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The Crystal Structure of Cesium Dodecachlorotrirhenate(III), a Compound with a New Type of Metal Atom Cluster[1a]

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A three-dimensional, X-ray crystallographic investigation of a compound with empirical formula $CsReCl_4$ shows it to contain anions of the composition $[Re_3Cl_{12}]^{3-}$. The structure of this anion consists of an equilateral triangle of chlorine atoms with a rhenium atom at the center of each edge so that the rhenium atoms also form an equilateral triangle (Re–Re, 2.477 Å.). Three more chlorine atoms are bound to each rhenium atom so that the five chlorine atoms bound to each rhenium atom lie, approximately, at five of the six apices of an octahedron. The three nonbridging chlorine atoms lying in the plane of the rhenium atoms are not as closely bound (Re–Cl, ~2.52 Å.) as are the other four (Re–Cl, 2.35–2.39 Å.). The similarity of the intermetal bonded Re_3 cluster discovered here to other sorts of metal atom clusters (triangular, tetrahedral, and octahedral) is briefly discussed.

Introduction

Little has been known with certainty about the structures of Re(III) compounds. It seems to have been generally supposed that those of the types M^IReX_4 and ReX_3L contain tetrahedrally coordinated rhenium. In order to obtain definite information about the structure and bonding in rhenium compounds, a program of chemical, physical, and, particularly, X-ray crystallographic studies has been initiated. This paper reports the first major result of these studies, namely, that the structure of $CsReCl_4$ is much more complex than had been supposed.[2] It has been found that the compound contains $[Re_3Cl_{12}]^{3-}$ anions. Thus its true molecular formula is $Cs_3Re_3Cl_{12}$ and its proper name is cesium dodecachlorotrirhenate(III). The latter formula and name will be used hereafter in this paper.

Experimental

Rhenium trichloride was prepared by thermal decomposition of the pentachloride.[5] $Cs_3[Re_3Cl_{12}]$ was obtained[6] by dissolving $ReCl_3$ in concentrated hydrochloric acid and adding a tenfold excess of CsCl. The dark red precipitate which formed rapidly was filtered and recrystallized twice from hydrochloric acid. A rhenium analysis[7] gave 39.9%; theory, 40.4%. The density, determined by displacement of benzene, was 4.5 g./cc. The magnetic susceptibility, determined by the Gouy method at ~300°K., was -390×10^{-6} c.g.s. unit per mole. The value which can be estimated, using Pascal's constants or other estimated gram-ionic susceptibilities[8] [-35×10^{-6} for Cs^+, -20×10^{-6} for Cl^-, and -30×10^{-6} for Re^{3+}] is -435×10^{-6}.

A positive piezoelectric test, indicating an acentric structure, was obtained.

Intensity data were recorded photographically using a Buerger precession camera and Mo Kα radiation, and the relative intensities were estimated visually using a set of timed exposures made with the same crystal. The crystal itself was of more or less spherical shape and had a mean cross section of ~0.05 mm. No absorption corrections were made.

The precession photographs provided data for determination of the unit cell and space group. The unit cell is orthorhombic, of dimensions $a = 10.69$, $b = 14.00$, and $c = 14.06$ Å., all ±0.02 Å. The following systematic absences were observed: for *hkl*, $k + l \neq 2n$; for *h0l*, $h \neq 2n$.

From the axial lengths, and assuming four formula units, $Cs_3Re_3Cl_{12}$, per cell, the density is calculated to be 4.38 g./cc., in satisfactory accord with the measured value.

TABLE I

TRIAL PARAMETERS FOR HEAVY ATOMS

Atom	Position	*x*	*y*	*z*	*B*
Re_I	8(*c*)	0.127	0.211	0.233	1.6
Re_{II}	4(*b*)	.250	.364	.267	1.6
Cs_I	4(*a*)	.000	.000	.000	3.0
Cs_{II}	4(*b*)	.250	.165	.664	3.0
Cs_{III}	4(*b*)	.250	.443	.900	3.0

Determination of Structure

The first problem was to identify the correct orthorhombic space group. The systematic absences reported above are consistent with each of the following three: Ama2 (No. 40), $A2_1am$ (No. 36), and Amam (No. 63), where the numbers are those of the International Tables,[9] although, in the last two, the *a* and *c* axes have been interchanged so that in all cases they are consistent with the edge lengths as identified above. The first two of these are acentric and thus consistent also with the observed piezoelectric effect, while the third, a centric space group, is not. However, due to the known tendency of our piezoelectric apparatus occasionally to give false signals, Amam was not completely eliminated from consideration at this point. A final decision was based on statistical tests of the centricity or acentricity of the principal zones following the

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(2) A preliminary note describing the completely refined structure, with final parameters, has previously appeared.[3] The structure, at a stage of incomplete refinement, has also been reported in a preliminary note by others.[4] The two studies are in complete accord to within the probable errors of the other results.

(3) J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *J. Am. Chem. Soc.*, **85**, 1349 (1963).

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

(5) L. C. Hurd and E. O. Brimm, *Inorg. Syn.* **1**, 180, 182 (1939).

(6) W. Geilman and F. W. Wrigge, *Z. anorg. allgem. Chem.*, **223**, 144 (1935).

(7) W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, "Applied Inorganic Analysis," John Wiley and Sons, New York, N.Y., 1953, p. 321.

(8) B. N. Figgis and J. Lewis, in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins Ed., Interscience, Publishers, New York, N.Y., 1960, p. 403.

(9) International Tables for X-ray Crystallography, Vol. I and III, Kynoch Press, Birmingham, England, 1952.

