(V) compound. Additional work designed to establish the composition of the tungsten(V) derivative was unsuccessful because of the difficulty of separation from the associated oxidation products. It is interesting to note, however, that the reduction was slowed in carbon tetrachloride and provided some evidence for one of the intermediates in the reduction of the hexachloride. The available evidence thus indicates that the reaction of WCl_6 with pyridine proceeds stepwise: $W(VI) \rightarrow W(V) \rightarrow W(IV)$, or that $W(V)$ is formed after initial reduction to W(IV) by the reaction $W(IV) + W(VI) = 2W(V)$. Evidence from the corresponding reactions of the niobium(V) halides[10] indicated that pyridine behaved as a two-electron reducing agent, hence the latter path seems more likely.[19]

(19) Note Added in Proof.—Although the X-ray powder pattern data[11,12] for the halides MX_4 (M = Nb, Ta, W; X = Cl, Br) have been indexed on the basis of an orthorhombic unit cell, more recent evidence from single crystal work indicates the true unit cell is monoclinic. According to a recent note [H. G. Schnering and H. Wöhrle, *Angew. Chem.*, **75**, 684 (1963)], it was found from single crystal data that $NbCl_4$ is monoclinic with $a = 12.32$, $b = 6.82$, $c = 8.21$ Å., and $\beta = 134°$.

Structural Studies of Zirconium Trihalides and Hafnium Triiodide[1]

By Lawrence F. Dahl,[2] Tao-I Chiang, Pyrtle W. Seabaugh, and Edwin M. Larsen

Structural studies of $ZrCl_3$, $ZrBr_3$, ZrI_3, and HfI_3 have been carried out from X-ray powder diffraction patterns. The isomorphous compounds contain two formula units in a hexagonal unit cell and have the following dimensions in Å. (all with e.s.d. ±0.01 Å.) and densities in g./cc. at 25°: $ZrCl_3$, $a = 6.36$, $c = 6.14$, $d_{exptl} = 2.95$, $d_{calcd} = 3.05$; $ZrBr_3$, $a = 6.75$, $c = 6.31_5$, $d_{exptl} = 4.52$, $d_{calcd} = 4.42$; ZrI_3, $a = 7.25$, $c = 6.64$, $d_{exptl} = 5.13$, $d_{calcd} = 5.20$; HfI_3, $a = 7.22_5$, $c = 6.59$, $d_{exptl} = 6.17$, $d_{calcd} = 6.25$. Systematic absences of l odd for $h0l$ reflections indicate as probable space groups, D^3_{6h}-$P6_3/mcm$, C^3_{6v}-$P6_3cm$, and D^2_{3h}-$P\bar{6}c2$. From space group assignment (D^3_{6h}-$P6_3/mcm$), intensity calculations, and stereochemical considerations (with the assumption of no order–disorder phenomenon) a structure based on a distorted hexagonal close-packing of the halogen atoms can be proposed which consists of infinite chains along the c axis formed by MX_6 octahedra joined at opposite faces with the metal atoms regularly spaced midway between the halogen atoms; the resulting metal–metal distance is equal to one-half the c lattice constant. Evidence is presented to show that previous powder work (made on relatively impure samples) by Holze[3] including another space group assignment (D^3_{3h}-$P\bar{6}2m$) and a formulated structure of linear chains of $(Zr_2X_6)_n$ units is not substantiated by our powder data. A qualitative MO theory of bonding is proposed from which direct metal–metal interactions can be postulated for a chain configuration.

Introduction

Preliminary X-ray powder diffraction studies of zirconium and hafnium trihalides were carried out first by Leddy[4] and later more thoroughly by Holze[3] on the zirconium trihalides alone. Holze[3] concluded that the zirconium trihalides are isostructural with TiI_3[3,5] and the β-form (designated by Holze[3] as the N-form) of $TiBr_3$ and $TiCl_3$.[3,6] On the basis of indexed powder lines obtained from samples highly contaminated with metal, Holze[3] assigned a space group (D^3_{3h}-$P\bar{6}2m$) and carried out a limited structural analysis which indicated that these solid zirconium trihalides consist of linear chains of $(Zr_2X_6)_n$ units (X = Cl, Br, I) in a hexagonal close-packed lattice of halogen atoms.[7]

The present investigation was virtually completed before Holze's Ph.D. thesis[3] was made available to us. This paper presents evidence that Holze's space group assignment and proposed structure for the zirconium trihalides are not substantiated by our powder patterns of these compounds. X-Ray powder diffraction data for HfI_3 which show this compound to be isomorphous with the zirconium trihalides are presented for the first time, and experimental densities and lattice constants are reported for the four compounds.

Several synthetic investigations of these compounds recently have been published which also are pertinent to this work. The preparation of pure, anhydrous zirconium trihalides by reduction of the corresponding zirconium tetrahalides with hydrogen under a glow discharge was described by Newnham and Watts,[8] but no characterization of the resulting products by X-ray analysis was given. The synthesis of ZrI_3 by the reduction of ZrI_4 with Al was carried out by Watt and Baker,[9] who state that their X-ray powder data attributable to only ZrI_3 are in good agreement with the unpublished data (presented here) obtained by Larsen and Chiang.[10] The preparation of pure $ZrBr_3$ from the reduction of $ZrBr_4$ with Zr metal was

(1) This article is based in part on a dissertation by Tao-I Chiang in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

(2) Fellow of the Alfred P. Sloan Foundation.

(3) E. Holze, Ph.D. Thesis, Westfälische Wilhelms Universität, Muenster, Germany, 1957.

(4) J. J. Leddy, Ph.D. Thesis, The University of Wisconsin, 1955.

(5) R. F. Rolsten and H. S. Sisler, *J. Am. Chem. Soc.*, **79**, 5891 (1957).

(6) G. Natta, P. Corradini, I. W. Bassi, and L. Porri, *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. Nat.*, **24**, 121 (1958).

(7) *Cf.* R. F. Rolsten, "Iodide Metals and Metal Iodides," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 46.

(8) I. E. Newnham and J. A. Watts, *J. Am. Chem. Soc.*, **82**, 2113 (1960).

(9) G. W. Watt and W. A. Baker, Jr., *J. Inorg. Nucl. Chem.*, **22**, 49 (1961).

