or only slowly, to $[Re_2X_8]^{2-}$. It is also puzzling that no other reducing agents have been found which lead to any isolable quantity of $[Re_2X_8]^{2-}$ salts, although $NaBH_4$ and hydrazine have been tried under a variety of conditions. The mechanism by which the binuclear ions are formed from the mononuclear starting material is at present entirely obscure.

Characteristic Properties of the $[Re_2X_8]^{2-}$ Ions.—The magnetic susceptibility of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ was found to be -530×10^{-6} c.g.s. unit at 25°. From Pascal's constants[21] for the cations and the chlorine atoms, and taking -40×10^{-6} for a rhenium atom, we estimate the diamagnetic susceptibility to be about -600×10^{-6}. Thus, while there may be a small, probably temperature-independent paramagnetism, the $[Re_2Cl_8]^{2-}$ ion is essentially diamagnetic. It has no unpaired electrons and thus consists entirely of closed shells of electrons. A treatment of its electronic structure must account for this fact.

Other properties of the $[Re_2X_8]^{2-}$ compounds have been mentioned and discussed above. It remains only to report their electronic spectra.

Electronic Absorption Spectra.—The electronic absorption spectra in the visible and near-ultraviolet regions for the $[Re_2Cl_8]^{2-}$ and $[Re_2Br_8]^{2-}$ ions have been measured by reflectance on all the compounds prepared and are essentially constant and characteristic. Figure 1 shows the complete spectrum of the $[Re_2Cl_8]^{2-}$ ion from 200 to 800 mμ and Table IV gives numerical data for this spectrum recorded in acidified methanol as well as for spectra recorded in other solvents.

Table IV

Spectral Data for $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$

Solvent	Maxima		Molar extinction coeff.	Oscillator strength[a]
	mμ	cm.$^{-1}$		
Methanol[b]	690	14,500	1530	0.023
	305	32,800	5650	0.31
	255	39,200	8840	0.65
Acetonitrile	680	14,700	2340	0.035
	307	32,600	8670	0.48
	250	40,000	9970	0.73
Acetone	680	14,700	2480	0.030

[a] Calculated from the formula $f = 4.6 \times 10^{-9}\epsilon_{\max}\Delta\nu$, where $\epsilon_{\max}$ is the decadic molar extinction coefficient and $\Delta\nu$ is the frequency difference, in cm.$^{-1}$, between the points where ϵ is ~0. For the higher energy peaks, $\Delta\nu$ is estimated by resolution of the observed envelope into Gaussian peaks. [b] Containing 1 ml. of concentrated aqueous HCl per 100 ml.

It may first be noted that this spectrum is quite different from that of the $[Re_3Cl_{12}]^{3-}$ ion, or those of any compounds containing the Re_3Cl_9 group,[4-6] and is sufficient evidence, in itself, that we are dealing here with a different type of compound.

The spectrum consists of three bands, one at ~14,500 cm.$^{-1}$ which, from its oscillator strength of ~0.03, is a forbidden band and two others at ~33,000 and ~40,000 cm.$^{-1}$ which are presumably electric-dipole-allowed transitions since their oscillator strengths are ~0.4 and ~0.7, respectively. Discussion of the assignments of these bands will be given in a later article. The spectrum of the $[Re_2Br_8]^{2-}$ ion is similar to that of the $[Re_2Cl_8]^{2-}$ ion in the red, but absorption rises sharply around 450 mμ. More extensive experimental studies of the spectra are being conducted.

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(21) See, for example, P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, New York, N. Y., 1956, p. 93.

Contribution from the Department of Chemistry,
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The Crystal and Molecular Structure of Dipotassium Octachlorodirhenate(III) Dihydrate, $K_2[Re_2Cl_8]\cdot 2H_2O$[1]

By F. A. Cotton and C. B. Harris

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A three-dimensional, single crystal X-ray diffraction study of the structure of $K_2[Re_2Cl_8]\cdot 2H_2O$ is reported. The crystals are triclinic with $a = 6.75$, $b = 7.86$, and $c = 7.61$ Å. and $\alpha = 102.0°$, $\beta = 109°$, and $\gamma = 105°$. There is one formula unit in the cell, and the space group is $P\bar{1}$. The $[Re_2Cl_8]^{2-}$ ion therefore has a center of symmetry; its idealized point symmetry is 4/mmm (D_{4h}). The mean Re–Cl distance is 2.29 Å., the mean Re–Re–Cl angle is 104°, the mean Cl–Re–Cl angle is 87°, and the Re–Re distance is 2.24 Å. The water molecules are coordinated to K^+ ions.