TABLE II

FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE PARAMETERS

Atom	Pos.	x	σ_x	y	σ_y	z	σ_z	B	σ_B
$\mathrm{Re_{I}}$	8(*c*)	0.1342	0.0002	0.2150	0.0002	0.2305	0.0007	1.57	0.05
$\mathrm{Re_{II}}$	4(*b*)	.2500	...	.3606	.0003	.2771	.0008	1.56	.08
$\mathrm{Cs_{I}}$	4(*a*)	.0000	...	.0000	...	.0000	...	3.02	.15
$\mathrm{Cs_{II}}$	4(*b*)	.2500	...	.1794	.0007	.6184	.0010	3.81	.18
$\mathrm{Cs_{III}}$	4(*b*)	.2500	...	.4083	.0008	.8943	.0012	4.89	.24
$\mathrm{Cl_{I}}$	4(*b*)	.2500	...	.0281	.0020	.8364	.0024	1.73	.42
$\mathrm{Cl_{II}}$	8(*c*)	.0723	.0019	.3690	.0015	.6998	.0020	2.90	.38
$\mathrm{Cl_{III}}$	4(*b*)	.2500	...	.3380	.0023	.4432	.0026	2.53	.55
$\mathrm{Cl_{IV}}$	8(*c*)	.0944	.0022	.1451	.0018	.3805	.0021	3.36	.44
$\mathrm{Cl_{V}}$	8(*c*)	.0252	.0020	.3557	.0017	.2842	.0024	3.14	.43
$\mathrm{Cl_{VI}}$	4(*b*)	.2500	...	.0784	.0022	.1832	.0026	2.32	.51
$\mathrm{Cl_{VII}}$	4(*b*)	.2500	...	.4446	.0022	.1319	.0026	2.26	.53
$\mathrm{Cl_{VIII}}$	8(*c*)	.0975	.0019	.2563	.0017	.0706	.0019	2.58	.38

method of Howells, Phillips, and Rogers.[10] The results clearly demonstrate that the (001) projection is centric, while (010) is not. This is consistent with Ama2, but not with Amam, where all three are centric, nor with $\mathrm{Ama2_1}$ in which (100) is centric while (001) and (010) are not.

Using the observed relative intensity values, placed on an approximation to absolute scale by Wilson's method,[11] for all reflections listed in Table III, a three-dimensional Patterson function was computed. The possible positions[9] for Cs and Re atoms were 8(*c*), 4(*a*), and 4(*b*). Only one large peak was observed on the Harker line, ($^1/_2 - 2x$, 0, 0), for the 8-fold set, corresponding to an internuclear distance of ~2.6 Å. For chemical reasons, it was assumed that this could only respond to a Re–Re separation, meaning that 8 of the 12 Re atoms lay at the 8(*c*) positions. Examination of the other Harker line, ($^1/_2$, $2y$, 0), for the 8(*c*) set and the Harker section, ($2x$, $2y$, 0), established a self-consistent assignment of the x and y coordinates of these rhenium atoms. Further attempts to extract information by inspection of the Patterson function directly proved fruitless.

A minimum function[12] was then prepared by superposing the point ($2x$, $2y$, 0) over the origin. Only two levels were necessary since all 4-fold sets appear at either $x = 0$ or $x = {}^1/_4$. In the $x = 0$ level, a weak peak remained at $y = 0$ and was assigned to a cesium atom in the 4(*a*) set. In the $x = {}^1/_4$ level, several peaks remained, the strongest appearing only ~2.6 Å. from the 8(*c*) rhenium. This was taken to mean that the remaining four rhenium atoms occupied 4(*b*) positions. Other peaks were assigned to cesium atoms of 4(*b*) sets. Since no z coordinates were fixed, this was done by placing one of the 4(*a*) cesium atoms at the origin and the other z coordinates were then taken from the minimum function. The positional and estimated thermal parameters thus available for the heavy atoms at this stage are listed in Table I.

A structure factor calculation using these parameters yielded a residual, $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, of 0.35.

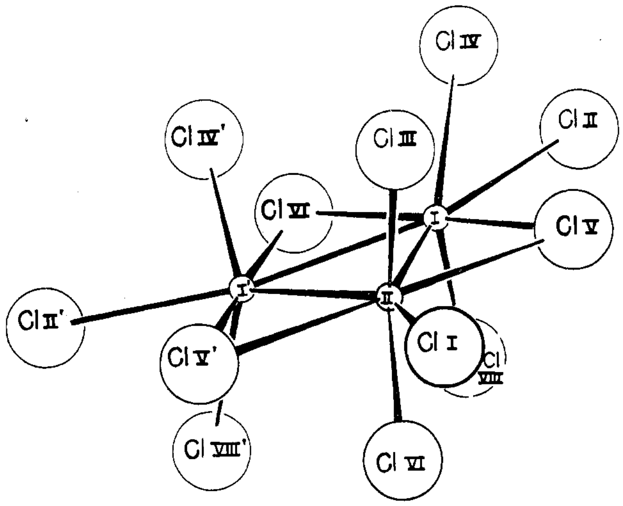

Fig. 1.—Perspective view of the anion $[\mathrm{Re_3Cl_{12}}]^{3-}$. Large circles are chlorine atoms; small circles are rhenium atoms. Roman numerals correspond with those in Tables I, II, and IV.

One cycle of least-squares refinement[13] was run varying the over-all scale factor, three positional parameters, and an isotropic temperature factor for each atom. A Geller correlation matrix[14] was written and examination of it showed that there was a high degree of parameter interaction between (a) the over-all scale factor and the temperature factors and (b) the z coordinates of different atoms. Consequently, refinement was continued allowing only those parameters to vary, in any one cycle, that did not interact strongly with one another. After ten such cycles the residual had dropped to 0.18.

A difference Fourier synthesis was now calculated[15] in which the contributions of the Re and Cs atoms, located at the positions given in the last of the preceding cycles of refinement, were subtracted out. Aside from some small anomalies at and near the positions of the heavy atoms, the difference synthesis showed six well-resolved peaks per asymmetric unit, $\mathrm{Cs_{1.5}Re_{1.5}Cl_6}$, four of them in the mirror plane at $x = {}^1/_4$. A trial structure factor calculation was again made to determine the extent of parameter interaction and it indicated re-

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(10) E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Cryst.*, **3**, 210 (1950).

(11) A. J. C. Wilson, *Nature*, **150**, 152 (1942).

(12) M. J. Buerger, "Vector Space," John Wiley and Sons, New York, N. Y., 1961.

(13) Using a program written by Dr. C. Prewitt for the IBM 7090 computer, which includes an optional subroutine for computing the Geller correlation matrix.[14]

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

(15) W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, ERFRZ IBM 709-7090 Fourier Program, 1962.