(10) E. M. Larsen and T. Chiang, communication to G. W. Watt, 1958

reported by Schäfer and Skoludek,[11] who represented their X-ray powder data in nonnumerical, line-diagram form without indexing the reflections and consequently without obtaining lattice parameters. The present study provides information which bears upon the preparation and purification procedures for these and related compounds.

Experimental

Preparation of Zirconium and Hafnium Trihalides.—The general method for the preparation and analysis of the trihalides has been reported previously.[12] The original zirconium with a hafnium impurity of 125 p.p.m. was obtained from the Atomic Energy Commission. Hafnium metal was obtained from A. D. MacKay, Inc.; correction was made for a zirconium impurity of about 1%. The composition of the samples used for X-ray powder work and the comparison of the purity of our samples with those prepared by Holze are given in Table I. The relatively high purity of our samples of $ZrBr_3$, ZrI_3, and HfI_3 was substantiated by the X-ray powder work. No diffraction lines characteristic of metallic zirconium were noted in our powder patterns, whereas the zirconium impurity in Holze's zirconium trihalide samples was sufficiently great that his resulting powder data were corrected by subtracting the known metallic zirconium powder lines from the experimental data. Only in listing our zirconium trichloride powder data did we follow the same procedure. Approximately 50 lines were obtained from each of our powder patterns of $ZrBr_3$, ZrI_3, and HfI_3, while 28 lines were recorded for $ZrCl_3$. (In contrast only 22 lines were given by Holze[8] for each of the three zirconium trihalides.) Efforts to prepare samples of hafnium trichloride and tribromide of high purity were unrewarding; the resulting samples were highly contaminated with metal, and their powder patterns were not of the same quality as those reported here.

Densities.—Densities were determined pycnometrically with carbon tetrachloride or kerosene at 25.0°. The results are reliable to ±0.05 g./cc. Corrections were applied for the density of the metal powder present.

X-Ray Powder Photographs.—The powder samples were loaded with the aid of a special holder[13] into Lindemann glass capillaries of 0.3-mm. diameter and then sealed with beeswax. All operations were performed inside a nitrogen atmosphere drybox. A 114.6-mm. diameter powder camera was used, and photographs of the diffraction patterns were taken with Ni-filtered Cu Kα radiation. Lattice constants with estimated standard deviations of ±0.01 Å. were obtained by the utilization of the Bradley–Jay extrapolation method.[14] Corrections were made for film shrinkage.

TABLE I
MOLE RATIO OF POWDER SAMPLES AND COMPARISON OF PER
CENT FREE METAL IMPURITY

Sample	Av. X/M mole ratio	% free metal This work	Holze[8]
$ZrCl_3$	3.01	38.8	46.2
$ZrBr_3$	2.95	3.0	28.2
ZrI_3	2.93	3.4	19.0
HfI_3	3.19	6.4	

Results

All of the observed X-ray diffraction lines from each of the four compounds were indexed with the aid of a hexagonal Bunn chart.[15] The lattice constants for

(11) H. L. Schäfer and H. Skoludek, *Z. anorg. allgem. Chem.*, **316**, 15 (1962).

(12) E. M. Larsen and J. J. Leddy, *J. Am. Chem. Soc.*, **78**, 5983 (1956).

(13) E. M. Larsen and J. J. Leddy, *Rev. Sci. Instr.*, **29**, 736 (1958).

(14) *Cf.* H. P. Klug and L. E. Alexander, "X-Ray Diffraction Procedures," John Wiley and Sons, New York, N. Y., 1954, p. 462.

(15) E. V. Azaroff and M. J. Buerger, "The Powder Method in X-Ray Crystallography," McGraw-Hill Book Co., Inc., New York, N. Y., 1958, p. 73.

these compounds are listed in Table II along with the values reported by previous workers for these and related compounds. The calculated densities for two MX_3 formula units per unit cell give good agreement with those measured experimentally (Table II). Systematic absences of the $h0l$ reflection for l odd indicate $P6_3/mcm$ (D^3_{6h}), $P6_3cm$ (C^3_{6v}), or $P\bar{6}c2$ (D^2_{3h}) as the probable space groups.[16] Any of these three probable space groups requires the two metals and six halogen atoms per unit cell to be in special positions. Stereochemical considerations restrict the possible combinations of symmetry. Table III shows the special positions and resulting point symmetry available to the metal and halogen atoms for each of the three probable space groups.[16] All three possible space groups demand that the metal and halogen layers of atoms each be regularly spaced along the c lattice direction. Consequently, it seems reasonable to assume that these alternating metal and halogen layers are equidistant from each other, corresponding to the z parameters of the metal and halogen atoms being restricted to $z = 0$ and $z = 1/4$, respectively. By this choice the noncentrosymmetric space group C^3_{6v}-$P6_3cm$ becomes equivalent to the centrosymmetric one, D^3_{6h}-$P6_3/mcm$, in which the metal atoms occupy the set 2b with point symmetry 3m and the halogen atoms are in set 6g with mm point symmetry. In order for the special positions of the other noncentrosymmetric space group, D^2_{3h}-$P\bar{6}c2$, to coincide with those of the centrosymmetric space group, the halogen y coordinate must be fixed at $y = 0$. Although D^2_{3h}-$P\bar{6}c2$ cannot be ruled out as a possibility, a structure consistent with the space group requirements of D^3_{6h}-$P6_3/mcm$ is supported by the intensity data.

For this centrosymmetric space group the two metal atoms are fixed in the special set 2b, while the placement of the six halogens in the one set 6g introduces an alterable x coordinate (Table III). The structure then is based only on one variable positional parameter and for an isotropic vibrational model on two independently variable thermal parameters (*i.e.*, one for each metal and the other for each halogen). Estimated values for these individual isotropic temperature factors of 1.9 and 1.5 Å.² were used for the halogen and metal atoms, respectively.

For a regular hexagonal close-packed structure of halogen atoms, the halogen x parameter ideally would be $1/3$. However, the c/a ratios suggest some distortion of the halogen lattice, and the actual intensity calculations carried out for several values of x (*e.g.*, $x = 0.333$, 0.325, 0.319, and 0.340) definitely indicated a better fit between the observed and calculated intensities, I_c, for a value of $x < 1/3$. For $ZrCl_3$ and $ZrBr_3$ the best agreement was obtained with an x value of 0.319, while for ZrI_3 and HfI_3 the best fit was found with an x parameter of 0.325. For all intensity calculations the form factors utilized for chlorine are those of Viervoll and

(16) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952.