Introduction

The preparation and characterization of compounds containing the octachlorodirhenate(III) and octabromodirhenate(III) ions, $[Re_2Cl_8]^{2-}$ and $[Re_2Br_8]^{2-}$, has been reported.[2] The full characterization of these species requires both chemical and X-ray evidence. The preceding paper[2] describes the chemistry and certain physical properties of various compounds; this paper reports an X-ray diffraction study of the crystal and molecular structure of one such compound, namely, $K_2[Re_2Cl_8]\cdot 2H_2O$, of sufficient accuracy to show unambiguously the structure of the $[Re_2Cl_8]^{2-}$ ion.

Experimental

The crystals of $K_2[Re_2Cl_8]\cdot 2H_2O$ were obtained from a sample of the compound prepared in a manner described elsewhere.[2]

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(1) Supported by the U. S. Atomic Energy Commission.

(2) F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, **4**, 326 (1965).

The crystal class and unit cell dimensions were established from zero layer Weissenberg photographs. The crystals are triclinic with the dimensions: $a = 6.75_2$ Å.; $b = 7.85_5$ Å.; $c = 7.61_0$ Å.; $\alpha = 102._0°$; $\beta = 108.9°$; $\gamma = 104.8°$. The calculated density assuming one formula weight per unit cell is 3.66 g. cm.$^{-3}$; the approximate density, estimated by flotation in CH_2I_2, is 3.5 g. cm.$^{-3}$, thus establishing that $Z = 1$.

Intensity data were collected by the equi-inclination Weissenberg method with Cu Kα radiation using a crystal with approximate dimensions 0.02 × 0.02 × 0.05 mm. The levels $0kl$–$4kl$ were recorded; 579 reflections within half a sphere ($h \geqslant 0$) with $\sin \theta/\lambda \leqslant 45°$ were recorded.

Intensities were estimated visually using an intensity wedge prepared by timed exposures of one reflection from the same crystal. On upper layers the elongated spots read were corrected for elongation. Lorentz and polarization corrections were made, but in view of the small size of the crystal, absorption corrections were omitted ($\mu = 480$ cm.$^{-1}$; $\mu t_{\max} = 2.5$).

Determination of Structure

Using the corrected intensities, a three-dimensional Patterson synthesis was computed.[3] The Re–Re vector was immediately obvious. Placing one Re atom at the origin, coordinates for the other were derived. A Fourier synthesis was then computed[3] using phases determined by Re atoms alone and assuming the acentric space group P1. The eight chlorine atoms and two potassium atoms were found in this Fourier map. The positional parameters for these atoms as well as five scale factors (one for each level) were subjected to one cycle of full-matrix least-squares refinement.[4] The atomic scattering factors used here and subsequently were taken from the International Tables.[5] Those of Table 3.3.1A were used for K^+, Cl^-, and O^0, while those for Re^0 were taken from Table 3.3.1B. No corrections were made for anomalous dispersion. The set of calculated structure factors now at hand was used to compute a three-dimensional difference Fourier function from which all Re, K, and Cl atoms were removed. Only two significant peaks appeared; these were assigned to the oxygen atoms.

The positional parameters of all 14 atoms as well as a scale factor for each level were now subjected to two cycles of full-matrix least-squares refinement. In these cycles, temperature parameters of 1.0 for Re, 2.0 for K and Cl, and 4.0 for O were assigned and kept fixed. The calculated structure factors obtained from the second of these cycles were used to compute a three-dimensional Fourier map, which showed no significant unexplained peaks and which also showed an essentially centric distribution of atoms about the midpoint of the Re–Re line. It was therefore concluded that the correct space group is $P\bar{1}$.

Using $P\bar{1}$ and assigning the above-mentioned initial temperature factors and using the average values of the pairs of atomic coordinates for the 21 coordinates now required, eight cycles of full-matrix least-squares refinement were now executed. The scale factors were not varied. Following this, one cycle was run in which the 21 positional parameters and the five scale factors were varied, but not the temperature factors. Finally, one cycle was run varying positional parameters and temperature parameters, but not the scale factors. The residual[6] was now 0.168 and the changes in positional parameters were less than the estimated standard deviations. As a final check on the correctness of the structure a three-dimensional difference Fourier map was computed. It showed no peaks of significant magnitude. The relatively high value of the final residual is probably due to inaccurate reading of spots from the very small crystal and to the lack of absorption corrections.

