84 |
| 4 | 8 | 4 | 58.72 | 54.05 |
| 4 | 10 | 4 | 3.95 | 6.37 |
| 4 | 12 | 4 | 15.58 | 12.05 |
| 4 | 14 | 4 | 14.56 | -2.31 |
| 4 | 16 | 4 | 16.61 | 17.16 |
| 4 | 18 | 4 | 21.16 | -21.56 |
| 4 | 20 | 4 | 5.05 | 2.91 |
| 4 | 2 | 5 | 10.10 | -1.82 |
| 4 | 4 | 5 | 3.65 | -12.50 |
| 4 | 6 | 5 | 28.06 | 35.86 |
| 4 | 8 | 5 | 98.54 | -93.04 |
| 4 | 10 | 5 | 4.15 | 9.28 |
| 4 | 12 | 5 | 40.82 | 35.56 |
| 4 | 14 | 5 | 15.42 | 8.47 |
| 4 | 16 | 5 | 5.16 | 2.88 |
| 4 | 18 | 5 | 26.39 | -38.97 |
| 4 | 20 | 5 | 31.34 | 40.88 |
| 4 | 0 | 6 | 33.61 | -38.66 |
| 4 | 2 | 6 | 37.20 | -27.46 |
| 4 | 4 | 6 | 71.74 | 80.06 |
| 4 | 6 | 6 | 22.88 | 18.59 |
| 4 | 8 | 6 | 59.51 | -60.34 |
| 4 | 10 | 6 | 14.10 | -5.37 |
| 4 | 12 | 6 | 11.39 | 3.15 |
| 4 | 14 | 6 | 20.52 | 26.89 |
| 4 | 16 | 6 | 20.75 | -22.46 |
| 4 | 18 | 6 | 5.33 | 3.12 |
| 4 | 2 | 7 | 4.13 | -13.17 |
| 4 | 4 | 7 | 4.40 | 13.79 |
| 4 | 6 | 7 | 55.72 | -57.71 |
| 4 | 8 | 7 | 46.22 | 51.24 |
| 4 | 10 | 7 | 8.95 | 5.02 |
| 4 | 12 | 7 | 27.23 | -21.97 |
| 4 | 14 | 7 | 29.18 | -21.78 |
| 4 | 18 | 7 | 37.71 | 51.00 |
| 4 | 0 | 8 | 80.18 | 49.34 |
| 4 | 16 | 7 | 23.48 | 10.71 |
| 4 | 2 | 8 | 29.77 | 28.17 |
| 4 | 4 | 8 | 76.93 | -58.73 |
| 4 | 6 | 8 | 4.80 | 2.36 |
| 4 | 8 | 8 | 30.61 | 32.53 |
| 4 | 10 | 8 | 19.84 | -18.71 |
| 4 | 12 | 8 | 5.13 | 3.38 |
| 4 | 14 | 8 | 26.41 | -32.50 |
| 4 | 16 | 8 | 5.44 | 2.11 |
| 4 | 2 | 9 | 44.05 | 38.64 |
| 4 | 4 | 9 | 4.71 | -7.00 |
| 4 | 6 | 9 | 29.91 | 34.61 |
| 4 | 8 | 9 | 41.37 | -37.15 |
| 4 | 10 | 9 | 5.24 | 6.20 |
| 4 | 12 | 9 | 37.43 | 29.07 |
| 4 | 14 | 9 | 5.43 | 9.03 |
| 4 | 0 | 10 | 32.36 | -25.92 |
| 4 | 2 | 10 | 21.97 | -19.09 |
| 4 | 4 | 10 | 47.61 | 35.41 |
| 4 | 6 | 10 | 4.95 | 0.17 |
| 4 | 8 | 10 | 25.32 | -19.71 |
| 4 | 10 | 10 | 17.13 | 18.28 |
| 4 | 12 | 10 | 15.91 | -10.85 |
| 4 | 2 | 11 | 10.27 | -13.16 |
| 4 | 4 | 11 | 4.98 | 5.61 |
| 4 | 6 | 11 | 20.67 | -22.82 |