TABLE II

X-RAY DATA FOR ZrX$_3$, HfI$_3$, β-TiCl$_3$, β-TiBr$_3$, AND TiI$_3$[a]

Compound	Proposed space group	a, Å.	c, Å.	c/a	D_{calcd} ($Z = 2$)	D_{exptl}	Source
ZrCl$_3$	D$^3_{6h}$-P6$_3$/mcm	6.36	6.14	0.965	3.05	2.95	Present work
	D$^3_{3h}$-P$\bar{6}$2m	6.41	6.25	0.975	2.96	. . .	Holze[3]
ZrBr$_3$	D$^3_{6h}$-P6$_3$/mcm	6.75	6.315	0.936	4.42	4.52	Present work
	D$^3_{3h}$-P$\bar{6}$2m	6.76	6.36	0.941	4.38	. . .	Holze[3]
ZrI$_3$	D$^3_{6h}$-P6$_3$/mcm	7.25	6.64	0.916	5.20	5.13	Present work
	D$^3_{3h}$-P$\bar{6}$2m	7.33	6.73	0.918	5.01	. . .	Holze[3]
HfI$_3$	D$^3_{6h}$-P6$_3$/mcm	7.225	6.59	0.912	6.25	6.17	Present work
β-TiCl$_3$	D$^3_{6h}$-P6$_3$/mcm	6.27	5.82	0.928	2.59	. . .	Natta, et al.[6]
β-TiBr$_3$	D$^3_{3h}$-P$\bar{6}$2m	6.69	6.13	0.916	4.04	. . .	Holze[3]
TiI$_3$	D$^3_{3h}$-P$\bar{6}$2m	7.13	6.49	0.910	5.00	. . .	Holze[3]
	D$^3_{3h}$-P$\bar{6}$2m	7.17	6.47	0.902	4.94	. . .	Rolsten[5]

[a] Holze's cell constants originally cited in kx. units[3] have been converted to Å.

TABLE III

POSSIBLE SPACE GROUP POSITIONS AND POINT SYMMETRY FOR Zr AND Hf TRIHALIDES

Atoms	Set	Point symmetry	Equiv. positions	Set	Point symmetry	Equiv. positions	Set	Point symmetry	Equiv. positions
		P$\bar{6}_3$/mcm (D$^3_{6h}$)			P6$_3$cm (C$^3_{6v}$)			P$\bar{6}$c2 (D$^2_{3h}$)	
6X	6g	mm	$x,0,^1/_4$; $0,x,^1/_4$; $\bar{x},\bar{x},^1/_4$ $\bar{x},0,^3/_4$; $0,\bar{x},^3/_4$; $x,x,^3/_4$	6c	m	$x,0,z$; $0,x,z$; $\bar{x},\bar{x},z$ $\bar{x},0,^1/_2 + z$; $0,\bar{x},^1/_2 + z$; $x,x,^1/_2 + z$	6k	m	$x,y,^1/_4$; $\bar{y},x - y,^1/_4$; $y - x,\bar{x},^1/_4$ $y - x,y,^3/_4$; $\bar{y},\bar{x},^3/_4$; $x,x - y,^3/_4$
2M	2b	$\bar{3}$m	$0,0,0$; $0,0,^1/_2$	2a	3m	$0,0,z$; $0,0,^1/_2 + z$	2a	32	$0,0,0$; $0,0,^1/_2$

Ögrim,[17] while the atomic form factors used for the metal and other halogen atoms are those of Thomas and Umeda.[18] The diffraction lines, proposed Miller indices, and relative intensities are listed in Table IV for the four compounds.

Discussion

The basic structure for each of these compounds consists of infinite chains along the c axis formed by MX$_6$ octahedra joined at opposite faces. The structure is based on a hexagonal close-packing of halogen atoms with the metal atoms occupying one-third of the available octahedral holes (Fig. 1). All of the octahedral holes along the corners of the unit cell parallel to the c axis are filled; the chains of octahedral holes parallel to c but with centers at $^1/_3$, $^2/_3$ and $^2/_3$, $^1/_3$ are unoccupied. The distance between each metal and its six surrounding halogen atoms calculated from the data for our model is 2.54 Å. for ZrCl$_3$, 2.67 Å. for ZrBr$_3$, 2.88 Å. for ZrI$_3$, and 2.87 Å. for HfI$_3$ (each with e.s.d. ± 0.03 Å.). A distortion in the hexagonal close-packing of the halogen atoms occurs such that the occupied octahedral holes are smaller than the unoccupied ones. This distortion can be explained readily from the bonding forces between each of the metal atoms and the octahedron of halogens surrounding it which no doubt draw the halogen atoms closer to one another (*i.e.*, $x < ^1/_3$) than to the other halogens which do not share between them a metal atom.

Our space group symmetry requires the metal atoms to be regularly spaced along the c direction midway between the halogen atoms at a distance corresponding to one-half of the "c" cell constant. This gives from our lattice constant measurements metal–

metal distances of 3.07 Å. for ZrCl$_3$, 3.16 Å. for ZrBr$_3$, 3.32 Å. for ZrI$_3$, and 3.30 Å. for HfI$_3$ (each with e.s.d. ± 0.005 Å.).

A detailed comparison of our structural analysis with that of Holze not only is informative but also is pertinent to other work on these and related compounds. Holze[3] selected from his X-ray powder data for the zirconium trihalides, β-TiBr$_3$, and TiI$_3$ (all classified by him as isostructural), a different space group P$\bar{6}$2m (D$^3_{3h}$) which, unlike our assignment, does not possess any symmetry restrictions corresponding to the systematic absence of $h0l$ reflections for l odd. For P$\bar{6}$2m Holze[3] placed the two metal atoms in one set of 2-fold special positions (2e) of point symmetry 3m, and the six halogen atoms in two sets of 3-fold special positions (3f and 3g) of point symmetry mm. The sets and coordinates of these equivalent positions[16] are

2e $0,0,z$; $0,0,\bar{z}$

3f $x_1,0,0$; $0,x_1,0$; $\bar{x}_1,\bar{x}_1,0$

3g $x_2,0,^1/_2$; $0,x_2,^1/_2$; $\bar{x}_2,\bar{x}_2,^1/_2$

The significant difference between the above equivalent positions and those for any of the three space groups considered by us (Table III) is that for P$\bar{6}$2m the z coordinates of the metal positions (set 2e) can be varied such that the metal atoms are not required to be regularly spaced along the c direction.