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $Cs_3[Re_3Cl_{12}]$

h	k	l	F_o	F_c
2	0	0	9.43	-9.37
4	0	0	6.40	6.44
6	0	0	7.81	-7.92
8	0	0	13.49	14.27
10	0	0	5.48	-5.87
12	0	0	2.24	2.52
3	2	0	7.35	-6.52
4	2	0	12.00	11.73
5	2	0	9.17	8.98
6	2	0	1.41	1.29
7	2	0	1.00	-0.96
8	2	0	3.61	-3.32
9	2	0	1.00	1.03
10	2	0	3.16	2.79
11	2	0	2.45	-2.38
12	2	0	2.83	2.96
13	2	0	2.83	2.74
14	2	0	1.41	-1.03
0	4	0	1.41	-1.26
1	4	0	8.12	8.01
2	4	0	7.14	6.84
3	4	0	2.24	1.62
5	4	0	4.36	-3.95
6	4	0	8.54	8.55
7	4	0	3.16	-3.21
8	4	0	1.73	1.66
9	4	0	3.61	3.71
10	4	0	2.65	2.50
12	4	0	3.16	-3.05
13	4	0	2.83	-2.53
14	4	0	3.00	2.84
0	6	0	3.74	3.69
1	6	0	11.58	-11.86
2	6	0	2.00	1.77
4	6	0	7.62	6.80
7	6	0	5.00	4.58
8	6	0	1.73	1.57
9	6	0	7.75	-7.51
11	6	0	2.00	1.83
12	6	0	2.24	2.17
13	6	0	1.41	1.35
3	11	1	3.00	2.79
4	11	1	6.56	-6.74
5	11	1	4.69	-4.80
6	11	1	3.74	3.25
1	13	1	6.78	-6.71
4	13	1	2.65	2.31
7	13	1	3.46	3.50
9	13	1	5.00	5.20
1	15	1	4.58	-4.17
9	15	1	3.46	-3.29
3	17	1	2.65	-2.58
5	17	1	2.83	-2.84
0	19	1	2.65	2.93
2	0	2	7.00	6.43
4	0	2	7.07	6.87
6	0	2	2.65	2.60
8	0	2	5.66	-5.49
10	0	2	6.08	6.23
2	2	2	4.00	3.69
4	2	2	3.74	-3.53
5	2	2	8.37	-7.90
6	2	2	5.74	5.25
7	2	2	3.16	3.00
8	2	2	6.40	6.39
9	2	2	4.47	4.28
0	4	2	8.31	7.85
1	4	2	4.12	-4.13
2	4	2	4.24	3.47
3	4	2	6.78	-5.98
4	4	2	10.20	9.96
5	4	2	7.14	7.16
6	4	2	3.16	-3.10
8	4	2	3.00	2.46
9	4	2	3.16	-3.35
12	4	2	3.46	3.86
13	4	2	2.83	2.94
1	6	2	10.82	9.73
2	6	2	3.87	3.91
3	6	2	4.80	4.66
4	6	2	2.83	-3.03
5	6	2	3.00	-3.05
6	6	2	3.61	3.73
0	8	0	3.46	3.81
1	8	0	5.10	5.03
2	8	0	4.47	4.47
3	8	0	3.00	3.05
4	8	0	2.00	2.02
5	8	0	4.12	-4.17
7	8	0	2.24	-1.36
9	8	0	4.80	5.36
10	8	0	1.41	1.48
12	8	0	2.00	1.77
13	8	0	2.24	-2.03
0	10	0	1.41	1.16
1	10	0	1.41	-0.99
2	10	0	1.73	1.37
3	10	0	3.74	-3.83
4	10	0	2.24	-2.58
6	10	0	4.12	4.59
8	10	0	1.73	1.68
9	10	0	2.24	-1.87
1	10	0	2.00	-1.46
2	10	0	2.00	-2.03
0	12	0	2.83	-2.69
1	12	0	1.73	-1.58
2	12	0	1.00	1.12
3	12	0	4.12	4.23
4	12	0	4.36	5.19
5	12	0	5.10	-5.20
8	12	0	1.41	-1.64
9	12	0	1.00	-0.85
10	12	0	2.24	2.41
11	12	0	1.41	1.69
3	14	0	1.41	0.05
4	14	0	1.41	-1.54
6	14	0	1.00	0.98
8	14	0	3.74	4.10
10	14	0	2.00	-1.84
2	1	1	7.21	6.65
3	1	1	5.66	-5.60
4	1	1	6.93	6.49
5	1	1	6.63	5.94
7	6	2	3.61	-3.94
9	6	2	6.16	5.96
0	8	2	3.00	3.11
1	8	2	8.37	-8.10
2	8	2	5.74	5.08
3	8	2	2.65	-2.37
4	8	2	4.12	-3.77
5	8	2	2.65	2.54
6	8	2	3.46	4.03
7	8	2	2.65	3.33
9	8	2	4.69	-5.26
10	8	2	2.65	2.64
1	10	2	2.65	2.28
3	10	2	4.36	4.44
4	10	2	7.21	7.38
5	10	2	6.63	-6.46
0	12	2	7.81	8.15
3	12	2	3.00	-3.05
5	12	2	3.87	4.19
8	12	2	3.87	4.19
0	14	2	5.92	-6.09
2	14	2	2.83	2.87
4	14	2	2.83	2.88
8	14	2	3.16	-3.42
10	14	2	2.65	2.81
0	16	2	3.61	3.80
4	16	2	2.65	-2.81
5	16	2	2.65	-2.54
6	16	2	2.65	2.26
8	16	2	2.65	2.43
4	18	2	3.46	3.82
1	1	3	11.09	-11.34
2	1	3	3.32	3.20