The final set of calculated structure factors (F_c) together with the observed absolute values of the structure factors are listed in Table I. The atom coordinates and isotropic temperature factors are listed in Table II. The standard deviations, σ, were obtained from the least-squares formula

$$\sigma^2(j) = a_{jj}(\Sigma w\Delta^2)/(m - n)$$

where a_{jj} is a diagonal element in the matrix inverse to the normal equation matrix.

Discussion

The $[Re_2Cl_8]^{2-}$ Ion.—The two $ReCl_4$ halves of the ion are related by a crystallographic center of symmetry. This fact requires that the rotomeric configuration of the $[Re_2Cl_8]^{2-}$ ion be the eclipsed one. The principal dimensions of the ion are listed in Table III. From these, it can be seen that the symmetry of the ion is D_{4h} (4/mmm) within the significance of the individual dimensions. Thus all Re–Cl bonds have lengths in the range 2.29 ± 0.03 Å., all Cl–Re–Cl angles are in the range 87 ± 2°, and all Re–Re–Cl angles are in the range 103.7 ± 2.1°. Figure 1 is a sketch of the

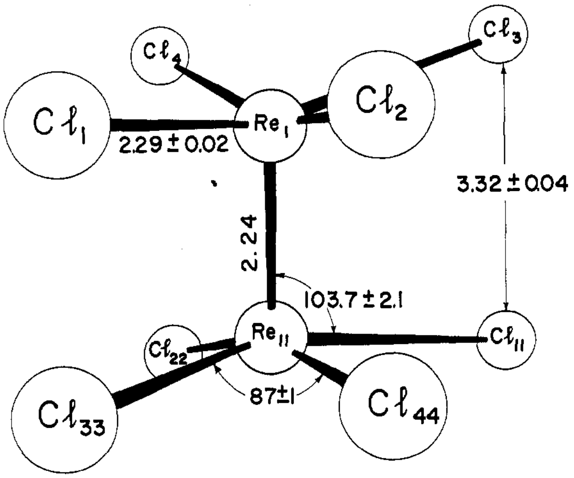

Figure 1.—A sketch of the $[Re_2Cl_8]^{2-}$ ion in $K_2[Re_2Cl_8]\cdot 2H_2O$. The numbering of atoms with single subscripts corresponds with that in Tables II and III. An atom with a double subscript is related to the atom with the corresponding single subscript by the center of inversion. The distances and angles are the averages of those in Table III, with the intervals representing mean deviations of the individual dimensions from these averages.

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(3) Using ERFR-2, a two- and three-dimensional Fourier program for the IBM 709/7090, 1962, by W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende.

(4) Using a full-matrix least-squares refinement program for the IBM 709/7090, 1962, by C. T. Prewitt.

(5) International Tables for X-Ray Crystallography, Vol. III, Kynoch Press, Birmingham, England, 1962.

(6) Residual is $\Sigma||F_o| - |F_c||/\Sigma|F_o|$; the refinement program, however, minimizes $\Sigma||F_o| - |F_c||^2/\Sigma|F_o|^2$.