From limited parameter calculations carried out only for the titanium trihalides in which the sets 3f and 3g were assumed to be interrelated by the condition $x_2 = 1 - x_1$, Holze[3] obtained bromine and titanium atomic coordinates ($x_1 = 0.318$ and $z = 0.290$) for β-TiBr$_3$ and an iodine coordinate ($x_1 = 0.314$) for TiI$_3$ (a titanium coordinate was not estimated for TiI$_3$). He

(17) H. Viervoll and O. Ögrim, *Acta Cryst.*, **2**, 227 (1949).
(18) L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957).

concluded that similar distortions from the so-called ideal structure (for his space group these parameters are $x_1 = 1/3$; $x_2 = 1 - x_1 = 2/3$; $z = 0.250$)[19] occur for the zirconium trihalides.

Holze's assignment[3,7] of this space group for the zirconium trihalides and his subsequently formulated structure with the zirconium atoms drawn together along the c direction toward one another in pairs to give linear chains of $(Zr_2X_6)_n$ units are based entirely on the presence of one observed reflection (an indexed 001 line designated by Holze[3] as a "metal line" attributable to the zirconium atom in ZrX_3) in his powder data. This 001 line is the only observed line in Holze's data which does not fit the systematic absences of l odd for $h0l$ data required by the $P6_3/mcm$ (D^3_{6h}) space group. Significantly, this line does not appear in any of our powder patterns nor in the data (indexed by us) of Watt and Baker[9] for ZrI_3, but it does appear in the powder data (indexed by us) reported by Schäfer and Skoludek[11] for $ZrBr_3$.

To compare the two models further, intensities based on Holze's model (and space group) were calculated for ZrX_3 ($X = Cl$, Br, I) and HfI_3 with metal z parameters of 0.27 and 0.29. The halogen x values utilized for Holze's model were identical with ours. The strongest pure "metal line" for the above metal parameters is the 001 reflection, but even for the most favorable ratio of metal to halogen scattering power (*i.e.*, $ZrCl_3$), the calculated intensity of the 001 line does not account for the relatively large experimental intensities of the 001 line observed by Holze[3] for ZrX_3 ($X = Cl$, Br, I) and by Schäfer and Skoludek[11] for $ZrBr_3$. Other reflections were found to give a more sensitive change in intensities due to small changes in parameter, but unfortunately the lack of resolution due to the accidental overlap of certain lines with similar Bragg angles does not allow a clear distinction to be made between the two models.

The basic assumption underlying our proposed model has been the absence of any order–disorder phenomenon. The method of preparation of the crystalline sample may result in a nonstoichiometric structure (*i.e.*, an "excess" structure with additional atoms occupying holes in the normal structure or a "deficient" structure with vacancies in the normal lattice positions) or may affect the degree of ordering of the atoms in the lattice (*i.e.*, lead to the formation of layer stacking faults). Variations of intensities due to such effects may account for the presence or absence of indexable lines (*e.g.*, the 001 reflection) for these compounds. These and the nonindexable lines (*e.g.*, the lowest-angle line (of largest d-spacing) observed by Watt and Baker[9] for ZrI_3 and by Schäfer and Skoludek[11] for $ZrBr_3$ cannot be indexed as a β-form reflection) may result from impurities or from the presence of a superlattice indicative of a larger unit cell with more complex grouping.
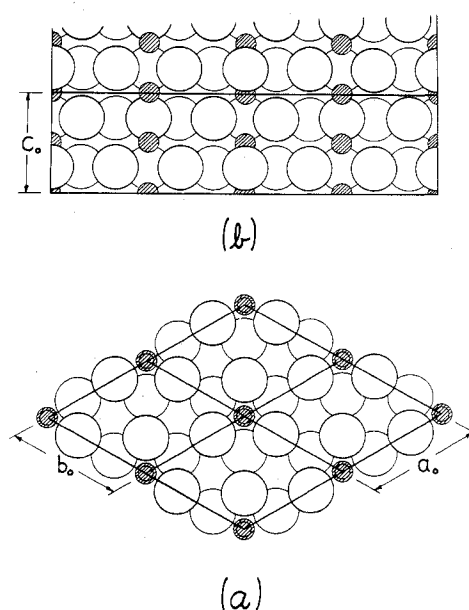
Fig. 1.—A packing drawing of the hexagonal structure for ZrX_3 ($X = Cl$, Br, I) and HfI_3 viewed in (a) along the c axis and in (b) along the [110] direction. The metal atoms are represented by the smaller line-shaded circles.

The similarity of cell dimensions, axial ratios, and diffraction symmetry (Table II) for the zirconium and β-form titanium trihalides certainly suggests that the atomic arrangements including distortions are similar for all these compounds. The space group D^3_{6h}-$P6_3/mcm$ obtained by Natta, *et al.*,[6] from the characteristic extinctions for β-$TiCl_3$ is identical with that chosen by us for ZrX_3 ($X = Cl$, Br, I) and HfI_3, and furthermore the model reported by Natta and co-workers from intensity calculations for β-$TiCl_3$ is essentially identical (*i.e.*, their fractional coordinate x for Cl is 0.315) with ours. The temporary designation by Rolsten and Sisler[5] of D^3_{3h}-$P\bar{6}2m$ (instead of D^3_{6h}-$P6_3/mcm$) for TiI_3 is based on the presence of a weakly observed 003 reflection in their powder pattern for which the 001 line was absent. In contrast to the powder data for β-$TiCl_3$ (for which the X-ray scattering power ratio of titanium with halogen is the most favorable), Holze[3] lists for β-$TiBr_3$ and TiI_3 three $h0l$ reflections (001, 003, and 005) with l odd. Although the above results do not indicate that Holze's model for β-$TiBr_3$ and TiI_3 can be discarded, on the basis of our powder data we feel that there is justification for the proposal of our symmetrical model for the zirconium trihalides and HfI_3. The apparent discrepancies in the powder work need to be investigated further.

Of interest is that the magnetic susceptibilities observed for the zirconium and titanium trihalides[20,21] certainly suggest some type of cooperative metal–metal interaction involving the one unpaired electron per metal atom. We wish to point out that simple

(19) An origin shift of $z = 1/4$ is required to transform Holze's parameters for the *undistorted* hexagonal close-packed arrangement into equivalent, idealized parameters for $P6_3/mcm$.