| 4 | 8 | 11 | 50.36 | 46.65 |
| 4 | 10 | 11 | 5.14 | -5.78 |
| 4 | 0 | 12 | 15.54 | 8.60 |
| 4 | 2 | 12 | 18.64 | 14.91 |
| 4 | 4 | 12 | 43.52 | -42.20 |
| 5 | 3 | 0 | 12.28 | -14.58 |
| 5 | 5 | 0 | 12.80 | -11.98 |
| 5 | 7 | 0 | 13.22 | 14.65 |
| 5 | 11 | 0 | 13.90 | -18.90 |
| 5 | 13 | 0 | 4.19 | -4.46 |
| 5 | 15 | 0 | 24.44 | -26.64 |
| 5 | 5 | 1 | 2.69 | 3.70 |
|  | 7 | 1 | 23.31 | 22.60 |
| 5 | 9 | 1 | 3.76 | -8.40 |
| 5 | 11 | 1 | 3.99 | -5.60 |
| 5 | 13 | 1 | 17.09 | 17.03 |
| 5 | 15 | 1 | 4.47 | -4.83 |
| 5 | 17 | 1 | 35.12 | -16.91 |
| 5 | 19 | 1 | 4.79 | -10.27 |
| 5 | 1 | 2 | 6.25 | -5.47 |
| 5 | 3 | 2 | 2.39 | -8.53 |
| 5 | 5 | 2 | 19.50 | 26.92 |
| 5 | 7 | 2 | 13.84 | -25.60 |
| 5 | 9 | 2 | 12.37 | 19.03 |
| 5 | 11 | 2 | 10.28 | -8.86 |
| 5 | 1 | 3 | 22.28 | -24.87 |
| 5 | 3 | 3 | 2.82 | 13.40 |
| 5 | 5 | 3 | 8.18 | -12.05 |
| 5 | 7 | 3 | 33.38 | 30.25 |
| 5 | 9 | 3 | 18.02 | 17.01 |
| 5 | 11 | 3 | 33.08 | -31.96 |
| 5 | 13 | 3 | 4.62 | 7.94 |
| 5 | 15 | 3 | 4.75 | -5.52 |
| 5 | 17 | 3 | 15.94 | 16.20 |
| 5 | 19 | 3 | 25.33 | -16.77 |
| 5 | 1 | 4 | 32.86 | -21.33 |
| 5 | 3 | 4 | 11.45 | 20.10 |
| 5 | 5 | 4 | 27.26 | -36.56 |
| 5 | 7 | 4 | 18.79 | 27.34 |
| 5 | 9 | 4 | 3.89 | -8.53 |
| 5 | 11 | 4 | 19.05 | 22.59 |
| 5 | 13 | 4 | 4.67 | -0.71 |
| 5 | 15 | 4 | 24.76 | 10.90 |
| 5 | 17 | 4 | 4.93 | 0.39 |
| 5 | 19 | 4 | 19.73 | -20.09 |
| 5 | 1 | 5 | 11.89 | -8.20 |
| 5 | 3 | 5 | 19.40 | -8.39 |
| 5 | 5 | 5 | 14.75 | 6.60 |
| 5 | 7 | 5 | 35.04 | -18.29 |
| 5 | 9 | 5 | 18.85 | -20.78 |
| 5 | 11 | 5 | 19.15 | 14.31 |
| 5 | 3 | 6 | 19.35 | 7.56 |
| 5 | 5 | 6 | 27.98 | 22.00 |
| 5 | 7 | 6 | 7.32 | -9.06 |
| 5 | 9 | 6 | 19.37 | -21.38 |
| 5 | 11 | 6 | 4.58 | 7.73 |
| 5 | 1 | 7 | 4.16 | 11.78 |
| 5 | 3 | 7 | 4.32 | -5.41 |
| 5 | 7 | 7 | 13.33 | -15.07 |
| 5 | 9 | 7 | 13.81 | 11.47 |
| 5 | 1 | 8 | 36.86 | 20.28 |
| 5 | 1 | 9 | 33.81 | 25.84 |