3	1	3	4.69	4.12
4	1	3	5.10	4.89
5	1	3	5.29	-5.07
6	1	3	3.32	3.17
7	1	3	3.74	4.07
9	1	3	8.00	8.68
2	3	3	7.14	5.07
3	3	3	8.06	-7.82
4	3	3	6.08	6.03
6	1	1	4.00	4.13
7	1	1	4.24	-3.75
9	1	1	7.21	6.51
0	3	1	5.92	5.13
1	3	1	5.57	-4.66
2	3	1	5.10	4.71
3	3	1	9.90	9.27
5	3	1	7.48	-7.27
6	3	1	3.46	3.44
9	3	1	2.83	-2.36
12	3	1	3.00	3.08
13	3	1	3.46	-3.35
14	3	1	2.83	2.65
0	5	1	6.08	5.75
1	5	1	7.35	-6.52
2	5	1	2.83	2.47
3	5	1	5.66	5.23
4	5	1	9.00	8.46
5	5	1	7.68	-6.47
6	5	1	4.58	4.69
7	5	1	4.00	3.59
8	5	1	4.24	4.21
12	5	1	3.16	2.74
13	5	1	3.61	-3.10
0	7	1	13.56	12.65
1	7	1	4.58	3.84
2	7	1	5.48	5.66
4	7	1	5.20	5.30
7	7	1	2.83	-2.44
8	7	1	7.55	8.14
10	7	1	5.00	4.75
0	9	1	9.27	8.82
1	9	1	2.83	2.71
2	9	1	3.00	2.69
3	9	1	5.00	-4.72
4	9	1	3.87	3.54
5	9	1	5.48	5.34
8	9	1	4.69	4.58
10	9	1	3.00	2.63
13	9	1	2.65	-2.60
2	11	1	4.36	4.35
5	3	3	8.00	8.04
6	3	3	3.61	3.78
13	3	3	3.16	3.53
0	5	3	13.11	12.64
1	5	3	8.00	6.56
2	5	3	6.56	6.18
3	5	3	5.74	-5.56
4	5	3	5.92	5.90
5	5	3	7.00	6.72
7	5	3	3.32	-3.23
8	5	3	6.00	6.48
10	5	3	3.32	3.53
0	7	3	12.00	10.89
2	7	3	4.36	3.83
4	7	3	5.00	-4.90
6	7	3	3.46	3.67
8	7	3	5.48	6.35
10	7	3	3.00	3.30
0	9	3	4.80	-4.44
1	9	3	3.61	-3.59
2	9	3	3.16	3.57
3	9	3	3.16	-3.37
4	9	3	6.86	7.57
5	9	3	3.00	-2.61
6	9	3	3.16	3.21
0	11	3	6.08	5.73
3	11	3	3.16	3.00
4	11	3	6.16	5.92
5	11	3	3.16	-3.34
1	13	3	3.32	3.61
5	13	3	3.00	3.54
9	13	3	2.83	-3.37
1	15	3	3.16	3.75
3	17	3	2.65	-2.93
4	17	3	3.00	3.02
5	17	3	3.00	-2.82
0	0	4	6.48	7.85
2	0	4	6.16	6.35
8	0	4	5.66	4.98
14	0	4	3.16	2.86
5	2	4	6.32	6.10
8	2	4	3.46	-3.26
9	2	4	3.46	-2.62
10	2	4	4.47	3.88
12	2	4	3.16	2.90
13	2	4	3.00	2.71
3	4	4	7.94	7.75
4	4	4	4.69	-4.14
6	4	4	3.87	4.39
8	4	4	4.47	3.80
9	4	4	2.65	2.29
13	4	4	3.87	-3.23
0	6	4	3.87	3.74
1	6	4	8.06	-6.80
2	6	4	3.87	3.19
3	6	4	6.56	-6.13
4	6	4	6.63	6.21
5	6	4	3.00	5.11
9	6	4	4.69	-4.39
13	6	4	3.32	2.61
0	8	4	6.24	5.99
1	8	4	9.06	9.14
2	8	4	2.65	-2.62
4	8	4	6.63	7.04
5	8	4	3.32	-3.05
7	8	4	4.47	-4.29
8	8	4	3.32	3.55
9	8	4	4.80	5.21
0	10	4	4.69	4.72
1	10	4	3.32	-3.32
2	10	4	3.74	3.84
3	10	4	3.00	-2.66
4	10	4	4.69	-4.38
5	10	4	3.87	4.26
6	10	4	3.16	3.31
8	10	4	3.00	2.58
9	10	4	3.32	-2.80
0	12	4	5.48	-4.82
1	12	4	3.16	2.97
2	12	4	3.87	3.73
4	12	4	4.24	4.84
5	12	4	3.16	-2.78
8	12	4	3.00	-2.54
10	12	4	2.65	2.44
0	14	4	7.55	7.18
3	14	4	1.41	1.53
0	4	8	8.00	9.01
1	4	8	6.93	7.04
2	4	8	4.90	4.76
5	4	8	3.00	2.84
6	4	8	3.74	3.93
7	4	8	3.61	-3.36
8	4	8	4.90	5.26
9	4	8	4.12	4.26
10	4	8	2.83	-2.77
0	1	9	2.65	2.68
2	1	9	3.87	3.66
3	1	9	4.12	-4.71
5	1	9	7.07	7.69
6	1	9	3.46	3.14
13	1	9	3.74	3.87
0	3	9	2.83	-3.34
1	3	9	2.83	3.42
4	3	9	3.16	3.27
5	3	9	3.46	-3.69
9	3	9	3.16	3.75
10	3	9	2.83	3.05
0	0	10	3.61	3.38
4	0	10	6.86	7.58
6	0	10	3.46	-3.67
12	0	10	3.46	3.37
0	2	10	5.20	5.44
1	2	10	5.20	5.58
2	2	10	2.24	1.95