(20) J. Lewis, D. J. Machin, I. E. Newnham, and R. S. Nyholm, *J. Chem. Soc.* 2036 (1962).

(21) W. Klemm, E. Holze, and W. Basualdo, "Inorganic Chemistry Papers, 16th International Congress of Pure and Applied Chemistry, Paris, 1957," Butterworth Scientific Publications, London, 1958, p. 43.

TABLE IV

X-RAY DIFFRACTION DATA (POWDER METHOD) FOR $ZrCl_3$, $ZrBr_3$, ZrI_3, AND HfI_3[a]

ZrCl₃

hkl	$Q_{obsd.}$	$Q_{calc.}$	I_o	I_c
100	0.0335	0.0330	s+	36.0
110} 002}	0.1013	0.0968	w	1.3
002		0.1062		0.2
111	0.1260	0.1254	s	11.0
200	0.1314	0.1318	w+	4.0
102	0.1402	0.1392	m-	9.0
112	0.2063	0.2050	s	12.0
210	0.2310	0.2305	m-	4.0
202	0.2382	0.2379	m-	5.0
211		0.2569	no	0.1
300	0.2972	0.2963	s-	5.5
212}	0.3381	0.3367	m	4.6
113}		0.3377		1.6
220		0.3951	no	0.2
302		0.4025	no	0.00
221}		0.4217		0.9
004}	0.4277	0.4247	m	2.7
310}		0.4279		1.7
311		0.4545	no	0.02
104	0.4582	0.4576	vw	1.3
213		0.4693	no	0.05
222	0.5018	0.5013	w	2.0
114}		0.5235		0.2
400}	0.5243	0.5267	vw	0.6
312}		0.5341		1.3
204		0.5563	no	0.7
320}		0.6255		0.4
402}	0.6352	0.6329	vw	0.4
223}		0.6339		0.4
321		0.6520	no	0.02
214	0.6573	0.6551	vw	1.0
410	0.6923	0.6914	vw	0.2
411}	0.7200	0.7178	vw	0.6
304}		0.7210		1.7
322}		0.7316		1.1
115		0.7623	no	0.3
412	0.7973	0.7976	w	1.6
224}		0.8198		0.1
500}	0.8223	0.8230	vvw	0.1
314		0.8526	no	0.8
323		0.8644	no	0.01
330	0.8898	0.8896	vw	0.6
215		0.8940	no	0.01
331		0.9154	no	0.00
420		0.9218	no	0.3
402}	0.9315	0.9292	w:d	0.4
413}		0.9302		0.4
421		0.9484	no	0.02
404		0.9514	no	0.4
006		0.9556	no	0.00
106		0.9684	no	0.02
332		0.9950	no	0.00
510		1.0206	no	0.2
422		1.0280	no	0.5
511		1.0471	no	0.05
324		1.0502	no	0.30
116		1.0544	no	0.40
225		1.0586	no	0.20
206		1.0872	no	0.30
315		1.0916	no	0.00
414		1.1160	no	0.10
512		1.1267	no	0.60
333		1.1277	no	0.00
423		1.1607	no	0.02
600}	1.1863	1.1851	vw	0.40
216}		1.1860		0.50
430		1.2181	no	0.30
431		1.2447	no	0.00
504		1.2477	no	0.10
306		1.2519	no	0.00
513		1.2595	no	0.02
325		1.2891	no	0.01
520		1.2911	no	0.07
602		1.2913	no	0.00
521		1.3105	no	0.20
334		1.3135	no	0.70
432		1.3243	no	0.20
424}		1.3465		0.50
226}	1.3477	1.3505	vvw	0.40
415}		1.3549		0.30
316}		1.3835		1.4
522}	1.3833	1.3900	vvw	1.0
610		1.4156	no	0.2
611		1.4422	no	0.02
514	1.4476	1.4453	vvv	0.4
433		1.4570	no	0.00
406	1.4868	1.4823	vvv	0.2
612}	1.5213	1.5218		0.3
523}		1.5228	vvv	0.3

ZrBr₃

hkl	$Q_{obsd.}$	$Q_{calc.}$	I_o	I_c
100	0.0291	0.0293	s	48.5
110	0.0887	0.0877	vvv	0.7
002	0.1013	0.1003	m-	6.4
111	0.1143	0.1127	s+	64.0
200	0.1180	0.1169	w	3.50
102	0.1307	0.1296	m	8.0
112	0.1890	0.1881	s	30.6
210	0.2065	0.2048	m-	4.3
202	0.2191	0.2172	m	7.3
211		0.2298	no	1.0
300	0.2654	0.2632	s-	20.8
212	0.3062	0.3051	m	6.1
113	0.3147	0.3135	s-	11.3
220		0.3510	no	0.04
302	0.3653	0.3635	w+	3.7
221}	0.3793	0.3761	m	7.4
310}		0.3803		2.9
004	0.4020	0.4012	w+	3.0
311		0.4054	no	0.1
213}	0.4313	0.4304		0.3
104}		0.4304	vw	1.68
222	0.4531	0.4513	m	5.7
400	0.4693	0.4630	w	1.3
312	0.4821	0.4806	w	0.99
114		0.4890	no	0.05
204	0.5203	0.5183	vvv	0.5
320	0.5583	0.5556	vvv	0.26
402		0.5682	no	0.16
223	0.5777	0.5767	m-	2.9
321		0.5807		0.2
313}	0.6066	0.6059		0.1
214}		0.6059	w	1.1
410		0.6142	no	0.01
411	0.6411	0.6393	m	4.4
322	0.6559	0.6559	w+	2.1
304	0.6640	0.6645	m-	5.9
412}	0.7143	0.7145		4.1
115}		0.7146	m	1.9
500		0.7311	no	0.05
224		0.7522	no	0.00
314}	0.7814	0.7814		1.3
323}		0.7814	w	.1
330	0.7902	0.7897	m	1.9
331		0.8148	no	0.00
420	0.8203	0.8190	w-	0.37
502}	0.8329	0.8314	vw	0.78
215}		0.8316		0.07
413	0.8408	0.8398	w+	2.5
421		0.8440	no	0.2
404		0.8691	no	0.7
332	0.8908	0.8900	vvv	0.4
006		0.9028	no	0.09
510		0.9066	no	0.14
422		0.9193	no	0.26
511		0.9317	no	0.2
106		0.9320	no	0.20
324		0.9569	no	0.19
225	.9773	0.9778	w-	0.99
116	.9903	0.9904	w-	1.2
512}	1.0076	1.0069		0.06
315}		1.0071	vw	0.85
333		1.0153	no	0.00
414		1.0153	no	0.02
205		1.0197	no	0.37
423		1.0446	no	0.14
600	1.0547	1.0529	m-	1.2
430	1.0830	1.0823	m-	0.67
431		1.1072	no	0.02
216		1.1074	no	0.50
513		1.1323	no	0.19
504		1.1324	no	0.06
520		1.1407	no	0.00
602		1.1515	no	0.25
521}	1.1659	1.1658	m-	1.4
306}		1.1659		0.3
432		1.1824	no	0.05
325		1.1826	no	0.05
334	1.1915	1.1908	m-	2.1
424	1.2196	1.2201	vw	0.48
522}	1.2410	1.2410		1.8
415}		1.2412	w:d	1.5
226		1.2536	no	0.96
610		1.2576	no	0.40
611}	1.2842	1.2827		0.10
316}		1.2829	vw	0.20
433}	1.3096	1.3078		0.02
514}		1.3078	w:d	0.20
612	1.3616	1.3579	vvv	0.17
523	1.3662	1.3663	w:d	1.3