TABLE II

FINAL POSITIONAL AND ISOTROPIC THERMAL PARAMETERS FOR $(QnH)_2[Re_4Br_{15}]$

| Atom[a] | $x/a$ ($\sigma_x$) | $y/b$ ($\sigma_y$) | $c/z$ ($\sigma_z$) | $B$ ($\sigma_B$) |
|---|---|---|---|---|
| $Re_{t2}$(8g) | 0.1353 (0.0009) | 0.2101 (0.0002) | $^1/_4$ | 3.1 (0.1) |
| $Re_{t1}$(4c) | 0.0 | 0.1346 (0.0002) | $^1/_4$ | 1.9 (0.1) |
| $Re_m$(4c) | 0.0 | 0.1031 (0.0002) | $^3/_4$ | 2.3 (0.2) |
| $Br_{t1}$(16h) | 0.1845 (0.0017) | 0.2207 (0.0002) | 0.0972 (0.0005) | 4.4 (0.2) |
| $Br_{t2}$(8f) | 0.0 | 0.1167 (0.0003) | 0.0969 (0.0007) | 3.2 (0.3) |
| $Br_{t3}$(8g) | 0.2809 (0.0030) | 0.1325 (0.0004) | $^1/_4$ | 4.9 (0.3) |
| $Br_{t4}$(4c) | 0.0 | 0.2870 (0.0006) | $^1/_4$ | 4.3 (0.4) |
| $Br_{m1}$(8f) | 0.0 | 0.1644 (0.0003) | 0.6343 (0.0007) | 3.1 (0.3) |
| $Br_{m2}$(8f) | 0.0 | 0.0421 (0.0004) | 0.6340 (0.0007) | 3.7 (0.3) |
| $Br_{m3}$(8g) | 0.2747 (0.0029) | 0.1036 (0.0004) | $^3/_4$ | 4.4 (0.3) |
| $C_1$(8f) | 0.0 | 0.279 (0.003) | 0.043 (0.006) | 11 (3) |
| $C_2$(8f) | 0.0 | 0.272 (0.003) | 0.949 (0.006) | 8 (3) |
| $C_3$(8f) | 0.0 | 0.319 (0.003) | 0.095 (0.006) | 11 (3) |
| $C_4$(8f) | 0.0 | 0.316 (0.003) | 0.909 (0.006) | 10 (3) |
| $C_5$(8f) | 0.0 | 0.358 (0.003) | 0.057 (0.006) | 11 (3) |
| $C_6$(8f) | 0.0 | 0.354 (0.003) | 0.944 (0.006) | 10 (3) |
| $C_7$(8f) | 0.0 | 0.394 (0.003) | 0.105 (0.006) | 10 (3) |
| $C_8$(8f) | 0.0 | 0.390 (0.003) | 0.901 (0.006) | 11 (3) |
| $C_9$(8f) | 0.0 | 0.433 (0.003) | 0.054 (0.006) | 9 (3) |
| $C_{10}$(8f) | 0.0 | 0.427 (0.003) | 0.950 (0.006) | 6 (3) |

[a] t = trimer; m = monomer; space group classification of atomic position, as given in ref. 18, is in parentheses beside each atom