3	2	10	3.00	2.67
4	2	10	3.46	-3.86
8	2	10	3.46	3.48
9	2	10	4.12	4.08
0	4	10	6.86	-7.41
1	4	10	4.90	5.39
2	4	10	3.74	3.56
4	4	10	2.00	1.55
6	4	10	3.00	2.66
8	4	10	4.24	-4.16
9	4	10	3.87	-3.96
10	4	10	3.32	3.19
1	1	11	3.16	2.51
2	1	11	3.16	2.79
4	14	4	2.65	3.00
8	14	4	4.47	4.39
0	16	4	3.00	-2.54
1	16	4	2.65	1.69
4	16	4	3.32	3.26
0	18	4	2.65	2.34
4	18	4	2.83	-2.17
0	1	5	12.41	14.05
1	1	5	9.85	-10.17
3	1	5	2.65	-2.62
4	1	5	6.93	7.21
5	1	5	6.16	5.96
6	1	5	3.32	-3.13
7	1	5	4.00	4.42
8	1	5	4.80	5.00
9	1	5	6.16	-5.96
13	1	5	2.65	2.58
0	3	5	8.25	-8.48
1	3	5	7.94	7.75
2	3	5	5.10	5.47
3	3	5	4.69	-5.27
4	3	5	5.66	5.88
5	3	5	5.00	4.80
6	3	5	5.57	6.14
7	3	5	2.83	-2.81
8	3	5	2.65	-2.48
9	3	5	4.00	4.34
10	3	5	3.16	3.34
0	0	6	7.81	-8.78
2	0	6	6.32	7.49
4	0	6	11.00	12.63
6	0	6	3.61	4.03
8	0	6	4.00	-4.12
10	0	6	3.16	3.56
12	0	6	2.83	3.30
0	2	6	11.62	11.46
1	2	6	3.87	-3.76
2	2	6	2.65	2.62
3	2	6	5.39	5.43
4	2	6	7.35	-7.69
5	2	6	4.90	-4.84
6	2	6	3.00	2.86
3	1	11	4.80	5.51
5	1	11	6.93	-6.76
0	3	11	6.71	7.60
1	3	11	4.47	-5.12
8	3	11	4.24	5.11
9	3	11	3.61	-3.79
0	0	12	3.32	-3.20
2	0	12	3.32	3.05
4	0	12	7.07	-7.71
6	0	12	4.00	4.33
0	2	12	4.00	4.40
1	2	12	2.65	-2.98
4	2	12	5.83	6.18
0	4	12	6.86	7.73
1	4	12	4.80	-4.64
7	4	12	2.83	2.32
8	4	12	3.74	3.68
9	4	12	3.16	-3.26
0	1	13	5.48	4.90
1	1	13	3.87	-3.61
3	1	13	4.58	-4.65
4	1	13	3.46	2.86
5	1	13	4.47	4.33
8	1	13	3.46	3.13
0	3	13	4.12	-4.59
1	3	13	4.36	4.73
2	3	13	4.00	3.93
4	3	13	2.65	2.62
7	3	13	2.65	-2.49
8	3	13	3.00	-3.09
9	3	13	3.16	3.35
10	3	13	2.65	2.52
0	0	14	3.00	3.27
2	0	14	2.65	2.29
4	0	14	7.07	6.43
6	0	14	3.32	3.38
0	2	14	4.00	-3.87
1	2	14	3.00	3.05
4	2	14	3.61	3.62
0	4	14	3.87	3.86
3	4	14	3.00	2.37
5	4	14	3.00	-2.78
8	2	6	5.29	5.57
9	2	6	3.46	-3.23
0	4	6	5.66	5.42
1	4	6	5.66	-5.38
2	4	6	2.83	-2.90
3	4	6	3.16	-3.15
4	4	6	8.49	8.98
5	4	6	3.61	3.69
8	4	6	4.36	4.52
9	4	6	4.12	-3.53
10	4	6	2.83	2.44
12	4	6	3.00	2.62
0	1	7	4.00	-3.97
1	1	7	3.16	3.15
2	1	7	4.80	4.41
3	1	7	7.87	8.23
5	1	7	8.25	-8.33
6	1	7	4.00	4.01
10	1	7	2.65	2.71
13	1	7	3.32	-3.22
0	3	7	11.36	12.66
1	3	7	6.56	-7.43
4	3	7	5.48	6.21
6	3	7	2.65	-2.67
7	3	7	3.00	3.32
8	3	7	5.10	5.72
9	3	7	4.00	-4.30
0	0	8	7.42	8.45
2	0	8	2.83	-3.24
4	0	8	8.72	9.67
6	0	8	3.74	3.76
8	0	8	4.47	5.25
12	0	8	2.65	-3.06
0	2	8	5.83	-5.84
1	2	8	7.07	-7.16
2	2	8	3.46	3.70
3	2	8	5.29	-5.15
4	2	8	5.92	6.21
5	2	8	3.46	2.76
7	2	8	3.46	3.46
8	2	8	3.16	-3.20
9	2	8	4.90	4.90
10	2	8	2.65	2.76
1	1	15	3.87	3.31
3	1	15	2.65	2.57
5	1	15	3.32	-3.10
9	1	15	3.00	2.65
0	3	15	3.32	3.36
5	3	15	2.65	2.47
8	3	15	2.65	2.43
4	0	16	3.61	3.45
6	0	16	3.00	2.46
0	2	16	3.46	3.39
1	2	16	3.46	-3.05
5	2	16	2.65	-2.20
0	4	16	3.61	3.01
4	4	16	2.83	2.82
5	1	17	2.65	2.55
4	3	17	2.65	2.76
0	0	18	6.86	5.39
4	2	18	2.65	2.62
4	4	18	3.00	-2.47
1	1	19	2.65	2.84