ZrBr₃ (continued)

hkl	$Q_{obsd.}$	$Q_{calc.}$	I_o	I_c
406		1.3707	no	0.06
440		1.4039	no	0.00
335		1.4165	no	0.00
441}	1.4301	1.4289		0.67
700}		1.4331	w-	0.43
530}		1.4331	no	0.04
425}		1.4459	no	0.14
604}	1.4542	1.4540		2.20
531}		1.4582	w	0.07
326}		1.4584		0.94
434}	1.4826	1.4833		1.40
613}		1.4833	vw	0.10
442		1.5042	no	0.99
416		1.5169	no	2.3
520		1.5208	no	0.05
702}		1.5334		0.00
515}		1.5336	w	0.20
532}	1.5338	1.5334		1.40
622	1.6213	1.6211	w-	2.0

ZrI₃

hkl	$Q_{obsd.}$	$Q_{calc.}$	I_o	I_c
100	0.0257	0.0254	s-	55.4
110	0.0772	0.0761	vv	11.2
002	0.0924	0.0907	v	26.9
111}	0.1001	0.0988	s+	190.0
200}		0.1015		4.40
102	0.1175	0.1161	v	9.7
112	0.1676	0.1668	s	65.10
210	0.1789	0.1777	m-	5.6
211		0.2002		1.08
202}	0.1935	0.1922	m-	8.90
300}	0.2287	0.2283	s-	53.2
212	0.2696	0.2684	v	7.49
113	0.2819	0.2802	m	35.60
220		0.3046	no	1.20
302	0.3195	0.3190	m-	20.50
221}	0.3290	0.3271	m	26.00
310}		0.3298		3.70
311		0.3525	no	0.31
004	0.3653	0.3628	m-	7.59
213}		0.3816		0.31
104}	0.3860	0.3882	vw	2.0
222	0.3959	0.3953	⊡	13.6
400	0.4069	0.4060	vw	1.6
312}	0.4220	0.4205	w:d	1.37
114}		0.4388		1.20
204	0.4659	0.4643	w:d	0.66
320	0.4826	0.4821	vvv	0.37
402	0.4991	0.4967	vvv	0.24
321		0.5048		0.22
223}	0.5107	0.5085	m	10.50
410}	0.5353	0.5329	w	0.72
313}		0.5339		0.12
214}		0.5405		1.39
411	0.5551	0.5555	m	17.00
322	0.5733	0.5728	w+	2.83
304	0.5925	0.5911	m	16.00
412	0.6239	0.6236	m	10.20
500		0.6344	no	0.06
115	0.6430	0.6430	w+	6.38
224		0.6674	no	0.44
330}	0.6857	0.6850	m-	5.68
323}		0.6862		0.12
314		0.6926	no	1.61
331		0.7077	no	0.00
420	0.7118	0.7104	vvv	0.53
502	0.7259	0.7251	vvv	1.04
421		0.7331	no	0.29
413	0.7395	0.7368	⊡	9.2
215		0.7444	no	0.22
404		0.7688	no	0.90
332	0.7766	0.7757	w:d	2.90
510		0.7866	no	0.20
422		0.8011	no	0.60
511		0.8092	no	0.29
006		0.8163	no	0.47
106		0.8417	no	0.25
324		0.8449	no	0.24
225}	0.8737	0.8713	w+	3.37
512}		0.8774		0.98
333		0.8891	no	0.00
116		0.8923	vvv	2.55
414		0.8957		0.46
315}	0.8965	0.8967		0.05
600}	0.9132	0.9135	v	3.20
423}		0.9145		0.19

TABLE IV (*Continued*)

ZrI₃ (continued)

hkl	Q_{obsd}	Q_{calc}	I_o	I_c
206)		0.9177		0.43
430	0.9359	0.9388	w:d	0.78
431		0.9615	no	0.03
520		0.9896	no	0.18
513		0.9906	no	0.19
216		0.9939	no	0.60
504		0.9972	no	0.12
602)		1.0042	m⁻	1.8
521)	1.0120	1.0123		5.0
432		1.0295	no	0.05
306)		1.0446		1.84
325)		1.0490		0.05
334)	1.0487	1.0478	m⁻	5.3
424)		1.0732		0.53
522)	1.0757	1.0803	m⁻	3.8
610		1.0911	no	0.48
415	1.1008	1.0996	w	4.7
611		1.1138	no	0.12
226		1.1208	no	1.87
433		1.1429	no	0.02
316)		1.1461		0.24
514)	1.1479	1.1494	vvw	0.24
612		1.1818	no	0.14
523	1.1942	1.1937	w⁺	4.3
440		1.2179	no	0.07
406		1.2223	no	0.12
441)	1.2403	1.2406	w:d	2.08
700)		1.2433		0.37
335		1.2519	no	0.00
531		1.2661	no	0.05
604	1.2767	1.2763	w	4.6
425		1.2773	no	0.13
613		1.2952	no	0.10
434)	1.3009	1.3015	w:d	1.20
442)		1.3086		1.68
620		1.3194	no	0.05
702)	1.3335	1.3340		0.00
522)		1.3340	vw	1.20
621		1.3421	no	0.19
416)		1.3492		3.50
524)	1.3534	1.3524	vw	0.26
515)		1.3534		0.17
622)	1.4096	1.4100	w:d	1.1
443)		1.4220		2.17
710		1.4463	no	0.13
506		1.4506	no	0.55
533		1.4474	no	0.06
614)	1.4560	1.4538	w⁻	0.98
711)		1.4690		4.49
435		1.5057	no	0.03
623)		1.5235		0.22
426)	1.5279	1.5267	w:d	0.48