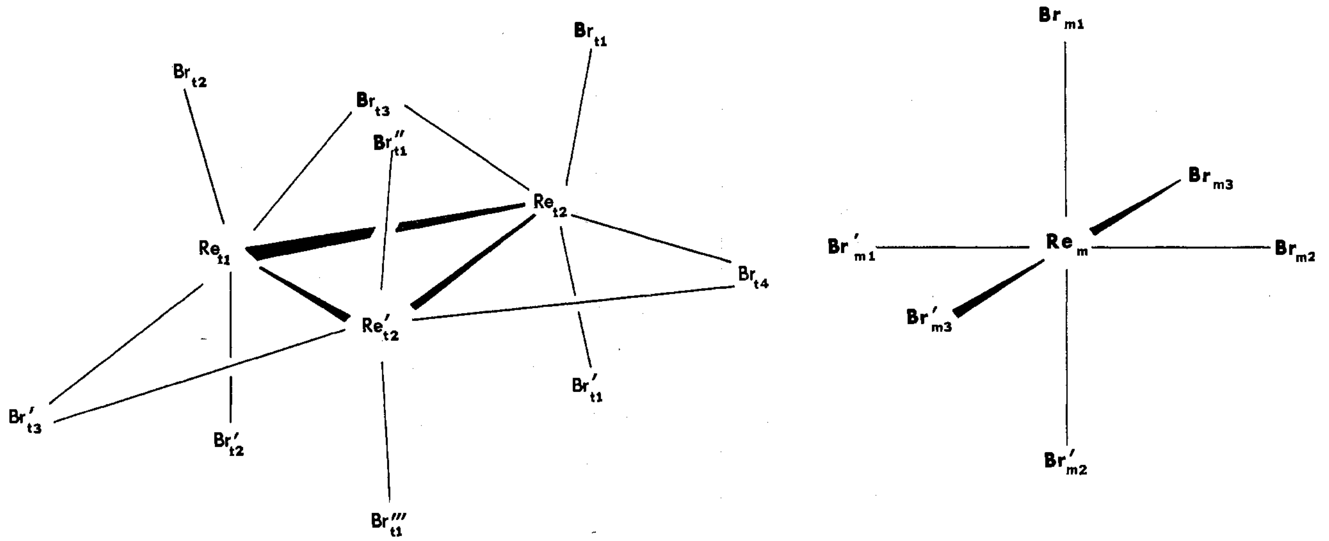

Figure 1.—Sketches of $Re_3Br_9$ and $[ReBr_6]^{2-}$ as they occur in $(QnH)_2Re_4Br_{15}$, showing the numbering of atoms, corresponding to that used in Tables II, III, and IV. No indication of the relative orientations of these moieties with respect to each other in the unit cell is implied.

TABLE III

BOND LENGTHS AND ANGLES IN $[ReBr_6]^{2-}$

| Bond or angle | Length, Å., or angle, deg. | Std. dev. |
|---|---|---|
| $Re_m$–$Br_{m1}$ | 2.51 | 0.01 |
| $Re_m$–$Br_{m2}$ | 2.51 | 0.01 |
| $Re_m$–$Br_{m3}$ | 2.50 | 0.01 |
| $Br_{m1}$–$Re_m$–$Br_{m3}$ | 89.8 | 0.4 |
| $Br_{m2}$–$Re_m$–$Br_{m3}$ | 90.2 | 0.3 |
| $Br_{m1}$–$Re_m$–$Br'_{m1}$ | 92.1 | 0.4 |
| $Br_{m2}$–$Re_m$–$Br'_{m2}$ | 92.4 | 0.5 |

The $ReBr_6$ group (to which the charge −2 may be assigned for reasons given later) is a slightly distorted octahedron. The Re–Br distances are all equal at 2.50 ± 0.01 Å.; two of the angles are insignificantly ($\Delta/\sigma$ = 0.5) different from 90° while the other two are different by a small but probably significant ($\Delta/\sigma \approx 5$) amount. Subtracting the Br covalent radius[20a] of 1.14 Å., a covalent radius of 1.36 Å. for Re(IV) is obtained. This is approximately the same as the radii of other ions of the third transition series in similar oxidation states.[20b]

**The $Re_3Br_9$ Group.**—This is the species of principal interest. A sketch of it is given in Figure 1 and the interatomic distances and angles are listed in Table IV. Two crystallographic planes of symmetry pass through it. One contains all the rhenium atoms and the three bridging bromine atoms; the other contains $Re_{t1}$, $Br_{t2}$, $Br'_{t2}$, and $Br_{t4}$. Thus the crystallographically required point symmetry is mm or $C_{2v}$. However, within the limits of significance of the data in Table IV, the group possesses point symmetry $\bar{3}$m or $D_{3d}$. Thus for the Re–Re distances $\Delta/\Sigma\sigma$ = 0.7, for the Re–Br(non-

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(20) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960: (a) Table 7-2, p. 224; (b) Table 7-15, p. 249.