currence of those previously encountered. Accordingly, precautions were again taken to minimize these interactions as nine cycles of refinement were carried out. In these cycles, the scattering curves were taken from Table 3.3.3A(1) of ref. 9 for Cs^+, Re^0, and Cl^0. After the final cycle, the residual had dropped to 0.073. A final difference Fourier synthesis was then calculated and it showed no anomalies. The final atom coordinates and thermal parameters and the estimated standard deviations of these quantities are given in Table II. Table III records the observed structure factors, $|F_o|$, and those calculated, F_c, from the parameters in Table II.

Discussion of the Structure

The $[Re_3Cl_{12}]^{3-}$ Anion.—The dimensions of the $[Re_3Cl_{12}]^{3-}$ ion (Fig. 1) are given in detail in Table IV. Crystallographically, it is required to possess but one sym-

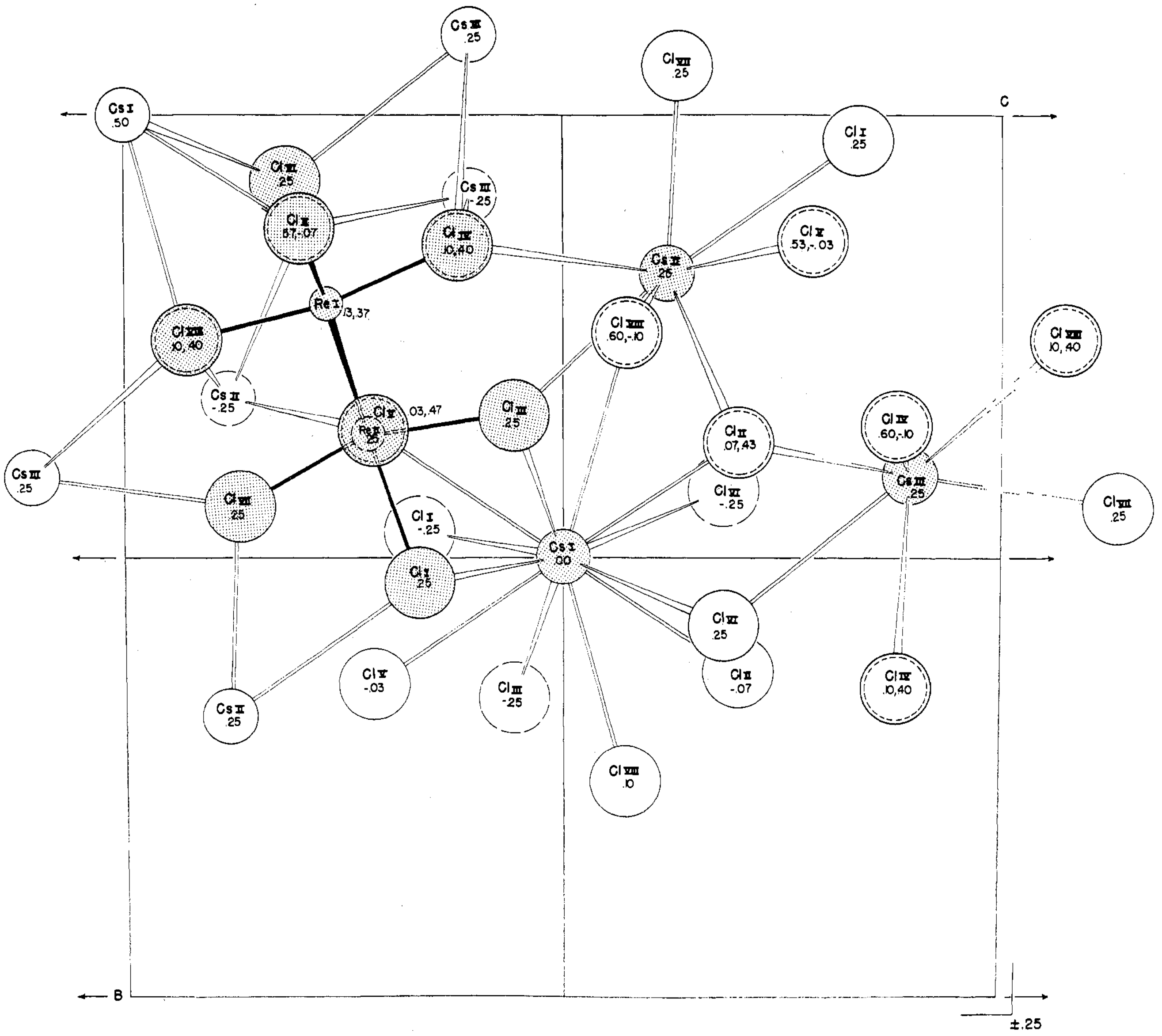

Fig. 2.—A projection of the crystal structure down the short, [100], axis, showing the packing of Cs^+ and $[Re_3Cl_{12}]^{3-}$ ions. Not all atoms are shown; shaded atoms are those for which all near neighbors are shown. Decimal fractions represent *x* coordinates.

metry element, a mirror plane passing through Re_{II}, Cl_I, Cl_{III}, Cl_{VI}, and Cl_{VII}. However, scrutiny of the quantities in Table IV shows that within the standard deviations, $[Re_3Cl_{12}]^{3-}$ actually has D_{3h} symmetry. This is further confirmed by a calculation of the deviations of Cl_I, Cl_{II}, Cl_V, and Cl_{VI} from the plane of the rhenium atoms. It is found that the greatest discrepancy (0.03 Å. by Cl_V) is less than the standard deviation and hence without significance. Table V gives the average values of the bond lengths and angles required in order to describe the ion within this idealized symmetry. For chemical purposes it is these average values which are of greatest interest, and they will be used throughout the following discussion.

The most noteworthy aspect of the crystal structure is, of course, the polynuclear nature of the anion, in which, as discussed below, the direct metal–metal bonding seems to be quite strong. Relatively few species containing clusters of transition metal atoms are known so that each new type which is discovered supplies valuable information about the essential features of such clusters. Neglecting the limiting case of diatomic clusters, *i.e.*, those having only a single, two-center metal–metal bond either supplemented by bridging groups (*e.g.*, $CO_2(CO)_8$, $W_2Cl_9^{3-}$) or not (*e.g.*, $Mn_2(CO)_{10}$), for which the theory of bonding is relatively uncomplicated, we may list the following types of compounds containing metal atom clusters. In each case, the shape of the idealized polygon or polyhedron formed by the metal atoms is stated, followed by the shortest metal–metal distance in Ångstroms.

I. Carbonyl Compounds:

(a) Clusters of three in $Ru_3(CO)_{12}$,[16] $Os_3(CO)_{12}$,[16] $Fe_3(CO)_{12}$[17] (with some uncertainty[18]), and in Ni_3-

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[16] E. R. Corey and L. F. Dahl, *Inorg. Chem.*, **1**, 521 (1962).

[17] L. F. Dahl and R. E. Rundle, *J. Chem. Phys.*, **26**, 1751 (1957).

[18] M. Kalvius, *et al.*, *Z. Naturforsch.*, **17a**, 400 (1962); R. H. Herber, W. R. Kingston, and G. K. Wertheim, *Inorg. Chem.*, **2**, 153 (1963).

TABLE IV

INTERNAL DIMENSIONS[a] OF THE $[Re_3Cl_{12}]^{3-}$ ANION

Distances, Å.		Angles, deg.	
Re_I–Re'_I	2.480	Re'_I–Re_I–Re_{II}	59.9
Re_I–Re_{II}	2.475	Re_I–Re_{II}–Re'_I	60.1
Re_I–Cl_{II}	2.54	Re'_I–Re_I–Cl_{VI}	58.5
Re_I–Cl_{IV}	2.36	Cl_V–Re_I–Re_{II}	59.1
Re_I–Cl_V	2.41	Cl_V–Re_I–Cl_{II}	90.5
Re_I–Cl_{VI}	2.37	Cl_{II}–Re_I–Cl_{VI}	92.0
Re_I–Cl_{VIII}	2.35	Cl_{II}–Re_I–Cl_{IV}	78.7
Re_{II}–Cl_I	2.49	Cl_{II}–Re_I–Cl_{VIII}	78.8
Re_{II}–Cl_{III}	2.36	Cl_V–Re_I–Cl_{IV}	88.4
Re_{II}–Cl_V	2.41	Cl_{VI}–Re_I–Cl_{IV}	90.6
Re_{II}–Cl_{VII}	2.36	Cl_V–Re_I–Cl_{VIII}	91.0
Cl_{VII}–Cl_{VIII}	3.22	Cl_{VI}–Re_I–Cl_{VIII}	89.0
Cl_{VIII}–Cl'_{VIII}	3.27	Cl_{IV}–Re_I–Re_{II}	111.3
Cl_{III}–Cl_{IV}	3.29	Cl_{IV}–Re_I–Re'_I	100.4
Cl_{IV}–Cl'_{IV}	3.33	Cl_{VIII}–Re_I–Re_{II}	97.7
Cl_{III}–Cl_I	3.06	Cl_{VIII}–Re_I–Re'_I	99.6
Cl_{III}–Cl_V	3.29	Re_I–Re_{II}–Cl_V	59.1
Cl_{VII}–Cl_I	3.10	Cl_V–Re_{II}–Cl_I	90.8
Cl_{VII}–Cl_V	3.45	Cl_{III}–Re_{II}–Cl_I	78.2
Cl_{IV}–Cl_{II}	3.11	Cl_{III}–Re_{II}–Re_I	98.7
Cl_{IV}–Cl_V	3.33	Cl_{III}–Re_{II}–Cl_V	87.4
Cl_{IV}–Cl_{VI}	3.37	Cl_{VII}–Re_{II}–Cl_I	79.6
Cl_{VIII}–Cl_{II}	3.11	Cl_{VII}–Re_{II}–Re_I	100.5
Cl_{VIII}–Cl_V	3.40	Cl_{VII}–Re_{II}–Cl_V	92.9
Cl_{VIII}–Cl_{VI}	3.37	Re_I–Cl_{VI}–Re'_I	63.0
		Re_I–Cl_V–Re_{II}	61.8