HfI₃

hkl	Q_{obsd}	Q_{calc}	I_o	I_c
100	0.0266	0.0256	m	164.6
110		0.0766	no	0.46
002	0.0924	0.0920	w	13.4

HfI₃ (continued)

hkl	Q_{obsd}	Q_{calc}	I_o	I_c
111)	0.1018	0.0996	s⁺	187.7
200)		0.1021		20.1
102	0.1186	0.1176	w	37.8
112	0.1701	0.1688	s	107.6
210	0.1812	0.1789	w⁺	21.6
202	0.1957	0.1944	m⁻	25.8
211		0.2018	no	1.08
300	0.2314	0.2299	s⁻	36.9
212	0.2723	0.2709	w⁺	25.3
113	0.2844	0.2839	s⁻	34.8
220		0.3062	no	0.00
302	0.3234	0.3221	m⁻	9.44
310)	0.3315	0.3320	m	10.9
221)		0.3295		25.8
311		0.3550	no	0.31
004	0.3675	0.3683	w⁺:d	10.4
213)		0.3860		0.31
104)	0.3906	0.3939	vw	6.67
222	0.4008	0.3986	m	23.3
400	0.4106	0.4087	vw	4.36
312	0.4249	0.4242	w	7.37
114		0.4452	no	0.00
204	0.4698	0.4706	vvw	3.24
320	0.4871	0.4853	vvw	2.47
402	0.5018	0.5008	vvw	2.04
321)		0.5083		0.22
223)	0.5144	0.5137	m	10.3
410		0.5364	no	0.00
313)		0.5393		0.12
214)	0.5398	0.5472	w:d	5.69
411	0.5613	0.5595	m	16.7
322	0.5790	0.5773	w⁺	7.97
304	0.5982	0.5984	m	22.5
412	0.6302	0.6285	m	17.9
500	0.6406	0.6386	w⁻	0.59
115	0.6541	0.6522	w⁻	6.19
224		0.6749	no	0.00
330)	0.6909	0.6896	m⁻	8.14
323)		0.6926		0.12
314)		0.7005		4.92
331		0.7126	no	0.00
420	0.7167	0.7151	vvw	1.93
502	0.7315	0.7306	vw	2.04
421		0.7582	no	0.29
413	0.7446	0.7436	m	9.07
215		0.7545	no	0.07
404)	0.7811	0.7771	vvw	2.39
332)		0.7818		1.19
510		0.7919	no	1.12
422		0.8074	no	2.66
511		0.8148	no	0.29
006		0.8287	no	0.19
106		0.8545	no	1.14
324		0.8558	no	1.66
225)	0.8839	0.8822	w:d	3.30
512)		0.8839		3.12
333		0.8969	no	0.00
414		0.9048	no	0.00

HfI₃ (continued)

hkl	Q_{obsd}	Q_{calc}	I_o	$I_c(Lp)$
116)		0.9056	vvw	4.48
315)	0.9075	0.9076		0.05
600)		0.9196	w	4.66
423)	0.9218	0.9225		0.19
206		0.9312	no	1.39
430	0.9468	0.9450	vvw	1.96
431		0.9681	no	0.02
520		0.9962	no	0.00
513		0.9990	no	0.19
504		1.0069	no	0.58
216		1.0078	no	2.21
602		1.0116	no	0.67
521)	1.0207	1.0192	w	4.99
432)		1.0372	no	0.94
334)	1.0576	1.0581	m	7.85
306)		1.0589		0.68
325)		1.0609	no	0.02
424)		1.0837		2.14
522)	1.0865	1.0882	w	7.08
610		1.0983	no	1.45
415	1.1124	1.1121	vw	4.68
611		1.1213	no	0.12
226		1.1355	no	3.50
433		1.1523	no	0.02
514)	1.1592	1.1602	vw	1.49
316)		1.1611		1.46
612		1.1905	no	1.22
523)	1.2023	1.2035	m⁻	4.25
440)		1.2260	no	0.01
406		1.2376	no	0.56
441)	1.2484	1.2491	vw	2.08
530)		1.2516		0.44
700)		1.2516		0.94
335		1.2654	no	0.00
531		1.2746	no	0.05
604)	1.2873	1.2879	w:d	6.97
425)		1.2908	no	0.14
613		1.3056	no	0.12
434)		1.3135	vw:d	3.22
326)	1.3152	1.3142		2.62
442)		1.3182		3.20
620		1.3281	no	0.50
702)	1.3440	1.3436		0.32
532)		1.3436	vw	3.26
621		1.3512	no	0.19
524)		1.3647		0.02
416)	1.3663	1.3653	vvw	6.70
515)		1.3675		0.17
622)	1.4220	1.4204	w⁻	3.17
443)		1.4333		2.20
710		1.4559	no	0.02
533)		1.4589	no	0.05
614)	1.4698	1.4668	vw	3.05
506)		1.4675		1.63
711)		1.4789		4.56
336		1.5186	no	0.6
435		1.5208	no	0.02
623)		1.5554		0.24
426)	1.5440	1.5442	vw	2.33

a Legend: $Q_{obsd} = (4 \sin^2 \theta_{obsd})/\lambda^2$; $Q_{calcd} = (4 \sin^2 \theta_{calcd})/\lambda^2$; no = not observed; s⁺, s, s⁻, m⁺, m, m⁻, w⁺, w, w⁻, vw, and vvw = order of relative (visually estimated) intensities in descending order; vw:d means a very weak diffuse line. The powder pattern for ZrCl₃ has been corrected for known metallic Zr lines.