Table I

H	K	L	FOB	FCAL
0	0	-1	102	143
0	0	1	93	143
0	0	-2	99	104
0	0	2	113	104
0	0	3	122	94
0	0	-3	116	94
0	0	4	19	18
0	0	4	19	18
0	0	-5	5	4
0	0	5	17	4
0	0	-6	47	-33
0	0	6	46	-33
0	0	-7	69	-52
0	0	7	65	-52
0	0	-8	37	-39
0	0	8	38	-39
0	-1	0	81	147
0	1	0	83	147
0	1	-1	130	131
0	-1	1	130	131
0	1	1	100	113
0	1	-2	120	104
0	-1	2	120	104
0	1	2	59	50
0	1	3	60	45
0	-1	3	116	80
0	1	-4	26	24
0	1	4	65	51
0	-1	4	32	24
0	-1	5	48	31
0	1	5	37	27
0	1	-5	41	31
0	1	-6	45	-34
0	1	6	42	-33
0	-1	6	51	-34
0	-1	7	90	-76
0	1	-7	92	-76
0	1	7	31	-25
0	-2	0	92	121
0	2	0	96	121
0	-2	1	129	131
0	2	1	27	27
0	2	-2	37	28
0	-2	2	38	28
0	2	2	116	102
0	2	-3	106	57
0	-2	3	76	57
0	2	3	41	29
0	2	-4	90	63
0	-2	4	90	63
0	2	4	26	19
0	2	5	5	5
0	-2	5	59	41
0	2	-5	62	41
0	-2	6	5	3
0	2	-6	5	3
0	2	6	66	-57
0	2	7	54	-50
0	-2	7	35	-26
0	-3	0	137	174
0	3	0	179	174
0	-3	1	134	177
0	3	1	104	91
0	3	2	61	53
0	-3	2	118	88
0	3	3	130	36
0	-3	3	143	107
0	3	-3	79	107
0	3	-4	14	52
0	3	4	18	0
0	-3	4	78	52
0	-3	5	21	19
0	3	-5	34	19
0	3	5	46	-38
0	3	-6	58	29
0	-3	6	38	29
0	3	6	76	-58
0	-3	7	61	-40
0	-4	0	105	91
0	4	0	105	91
0	4	1	89	74
0	-4	1	149	151
0	-4	2	138	123
0	4	2	64	50
0	4	3	5	8
0	-4	3	102	83
0	4	4	42	33
0	-4	4	78	59
0	-4	5	56	44
0	4	5	29	-19
0	-4	6	5	1
0	-4	7	64	-48
0	-5	0	50	45
0	5	0	52	45
0	5	1	56	40
0	5	2	61	44
0	5	3	27	23
0	-6	0	62	71
0	-7	0	57	45
0	-8	0	39	30
0	-9	0	47	36
1	0	1	13	12
1	0	-2	121	117
1	0	2	42	-33
1	0	-3	195	221
1	0	3	92	-93
1	0	-4	140	125
1	0	4	69	-62
1	0	-5	89	88
1	0	5	65	-75
1	0	-6	77	75
1	0	6	59	-62
1	0	-7	21	25
1	0	7	46	-54
1	1	0	14	15
1	-1	-1	99	113
1	1	1	67	80
1	-1	1	4	-0
1	1	-2	115	85
1	-1	2	14	10
1	-1	-2	84	64
1	1	2	26	19
1	-1	3	100	-83
1	1	-3	111	90
1	-1	-3	135	136
1	1	3	70	-69
1	-1	4	138	-124
1	-1	-4	126	100
1	1	-4	164	138
1	1	4	34	-37
1	1	-5	79	78
1	-1	-5	30	34
1	1	5	44	-48
1	-1	5	65	-63
1	-1	-6	54	51
1	1	-6	67	63
1	-1	6	73	-76
1	1	6	71	-74
1	1	-7	37	40
1	1	7	40	-56
1	-1	7	51	-63
1	2	0	29	32
1	-2	-1	42	44
1	2	1	10	6
1	2	-1	64	94
1	-2	1	69	59
1	-2	2	107	80
1	-2	-2	93	91
1	2	2	30	-32
1	-2	-3	114	101
1	2	-3	119	94
1	2	3	77	-88
1	-2	3	54	-44
1	2	-4	154	115
1	-2	-4	55	58
1	2	4	71	-73
1	-2	4	53	-44
1	-2	-5	63	68
1	2	-5	36	39
1	-2	5	31	-39
1	2	5	66	-70
1	2	-6	41	47
1	-2	-6	31	34
1	-2	6	72	-75
1	2	6	49	-52
1	2	-7	58	52
1	2	7	39	-53
1	-2	7	53	-59
1	3	0	16	12
1	-3	-1	78	69
1	3	-1	21	18
1	-3	1	61	52
1	3	1	15	-8
1	-3	2	6	3
1	-3	-2	128	136
1	3	2	91	-98
1	-3	3	4	6
1	-3	-3	155	161
1	3	3	84	-84
1	-3	-4	61	74
1	-3	4	73	-66
1	3	4	54	-59
1	-3	-5	52	62
1	3	-5	118	94
1	-3	5	51	-50
1	3	5	66	-70
1	3	-6	64	76
1	3	6	40	-48
1	-3	6	47	-47
1	-3	7	51	-59
1	4	0	4	-2
1	-4	1	21	23
1	4	1	33	21
1	-4	-1	104	93
1	-4	-2	115	117
1	-4	2	35	38
1	4	2	43	-44
1	-4	-3	97	102