[a] Estimated standard deviations: 0.01 Å. for Re–Re; 0.03 Å. for Re–Cl; 0.05 Å. for Cl–Cl.

TABLE V

INTERNAL DIMENSIONS OF THE $[Re_3Cl_{12}]^{3-}$ ANION AVERAGED FOR D_{3h} SYMMETRY[a]

Distances, Å.		
Re–Re	2.477 ± 0.003	
Re–Cl_a (out of plane)	2.359 ± .004	
Re–Cl_b (bridging)	2.39 ± .02	
Re–Cl_c (in plane)	2.52 ± .03	
Cl_a–Cl_a	3.28 ± .06	(closest contacts)
Cl_a–Cl_b	3.37 ± .08	(closest contacts)
Cl_a–Cl_c	3.08 ± .04	(closest contacts)
Cl_b–Cl_c	3.51 ± .03	(closest contacts)
Angles, deg.		
Re–Re–Cl_b	58.8 ± 0.3	
Re–Cl_b–Re	62.4 ± .6	
Cl_a–Re–Cl_c	78.9 ± .7	
Cl_c–Re–Cl_b	91.3 ± .7	
Cl_a–Re–Cl_b	89.9 ± 2.0	

[a] Uncertainties are standard errors of the mean of the crystallographically different but "molecularly" equivalent distances which have been averaged. Standard deviations of individual bond lengths have not been included.

TABLE VI

CESIUM–CHLORINE PACKING DISTANCES

About Cs_I	$2Cl_I$	at 3.55
	$2Cl_{II}$	at 3.44
	$2Cl_{III}$	at 3.60
	$2Cl_V$	at 3.66
	$2Cl_{VI}$	at 3.87
	$2Cl_{VIII}$	at 3.87
About Cs_{II}	Cl_I	at 3.73
	$2Cl_{II}$	at 3.46
	Cl_{III}	at 3.32
	$2Cl_{IV}$	at 3.77
	$2Cl_V$	at 3.79
	Cl_{VII}	at 3.29
	$2Cl_{VIII}$	at 3.89
About Cs_{III}	$2Cl_{II}$	at 3.38
	$2Cl_{IV}$	at 3.72
	$2Cl_{IV}$	at 3.77
	Cl_{VI}	at 3.81
	Cl_{VII}	at 3.38
	$2Cl_{VIII}$	at 3.65

$(C_5H_5)_3(CO)_2$[19]; equilateral triangle; 2.88 (Os), ~2.8 (Fe), 2.39 (Ni).

(b) A cluster of four in $Co_4(CO)_{12}$[20]; tetrahedron; 2.50 ± 0.05.

(c) A cluster of six in $Rh_6(CO)_{16}$[21]; octahedron; 2.776.

II. Halogen Compounds:

(a) A cluster of three in $[Re_3Cl_{12}]^{3-}$; equilateral triangle; 2.477.

(b) Clusters of four: none yet known.

(c) Clusters of six in $[Nb_6Cl_{12}]^{2+}$,[22] $[Ta_6Cl_{12}]^{2+}$,[22] $[Ta_6Br_{12}]^{2+}$,[22] and in $[Mo_6Cl_8]^{4+}$[23,24]; octahedra; 2.85 (Nb), ~2.90 (Ta), 2.63 (Mo).

It must be carefully noted that the above classification covers only compounds with symmetrical and "closed" clusters of metal atoms. These are emphasized because it seems probable that they will be the most amenable to molecular orbital treatment of the intermetal bonding. It is not likely, however, that the intermetal bonding in these compounds differs in any essential way from that in less symmetrical clusters in which the polyhedra have been "opened" by the intimate inclusion of nonmetal atoms. The work of Dahl has recently provided several examples of the more open clusters, *e.g.*, $Fe_5(CO)_{15}C$,[25] $Co_4(CO)_{10}(C_2H_5C_2C_2H_5)$,[26] and $Co_3(CO)_9CCH_3$.[27]

The mean Re–Re separation in $[Re_3Cl_{12}]^{2-}$ of 2.48 Å. is notably short and indicates that the extent of direct intermetal bonding in the Re_3 cluster is at least as great as in the other metal atom clusters cited. Thus, in rhenium metal,[28] the Re–Re distances are 2.74 and 2.76 Å., and Pauling[29] has estimated that a Re–Re single bond would be about 2.56 Å. in length. As noted earlier,[3] an LCAO–MO treatment of the intermetal bonding leads straightforwardly and in a manner little dependent on quantitative choices of orbital parameters to the prediction of six bonding molecular orbitals. These can just accommodate the twelve electrons (four from each Re^{III}) and thus the diamagnetism of the compound is explained.[30]

An interesting aspect of the $[Re_3Cl_{12}]^{3-}$ structure becomes apparent from consideration of the Re–Cl distances and Cl–Re–Cl angles, Table V. For a Re–Cl single bond one might anticipate a length of about 2.35 Å., either from consideration of covalent radii[31] or direct comparison with bond lengths in chloro complexes of other heavy transition elements.[31,32] On this basis,

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[19] A. A. Hock and O. S. Mills, "Advances in the Coordination Compounds," S. Kirschner, Ed., the Macmillan Co., New York, N. Y., 1961, p. 640.

[20] P. Corradini, *J. Chem. Phys.*, **31**, 1676 (1959).