Table IV

Interatomic Distances and Angles in the $Re_3Br_9$ Group[a]

| | |
|---|---|
| Bond distances, Å. | |
| $Re_{t2}$–$Re'_{t2}$ | 2.454 ± 0.015 |
| $Re_{t1}$–$Re_{t2}$ | 2.470 ± 0.007 |
| $Re_{t2}$–$Br_{t1}$ | 2.45 ± 0.01 |
| $Re_{t1}$–$Br_{t2}$ | 2.44 ± 0.01 |
| $Re_{t2}$–$Br_{t3}$ | 2.57 ± 0.02 |
| $Re_{t2}$–$Br_{t4}$ | 2.51 ± 0.01 |
| $Re_{t1}$–$Br_{t3}$ | 2.55 ± 0.03 |
| Angles, deg. | |
| $Re_{t1}$–$Re_{t2}$–$Re'_{t2}$ | 60.22 ± 0.06 |
| $Re_{t2}$–$Re_{t1}$–$Re'_{t2}$ | 59.6 ± 0.2 |
| $Br_{t3}$–$Re_{t2}$–$Br_{t4}$ | 178.4 ± 0.4[b] |
| $Br_{t3}$–$Re_{t1}$–$Br'_{t3}$ | 177.2 ± 0.4[b] |
| $Br_{t1}$–$Re_{t2}$–$Br'_{t1}$ | 154.5 ± 0.4[b] |
| $Br_{t2}$–$Re_{t1}$–$Br'_{t2}$ | 155.9 ± 0.5[b] |
| $Re_{t2}$–$Br_{t4}$–$Re'_{t2}$ | 58.6 ± 0.4 |
| $Re_{t2}$–$Br_{t3}$–$Re_{t1}$ | 57.7 ± 0.3 |
| $Br_{t1}$–$Re_{t2}$–$Br_{t3}$ | 90.7 ± 0.2 |
| $Br_{t1}$–$Re_{t2}$–$Br_{t4}$ | 89.0 ± 0.4 |
| $Br_{t2}$–$Re_{t1}$–$Br_{t3}$ | 89.7 ± 0.3 |
| Nonbonded distances, Å. | |
| $Br_{t1}$–$Br_{t2}$ | 3.40 ± 0.02 |
| $Br_{t1}$–$Br''_{t1}$ | 3.35 ± 0.03 |
| $Br_{t1}$–$Br'_{t1}$ | 4.77 ± 0.02 |
| $Br_{t2}$–$Br'_{t2}$ | 4.78 ± 0.02 |
| $Br_{t1}$–$Br_{t3}$ | 3.57 ± 0.03 |
| $Br_{t1}$–$Br_{t4}$ | 3.46 ± 0.03 |
| $Br_{t2}$–$Br_{t3}$ | 3.52 ± 0.02 |

[a] Intervals given are standard deviations. [b] These angles are measured on the outside of the molecule and are thus <180° since the angles $Re_{t2}$–$Br_{t4}$–$Re'_{t2}$ and $Re_{t2}$–$Br_{t3}$–$Re_{t1}$ are <60°.

Table V

Mean Distances and Angles in $Re_3Br_9$ Averaged According to $D_{3h}$ Symmetry[a,b]

| | |
|---|---|
| Re–Re, Å. | 2.465 ± 0.008 |
| Re–$Br_n$, Å. | 2.447 ± 0.007 |
| Re–$Br_b$, Å. | 2.543 ± 0.015 |
| Re–Re–Re, deg. | 60.00 ...[c] |
| $Br_n$–Re–$Br_n$, deg. | 155.0 ± 0.3 |
| $Br_b$–Re–$Br_b$, deg. | 178.0 ± 0.3 |
| Re–$Br_b$–Re, deg. | 58.0 ± 0.3 |
| $Br_n$–Re–$Br_b$, deg. | 89.8 ± 0.2 |

[a] Intervals represent standard deviations of the mean. [b] $Br_b$ = bridging bromine; $Br_n$ = nonbridging bromine. [c] This result is required by geometry.

bridging) distances $\Delta/\Sigma\sigma = 0.5$, and for the Re–Br(bridging) distances the several $\Delta/\Sigma\sigma$ values are 2.0, 1.0, and 0.4. Similar statements can be made concerning the angles. For purposes of discussion, we shall use distances and angles which are weighted averages according to $D_{3h}$ symmetry; these are given in Table V.