1	4	3	57	-58
1	-4	3	29	-25
1	-4	4	111	-106
1	-4	-4	54	63
1	4	4	35	-40
1	-4	-5	36	42
1	-4	5	77	-66
1	4	5	44	-54
1	-4	6	57	-63
1	-4	7	62	-73
1	5	0	38	34
1	-5	-1	50	48
1	-5	1	65	72
1	5	1	16	-14
1	-5	-2	83	93
1	-5	2	50	32
1	5	2	53	-52
1	-5	3	14	13
1	-5	-3	52	51
1	5	3	55	-44
1	-5	4	31	-36
1	-5	6	44	-54
1	-5	7	44	-62
1	-6	0	67	67
1	-6	1	50	51
1	-6	-1	64	57
1	-6	2	22	23
1	-6	-2	96	102
1	6	2	31	-84
1	-6	3	23	39
1	-6	4	4	-14
1	-6	5	37	-42
1	-6	6	15	-18
1	-7	0	64	60
1	-7	-1	87	97
1	-7	1	58	59
1	-7	2	33	36
1	-7	3	4	15
1	-7	4	33	-33
1	-7	5	47	-55
1	-8	0	26	33
2	0	0	107	-156
2	0	1	53	-58
2	0	2	122	-116
2	0	-2	28	7
2	0	-3	36	16
2	0	3	89	-91
2	0	-4	57	39
2	0	4	69	-73
2	0	-5	101	78
2	0	5	80	-93
2	0	-6	117	106
2	0	6	25	-33
2	-1	0	102	-129
2	1	0	61	-87
2	-1	1	147	-151
2	1	1	52	-60
2	-1	2	114	-106
2	1	2	68	-71
2	-1	-2	8	-4
2	-1	-3	49	37
2	1	-3	12	0
2	1	3	87	-98
2	-1	3	92	-86
2	-1	-4	88	71
2	1	-4	90	64
2	-1	4	89	-83
2	1	4	88	-93
2	-1	-5	50	36
2	1	-5	68	50
2	1	5	57	-63
2	-1	5	73	-68
2	-1	-6	93	90
2	1	-6	59	51
2	1	6	15	-22
2	-1	6	5	-14
2	1	-7	115	101
2	-2	0	126	-92
2	2	0	99	-96
2	-2	-1	79	75
2	-2	1	56	-61
2	2	1	96	-93
2	2	-1	73	-86
2	2	2	111	-102
2	-2	-2	46	37
2	-2	2	43	-45
2	-2	3	119	-116
2	-2	-3	42	33
2	2	3	56	-53
2	-2	-4	62	53
2	2	-4	60	39
2	-2	4	80	-81
2	2	4	65	-72
2	2	-5	48	31
2	-2	-5	53	48
2	2	5	27	-33
2	-2	5	73	-81
2	2	-6	80	56
2	-2	-6	70	68
2	-2	6	52	-50
2	2	-7	96	75
2	3	0	91	-98
2	-3	0	65	-55
2	3	-1	158	-145
2	-3	1	70	-68
2	3	1	77	-76
2	-3	-1	5	-9
2	-3	-2	43	36
2	3	2	85	-86
2	-3	2	73	-73
2	-3	-3	60	51
2	-3	3	92	-84
2	3	3	66	-65
2	-3	-4	53	51
2	3	4	55	-59
2	-3	4	73	-76
2	-3	-5	59	80
2	-3	5	88	-100
2	3	5	30	-34
2	-3	6	79	-79
2	-4	0	73	-58
2	4	0	73	-68
2	-4	1	141	-148
2	-4	-1	5	8
2	4	-1	57	-58
2	4	1	73	-68
2	-4	2	97	-83
2	4	2	72	-66
2	-4	-2	5	-2
2	-4	-3	77	71
2	-4	3	89	-89
2	4	3	72	-74
2	-4	-4	62	58
2	-4	4	91	-91
2	4	4	77	-76
2	-4	-5	70	69
2	-4	5	67	-74
2	-4	6	77	-53
2	-5	0	16	-18
2	5	0	58	-46
2	-5	-1	49	38
2	5	1	88	-79
2	-5	1	60	-67
2	-5	-2	48	40
2	-5	2	45	-52
2	5	2	65	-59
2	-5	-3	39	33
2	5	3	48	-50
2	-5	3	73	-81
2	-5	-4	41	38
2	-5	4	78	-86
2	-5	5	44	-59
2	-5	6	61	-73
2	-6	0	22	19
2	-6	-1	20	12
2	-6	1	34	-37
2	-6	-2	48	39
2	-6	2	38	-46
2	-6	3	33	-41
2	-6	4	49	-60
2	-6	5	63	-78
2	-7	0	21	2
2	-7	-1	19	17
2	-7	1	64	-65
2	-7	2	70	-70
2	-7	3	44	-43
2	-7	4	63	-79
2	-7	5	41	-58
3	0	0	90	-113
3	0	-1	59	-119
3	0	1	73	-90
3	0	2	96	-95
3	0	-2	58	-63
3	0	-3	177	-132
3	0	3	29	-27
3	0	-4	135	-96
3	0	4	19	-15
3	0	5	6	5
3	0	-5	15	-9
3	0	-6	6	-11
3	-1	0	54	-68
3	1	0	83	-103
3	1	1	109	-133
3	1	-1	63	-88
3	-1	1	80	-93
3	1	2	53	-49
3	-1	2	68	-70
3	-1	-2	87	-112
3	-1	-3	143	-111
3	-1	3	31	14
3	1	-3	89	-69
3	1	3	6	-13
3	-1	-4	119	-81
3	-1	4	6	6
3	1	-4	67	-50