[21] E. R. Corey, L. F. Dahl, and W. Beck, *J. Am. Chem. Soc.*, **85**, 1202 (1963).

[22] P. A. Vaughan, J. H. Sturdivant, and L. Pauling, *ibid.*, **72**, 5477 (1950).

[23] C. Brosset, *Arkiv Kemi, Mineral., Geol.*, **A20** (1945); **A22** (1946).

[24] P. A. Vaughan, *Proc. Natl. Acad. Sci. U.S.*, **36**, 461 (1950).

[25] E. H. Braye, L. F. Dahl, W. Hübel, and D. L. Wampler, *J. Am. Chem. Soc.*, **84**, 4633 (1962).

[26] L. F. Dahl and D. L. Smith, *ibid.*, **84**, 2450 (1962).

[27] L. F. Dahl, private communication, to be published.

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

[29] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 440.

[30] F. A. Cotton and T. E. Haas, *Inorg. Chem.*, in press.

[31] Reference 29, pp. 248–252.

[32] "Tables of Interatomic Distances and Configuration in Molecules and Ions," Spec. Publ. No. 11, The Chemical Society, London, 1958.

the Re–Cl_a and Re–Cl_b distances are to be regarded as indicating the existence of normal, single bonds. The Re–Cl_c distances of 2.52 Å. are about 0.15 Å. longer, however. This lengthening is definitely significant, being *much* greater than the sum of the standard deviations in the short (σ = 0.02, 0.04) and in the long (σ = 0.03) Re–Cl distances, and indicates that the Re–Cl_c bonds are weaker than the other, normal ones. This may be partly, or even entirely due to steric pressure of the Cl_a atoms on the Cl_c atom, rather than to any inherent tendency of the Re–Cl_c bond to be weaker.

All Cl–Re–Cl angles are within 1–2° of 90° except for the Cl_a–Re–Cl_c angles, which are only 80°. This, however, is due in large part at least to van der Waals repulsions between the Cl_a atoms. Thus, it is possible to describe the structure and bonding in the following way. Each rhenium atom lies in an approximately square $ReCl_4$ group, for which four of its oribitals are required. It uses an orbital on one side of this plane to bind a fifth chlorine atom, somewhat more loosely. Its remaining orbitals are used in the intermetal bonding in the Re_3 cluster.

Crystal Packing.—The crystal packing is illustrated in Fig. 2, which shows the projection down the [100] axis. All Cs···Cl distances (Table VI) are within an acceptable range, 3.3–3.9 Å. (*cf.* 3.6 in CsCl). In particular, there is no indication that any Cs···Cl interactions are seriously perturbing the $[Re_3Cl_{12}]^{3-}$ structure. The coordination numbers of the cesium atoms cannot be defined rigorously because of the range of Cs···Cl distances. If we arbitrarily select 3.9 Å. as a cut-off for the coordination sphere, the coordination numbers of Cs_I, Cs_{II}, and Cs_{III} are, respectively, 12, 11, and 10. The polyhedra so defined are all rather irregular, although the arrangement about Cs_I is somewhat similar to the 3, 6, 3 set of neighbors about a sphere which is in a close-packed structure.

CONTRIBUTION FROM THE EVANS AND MCPHERSON CHEMICAL LABORATORIES,
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Complexes Derived from Strong Field Ligands. XVI.
The Transition Metal Complexes of 2-Pyridinalhydrazones

BY MARTIN A. ROBINSON AND DARYLE H. BUSCH

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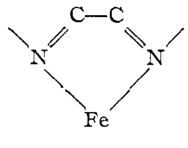
A variety of complexes have been synthesized with methyl and phenyl substituted 2-pyridinalhydrazones. Magnetic moments, molar conductances, and spectral data have been applied to the characterization of the compounds. The properties of the cobalt(II) and nickel(II) complexes are typical of spin-free octahedral species, while the behavior of the iron(II) complexes provides evidence for an interesting steric effect. Although all the other known complexes of iron(II) with pyridinal imines and hydrazones are spin-paired, tris-(2-pyridinaldimethylhydrazone)-iron(II) iodide is paramagnetic with a magnetic moment of 5.45 Bohr Magnetons. This is explained on the assumption that the –NNR′ group of the hydrazone group is planar. The hypothesis is supported by spectral and other results. Similar steric effects limit the number of molecules of pyridinalphenylhydrazone that may enter an octahedral coordination sphere.

Introduction

Since the first observations by Blau[1] on the complexing abilities of 2,2′-bipyridine and 1,10-phenanthroline, much interest has been found in the metal derivatives of ligands containing the –N=C—C=N– linkages. Earlier efforts centered on the original aromatic ligands and their derivatives. More recently, investigations in this series have directed attention toward the similar behavior of pyridinalimines,[3] α-diketoimines,[3] pyridinalhydrazones,[4] α-diketodihydrazones,[4] and pyridinaldazine.[5]

Typically the octahedral, tris-chelated iron(II) derivatives of these ligands exhibit spin-paired ground states and spectral properties provide evidence for extensive metal–ligand π-bonding. Infrared spectral studies have revealed that the



chelate ring is best considered to be an aromatic system.[2,4,6] Further, the characteristic low energy charge-transfer spectra of such compounds support this conclusion.[7] In contrast, the majority of the bidentate ligands of this class yield three-to-one octahedral complexes of cobalt(II) and nickel(II) which are of the high-spin type.[3–5] Infrared data indicate that the degree of metal–ligand π-bonding decreases in the order Fe(II) > Co(II) > Ni(II). In the case of tris-

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[1] F. Blau, *Ber.*, **21**, 1007 (1888); *Monatsh. Chem.*, **19**, 647 (1898).

[2] W. W. Brandt, F. P. Dwyer, and E. C. Gyarfas, *Chem. Rev.*, **54**, 959 (1954).

[3] P. E. Figgins and D. H. Busch, *J. Am. Chem. Soc.*, **82**, 820 (1960); *J. Phys. Chem.*, **65**, 2236 (1961).

[4] R. C. Stoufer and D. H. Busch, *ibid.*, **78**, 6016 (1956); *ibid.*, **82**, 3491 (1960).

[5] W. J. Stratton and D. H. Busch, *ibid.*, **80**, 1286 (1958); *ibid.*, **80**, 3191 (1958); *ibid.*, **82**, 4834 (1960).

[6] K. Nakamoto, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 437.

[7] D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **78**, 1137 (1956).