The dimensions of the $Re_3Br_9$ group may be compared with those of the $Re_3Cl_9$ group as it occurs in various compounds.[3,5,6,8,9] Most important is the presence of a triangular cluster of rhenium atoms with a mean Re–Re distance, 2.465 ± 0.008 Å., which is not significantly different from those in the $Re_3$ clusters in the chloro compounds where Re–Re distances of 2.48 ± 0.01,[3] 2.493 ± 0.004,[6] and 2.489 ± 0.006[5] Å. have been found. Further, the general structure of the $Re_3Br_9$ group is very similar to that of the $Re_3Cl_9$ group in all respects. The difference between Re–Br(nonbridging) and Re–Br(bridging) distances, 0.09 ± 0.02 Å., is outside the probable uncertainty, whereas in the $Re_3Cl_9$ species the corresponding differences, 0.03 ± 0.06,[3] 0.06 ± 0.03,[6] and ~0.1 ± 0.1[5] Å., were not significant. Taking the covalent radii[20a] of Br and Cl as 1.14 and 0.99 Å., respectively, the radius of the Re atom in the $Re_3$ cluster for bonding the nonbridging halogen atoms is found to be 1.31 ± 0.01 Å. for $Re_3Br_9$ and in the several $Re_3Cl_9$ species 1.37 ± 0.03,[3] 1.33 ± 0.02,[6] and 1.30 ± 0.06[5] Å.; these four radii are not significantly different from one another.

**The Quinolinium Ion.**—The dimensions obtained for the quinolinium ion, which lies in a plane of symmetry, are not very precise because of the presence of so many heavy atoms in the cell. There is no point, therefore, in reporting them individually. The eleven C–C (or C–N) distances, each with a standard deviation of 0.14 Å., range from a low one of 1.19 Å. to a high one of 1.77 Å. The mean is 1.39 ± 0.04 Å., which is in good agreement with the value to be expected. The C–C–C angles range from 108 to 132°, with individual standard deviations of 8–10°; the mean value of the angles is, for geometrical reasons, 120°.

On the basis of electrostatic considerations, assuming the charge to reside predominantly on the N atom, we tentatively suggest that "$C_3$" may be the nitrogen atom, but the possibilities that $C_4$, $C_7$, or $C_8$ might be N cannot be ruled out with any certainty.

**Electronic Spectra.**—The electronic spectra of the $M_2Re_4Br_{15}$ compounds have been recorded from 300 to 1000 mμ. The results are given in Table VI, along with data on other compounds for comparison, and the spectrum of $(pyH)_2Re_4Br_{15}$, which is typical, is shown in Figure 2. It seems evident from these data that the spectra of the $[Re_4Br_{15}]^{2-}$ compounds are composites of the spectra of $Re_3Br_9$ and $[ReBr_6]^{2-}$. The presence of

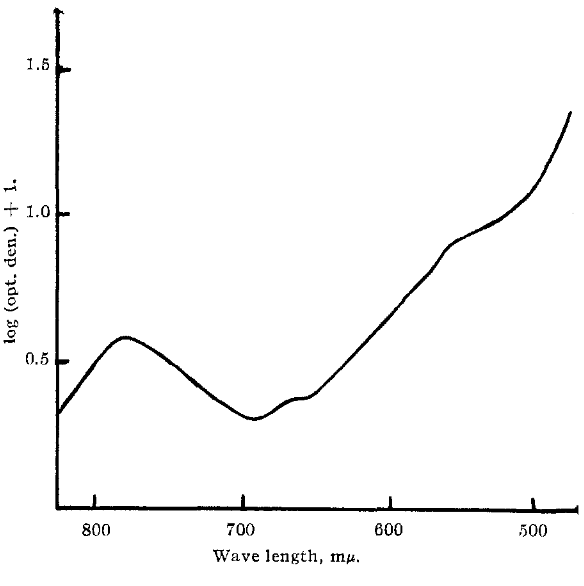

Figure 2.—The visible spectrum of $(pyridinium)_2Re_4Br_{15}$ in acetone solution. The concentration is unknown but is approximately that of a saturated solution.