3	1	4	6	-12
3	-1	5	6	0
3	1	-5	28	6
3	-1	-5	6	-7
3	1	-6	17	3
3	-1	-6	22	12
3	1	-7	44	29
3	-2	0	129	-125
3	2	0	56	-54
3	-2	-1	47	-60
3	-2	1	95	-107
3	2	1	68	-70
3	2	-1	87	-107
3	2	-2	97	-96
3	-2	2	96	-94
3	2	2	19	-18
3	-2	-2	85	-72
3	-2	-3	108	-82
3	2	3	37	27
3	-2	3	30	-27
3	2	4	6	7
3	-2	-4	29	13
3	2	-4	45	-101
3	-2	4	6	-9
3	-2	5	6	9
3	-2	-5	35	17
3	2	-5	35	-32
3	2	-6	6	21
3	-2	-6	23	15
3	2	-7	6	6
3	-3	0	89	-109
3	3	0	87	-81
3	-3	-1	122	-57
3	-3	1	93	-90
3	3	1	76	-60
3	3	-1	87	-76
3	-3	2	118	-126
3	-3	-2	54	-50
3	3	2	21	-12
3	-3	3	95	-85
3	-3	-3	99	-89
3	3	3	22	-11
3	3	4	6	8
3	-3	-4	22	-21
3	-3	4	6	-16
3	-3	-5	26	14
3	-3	5	30	-28
3	4	0	104	-89
3	-4	0	82	-97
3	-4	-1	120	-91
3	-4	1	87	-85
3	4	1	88	-82
3	-4	-2	138	-122
3	-4	2	105	-98
3	4	2	18	-11
3	-4	3	37	-39
3	-4	-3	81	-74
3	4	3	6	-7
3	-4	-4	19	-21
3	-4	4	6	-6
3	-4	5	19	-20
3	-5	0	80	-93
3	5	0	83	-57
3	-5	1	90	-96
3	-5	-1	61	-50
3	5	1	28	-29
3	5	2	15	5
3	-5	2	66	-67
3	-5	-2	78	-72
3	-5	3	65	-67
3	-5	-3	42	-41
3	-5	4	6	-6
3	-5	5	6	9
3	-6	0	71	-66
3	-6	1	62	-67
3	-6	-1	42	-40
3	-6	-2	48	-45
3	-6	2	85	-92
3	-6	3	96	-99
3	-6	4	28	-31
3	-6	5	21	-26
3	-7	0	58	-52
3	-7	-1	80	-67
3	-7	1	84	-82
3	-7	2	64	-71
3	-7	3	48	-66
3	-7	4	32	-43
4	0	0	25	-22
4	0	-1	47	-54
4	0	1	6	-8
4	0	2	34	36
4	0	-2	56	-92
4	0	-3	116	-102
4	0	3	39	38
4	0	-4	106	-81
4	0	4	62	75
4	0	-5	84	-68
4	0	-6	100	-84
4	0	-7	84	-78
4	-1	0	38	36
4	1	0	6	-1
4	-1	1	25	17
4	1	-1	20	-22
4	-1	-1	33	-43
4	1	1	6	-3
4	-1	2	20	18
4	1	2	39	42
4	1	-2	74	-129
4	-1	-2	7	-76
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4	1	3	46	47
4	-1	-3	52	-51
4	-1	-4	144	-111
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4	1	4	50	58
4	1	-4	97	-83
4	1	-5	104	-84
4	-1	5	44	64
4	-1	-5	87	-72
4	1	-6	58	-49
4	-1	-6	94	-76
4	-2	0	13	6
4	2	0	36	29
4	2	-1	17	3
4	2	1	29	27
4	-2	-1	61	-76
4	-2	1	17	-11
4	-2	2	26	25
4	2	2	35	30
4	-2	-2	80	-112
4	2	-2	36	-40
4	-2	3	56	48
4	2	3	34	38
4	-2	-3	97	-90
4	-2	4	29	33
4	-2	-4	78	-71
4	-2	5	57	67
4	-2	-5	78	-65
4	-2	-6	71	-56
4	2	-7	66	-80
4	-3	0	61	-62
4	3	0	24	-11
4	-3	-1	114	-109
4	3	-1	6	14
4	3	1	27	27
4	-3	1	25	-19
4	3	2	43	41
4	3	-2	50	-42
4	-3	-2	97	-92
4	-3	2	6	-4
4	-3	-3	111	-97
4	-3	3	20	21
4	3	3	49	48
4	-3	4	47	55
4	-3	-4	82	-76
4	-3	5	59	79
4	-3	-5	43	-42
4	4	0	6	5
4	-4	0	6	-12
4	-4	-1	107	-91
4	-4	1	20	12
4	4	1	24	21
4	4	2	45	41
4	-4	2	23	-20
4	-4	-2	85	-64
4	-4	3	39	36
4	-4	-3	84	-77
4	-4	4	42	40
4	-4	-4	95	-82
4	-4	5	41	61
4	-5	0	28	-31
4	-5	1	6	1
4	-5	-1	80	-70
4	-5	-2	100	-82
4	-5	2	20	14
4	-5	3	30	27
4	-5	-3	80	-78
4	-5	4	29	29
4	-5	5	33	46
4	-6	0	82	-90
4	-6	1	24	-15
4	-6	-1	99	-88
4	-6	-2	76	-64
4	-6	2	29	-23
4	-6	3	6	-3
4	-6	4	28	34
4	-7	0	47	-56
4	-7	1	20	-20
4	-7	2	22	-22

Table II

Final Positional and Isotropic Temperature Parameters[a]

Atom	*x/a*	*y/b*	*z/c*	*B*
Re	0.8193 (8)	0.9854 (5)	0.9504 (5)	0.91 (7)
Cl_1	0.754 (5)	0.046 (3)	0.226 (3)	1.3 (4)
Cl_2	0.826 (6)	0.279 (4)	0.957 (3)	2.1 (5)
Cl_3	0.709 (5)	0.909 (3)	0.615 (3)	1.5 (5)
Cl_4	0.639 (5)	0.675 (4)	0.892 (3)	1.7 (5)
K	0.878 (5)	0.659 (4)	0.326 (3)	2.7 (5)
O	0.78 (2)	0.46 (1)	0.56 (1)	3 (2)

[a] Numbers in parentheses are standard deviations occurring in the last significant figure for each parameter.

$[Re_2Cl_8]^{2-}$ ion showing the numbering system for the atoms and giving the mean values for each type of principal dimension together with the mean deviation of the individual dimensions of each type from their mean value. The eight chlorine atoms lie approximately at the corners of a cube with edges *ca.* 3.2 Å. in length.

Table III

Crystallographically Independent[a] Distances and Angles in $[Re_2Cl_8]^{2-}$

Distances, Å.		Angles, deg.	
Re_I–Re_{II}	2.241 (7)	Cl_1–Re_I–Cl_2	85.4 (8)
Re_I–Cl_1	2.26 (2)	Cl_2–Re_I–Cl_3	88 (1)
Re_I–Cl_2	2.29 (3)	Cl_3–Re_I–Cl_4	86.0 (9)
Re_I–Cl_3	2.31 (2)	Cl_4–Re_I–Cl_1	87.9 (8)
Re_I–Cl_4	2.31 (3)	Re_{II}–Re_I–Cl_1	105.8 (6)
Cl_2–Cl_{44}	3.31 (5)	Re_{II}–Re_I–Cl_2	103.4 (7)
Cl_3–Cl_{11}	3.33 (4)	Re_{II}–Re_I–Cl_3	101.7 (6)
		Re_{II}–Re_I–Cl_4	103.6 (6)

[a] The numbers in parentheses are standard deviations occurring in the last significant figure of each dimension. They were calculated from the standard deviations in Table II by the method of D. W. J. Cruickshank and A. P. Robertson, *Acta Cryst.*, 6, 698 (1949), using a molecular geometry program for the IBM 709/7090/7094 computer written by Dr. J. S. Wood.