TABLE VI

ELECTRONIC ABSORPTION SPECTRA OF $M_2Re_4Br_{15}$ COMPOUNDS

| Compd. and state or solvent | Wave lengths of maximum ($\epsilon^a$ or rel. intens.) | | | | | | |
|---|---|---|---|---|---|---|---|
| (1) $(QnH)_2Re_4Br_{15}$ (mull) | 775–800 (m) | 667 (vw) | 560 (m, sh) | 470 (s) | 440 (s) | 375 (s) | 335 (s) |
| (2) $[(C_2H_5)_4N]_2Re_4Br_{15}$ (acetone) | 778 (~600) | 670 (~13) | ~540 (sh$^b$) | | | | |
| (3) $(pyH)_2Re_4Br_{15}$ (acetone) | 777 (~600) | 672 (~13) | ~540 (sh$^b$) | | | | |
| (4) $(QnH)_2Re_3Br_{11}$ (acetone) | 777 (606) | | 535 (sh) | | | | |
| (5) $Re_3Br_9((C_2H_5)_2C_6H_5P)_3$ (chloroform) | 770 (600) | | 535 (sh) | | | | |
| (6) $K_2ReBr_6$ (1 *N* HBr)$^c$ | 755 (11.3) | 665 (11.8) | | | | 353 ($10^4$) | 325 ($10^4$) |

[a] $\epsilon$ represents decadic molar extinction coefficient. [b] sh indicates that the shoulder was so poorly resolved as to preclude a meaningful intensity estimate, that is, one which does not include a major contribution from the underlying absorption which is rising steeply into the ultraviolet; see Figure 2. [c] Taken from C. Rulfs and R. Meyer, *J. Am. Chem. Soc.*, **77,** 4505 (1955).

an $Re_3Br_9$ group in compound 5 has already been demonstrated by the isomorphism of that compound with $Re_3Cl_9[(C_6H_5)(C_2H_5)_2P]_3$, which has been shown by X-ray structural work[6] to contain the $Re_3Cl_9$ group. An extensive series of other compounds,[21] including compound 4, also contain the $Re_3Br_9$ group and characteristically have absorption bands at ~780 and ~540 mμ.

**Acknowledgments.**—We thank the M.I.T. Computation Center for use of the I.B.M. 7094 computer and Dr. R. M. Wing for helpful discussions.

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CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY,
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# Analysis of the Absorption Spectrum of Cesium Uranium(V) Hexafluoride[1]

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The optical absorption spectrum of $CsUF_6$ has been measured from 300 to 50,000 cm.$^{-1}$, and the results have been analyzed in terms of the crystal field theory. The $UF_6^-$ ion, characterized by a single 5f electron on the uranium, has a slightly distorted octahedral configuration. The crystal field parameters found are $\zeta_{5f}$ = 1955 cm.$^{-1}$, $A_4^0\langle r^4\rangle$ = 2351 cm.$^{-1}$, and $A_6^0\langle r^6\rangle$ = 208.8 cm.$^{-1}$. The spectrum is largely vibronic in character, and values of the fundamental vibrational frequencies have been deduced from the splittings observed in the near-infrared and visible regions.

We have previously reported some preliminary results on the near-infrared absorption spectrum of several compounds of the type $MUF_6$, containing uranium in the pentavalent state.[2] It is the purpose of this work to report on the complete spectral analysis of $CsUF_6$ and to ascertain the magnitude of the crystal field parameters responsible for the salient features of the observed absorption spectrum.

Although intensive investigation of the optical behavior of the first inner transition series, characterized by the presence of 4f electrons, has been carried out, relatively little data have appeared on the actinide elements with the $5f^n$ electronic configuration.[3–5] In particular, of those elements possessing a $5f^1$ configuration in chemically accessible valence states, only three have been prepared: Pa(IV), U(V), and Np(VI). The optical and magnetic properties of Pa(IV) have previously been treated[6] as have those for Np(VI),[7–9] and it was therefore felt to be desirable to augment these data with information on U(V).

The optical absorption spectra of compounds containing actinide ions may be explained in terms of the incomplete 5f electronic shell, and consist in the main of fairly sharp groups of lines corresponding to transitions between the ground state and the upper Stark levels of the ions. The free ion splittings, due to interelectronic repulsion and spin–orbit coupling, are further augmented by the electrostatic field generated by the other ions present in the environment. These surrounding charges distort the free-ion electronic wave functions and give rise to crystal field splittings of the order of several thousand cm.$^{-1}$, whereas the analogous splittings in lanthanide complexes are a factor of ten smaller. We may envision the following cases according to the relative strengths

[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

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