The dimensions of the $[Re_2Cl_8]^{2-}$ ion may be compared with those of the Re_3Cl_9 group which has been found in Re(III) compounds derived directly from rhenium(III) chloride[7-10] and in rhenium(III) chloride itself.[11] The average Re–Re distance in the triangular Re_3 cluster which occurs in these compounds is 2.48 Å. Since the order of the Re–Re bond is found to be 2.0 by a molecular orbital treatment,[12,13] it is evident that the Re–Re bond order in $[Re_2Cl_8]^{2-}$ must be quite high indeed, since the bond is some 0.24 Å. shorter. It will be shown subsequently[13] that it is, in fact, a quadruple bond. The Re–Cl distance in $[Re_2Cl_8]^{2-}$, 2.29 ± 0.02 Å., is approximately the same as those for Re to nonbridging Cl atoms in the Re_3Cl_9 derivatives. Thus, for $[Re_3Cl_{12}]^{3-}$ we have[7] 2.36 ± 0.03 Å., and for $Re_3Cl_9[(C_2H_5)_2C_6H_5P]_3$ the crystallographically independent distances[10] of this kind are 2.32 ± 0.02 and 2.31 ± 0.02 Å.

Crystal Packing.—The crystal of $K_2[Re_2Cl_8]\cdot 2H_2O$ is an array of K^+ and $[Re_2Cl_8]^{2-}$ ions and H_2O molecules. The arrangement of nearest neighbors around the potassium ions (both of which are crystallographically equivalent) is quite irregular. The K^+ ion lies approximately above the center of the square set of four Cl atoms, Cl_1, Cl_4, Cl_{22}, Cl_{33}, of one $[Re_2Cl_8]^{2-}$ ion. These four chlorine atoms lie at distances of 3.52, 3.21, 3.41, and 3.63 Å., respectively, from K^+, each distance having a standard deviation of 0.03–0.04 Å. In other directions about the K^+ ion there are Cl atoms of other $[Re_2Cl_8]^{2-}$ ions at distances of 3.31, 3.38, 3.40, 3.50, 4.52, and 4.98 Å.; at least the first four of these are to be considered coordinated. Finally, the oxygen atom is 2.66 ± 0.08 Å. from K^+. The O atom has six Cl atoms at distances of 3.3–3.7 Å. from it, in directions such that O–H···Cl bonds might exist; however, these distances are all somewhat greater than those considered typical of $HOH\cdots Cl^-$ bonds.[14] The eight K^+–Cl distances in the range 3.21–3.63 Å. and the K^+–O distance of 2.66 Å. are all reasonable.

The closest intermolecular Re···Cl contacts are 3.58, 4.66, and 4.84 Å., all with standard deviations of 0.03 Å. None of these Cl atoms lies at all close to the extended Re–Re line. Thus, each Re atom can be considered to be coordinated by only the four Cl atoms to which it is bound in its own $[Re_2Cl_8]^{2-}$ ion.

Comparison With Previous Work.—As shown in the preceding paper,[2] $K_2[Re_2Cl_8]\cdot 2H_2O$ is the correct formula for a compound previously reported[15] as $KH[ReCl_4]\cdot H_2O$, that is, as a compound of Re(II). An X-ray study has recently been carried out on the corresponding pyridinium compound, written by the Russian workers[15] as $(C_5H_6N)H[ReCl_4]$, by Kuznetsov and Koz'min.[16] They found it to contain a dimeric group, but the formula they assigned to it was $[Re_2Cl_8]^{4-}$. Some of the dimensions they report disagree rather markedly with those we have found in $K_2[Re_2Cl_8]\cdot 2H_2O$; thus they give the Re–Re distance as 2.22 ± 0.02 Å. and the Re–Cl distance as 2.43 ± 0.03 Å. Their method of refinement was described simply as "trial and error," however, and on subjecting their intensity data to full-matrix least-squares refinement, we[17] have effected marked changes in atom coordinates such as to bring the dimensions of the $[Re_2Cl_8]^{2-}$ ion in their compound in good agreement with those of Figure 1. Our reinvestigation of the structure of $(C_5H_6N)_2[Re_2Cl_8]$ as well as an investigation[17] of the corresponding collidinium compound, $(C_8H_{12}N)_2[Re_2Cl_8]$, which has the advantage over the pyridinium salt that it does not form twinned crystals, will be reported in detail later.

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