molecular orbital theory can be utilized to explain qualitatively a direct metal–metal interaction for a system of regularly spaced metal atoms in a linear polymeric configuration. For our proposed zirconium trihalide model the local crystallographic point group symmetry about each zirconium is $\bar{3}m$ (D_{3d}). The nine relevant zirconium orbitals available for bonding transform under this point group to give the sum $2A_{1g} + A_{2u} + 2E_g + E_u$ where A_{1g} is the symmetry representation of the s and d_{z^2} orbitals, A_{2u} that of p_z, E_g that of the ($d_{x^2-y^2}$, d_{xy}) and (d_{xz}, d_{yz}) pairs, and E_u that of the (p_x, p_y) pair. Six of these zirconium orbitals of representation $A_{1g} + A_{2u} + E_g + E_u$ are combined under this trigonal ligand field with the appropriate symmetry orbitals of the six coordinated halogens to give the usual six σ-bonds. The essential feature of this description is that after σ-bonding, there are left three orbitals on each zirconium available for

possible metal–metal interaction involving the remaining electron per metal atom. These consist of a σ-type metal orbital of A_{1g} symmetry which points along the chain axis and two other degenerate orbitals of E_g symmetry.

These orbitals as well as higher energy zirconium AO's can interact with the corresponding orbitals (of identical symmetry) of the neighboring metals in the chain to give molecular orbitals. For an infinite linear array of equidistant zirconium atoms the energy levels become bands. Since these bands presumably overlap and since "configuration interaction" involving higher energy states also may contribute to the ground state, the assignment of electrons to these bands cannot be made unambiguously, but in any case the band(s) are only partially filled. This MO description of bonding thereby provides a qualitative picture by which the zirconium atoms conforming

to our proposed model can interact directly with one another.[22] The presumed antiferromagnetic behavior[20,21] then may arise by direct metal–metal interaction and/or by super-exchange *via* the bridging halogen atoms.

(22) This bonding description also is applicable to Holze's $(Zr_2X_6)_n$ model[3,7] of alternating short and long interatomic distances. The local point group symmetry about each zirconium is decreased to C_{3v} for which the s, p_z, and d_{z^2} orbitals transform as A_1, and the three pairs (p_x, p_y), $(d_{x^2-y^2}, d_{xy})$, and (d_{xz}, d_{yz}) as E. Similarly, after σ-bonding the three orbitals remain on each zirconium with the symmetry $A_1 + E$. The non-equivalent bond distances will result in the energy levels splitting into gaps of bonding and antibonding states; if the dimeric $(Zr_2X_6)_n$ units are sufficiently separated from one another, the interaction of the zirconium atoms can be considered as distinct pairs. Since for a given (Zr_2X_6) unit the axially symmetric A_1 atomic orbitals presumably interact with each other more strongly than the degenerate orbitals making up the E representation, the two coupling electrons can be assigned to the totally symmetric bonding MO with the resulting formation of a direct metal–metal bond. This electron coupling in pairs is similar to that found for α-NbI$_4$ and TaI$_4$ which are diamagnetic.[23] The structure of solid α-NbI$_4$ and the isomorphous TaI$_4$ consists of infinite chains formed by MI$_6$ octahedra sharing two opposite edges; the metal atoms are shifted from the centers of the iodine octahedra toward one another in pairs to give a resulting metal–metal distance of 3.31 Å.[23]

(23) L. F. Dahl and D. L. Wampler, *Acta Cryst.*, **15**, 903 (1962).

Of significance would be a measurement of electrical conductivity of pure single crystals (attempts to prepare suitable crystals for X-ray diffraction as yet have been unsuccessful) to determine the metallic nature of these compounds. Also, a low-temperature neutron diffraction study is needed to elucidate the atomic magnetic moment orientation of these presumed antiferromagnetic substances.

The Role of the Monofluoroiron(III) Ion in the Iron(II)–Iron(III)–Fluoride Ion Isotope Exchange Reaction

By JAMEEL MENASHI, SHOUZOW FUKUSHIMA,[1] CHARLES FOXX, and WARREN L. REYNOLDS

The iron(II) + iron(III) exchange rate was measured in NaF–NaClO$_4$–HClO$_4$ media at constant pH and ionic strength. The iron(II) concentration was increased so as to make the isotope exchange rate comparable to the rate of formation of the inner coordination shell complex FeF^{+2}. The observed isotope exchange rate was dependent on the rate of formation of FeF^{+2} in the manner expected if the activated complex [Fe$_2$F^{+4}]* was formed from Fe^{+2}(aq) and FeF^{+2}(aq).

A considerable number of anionic catalysts for the iron(II) + iron(III) isotope exchange reaction have been reported.[2] In each of these cases it has been postulated that isotope exchange occurs between Fe^{+2} and FeX$_n^{+3-nq}$, the latter species being a complex between Fe^{+3} and the anion X^{-q} which is formed reversibly and rapidly compared to the rate of isotope exchange. As a result of the postulate the rate of the isotope exchange reaction is written as

$$R = \left\{ k_0 + \frac{k_h K_h}{[H^+]} + k_1 K_1 [X^{-q}] + k_2 K_1 K_2 [X^{-q}]^2 + \ldots \right\} [Fe^{+2}][Fe^{+3}] \quad (1)$$

where k_0, k_h, k_1, k_2 are the rate constants for isotope

exchange between Fe^{+2} and Fe^{+3}, Fe(OH)$^{+2}$, FeX^{+3-q}, FeX$_2^{+3-2q}$, respectively, K_h is the acid dissociation constant of aquo ferric ion, and K_1 and K_2 are the stepwise formation constants of the Fe(III)–X^{-q} complexes. The products $k_1 K_1$, $k_2 K_1 K_2$, ... in (1) are obtained from the variation of observed rate constants with change of X^{-q} concentration. From these products values of k_1, k_2, ... are calculated using independently determined values of K_1, K_2, ... for the inner coordination sphere complexes of Fe(III). The theories concerning mechanisms of electron transfer use these rate constants without it being known whether or not the rate constant values are valid. If, for example, the exchange path involving one Fe^{+2}, one Fe^{+3}, and one X^{-q} in the activated complex was a reaction between FeX^{+2-q} and Fe^{+3} or between Fe^{+2} and an outer-sphere complex, Fe(H$_2$O)$_6$X^{+3-q}, of Fe(H$_2$O)$_6^{+3}$ and X^{-q}, then the values of K_1 and k_1 would be very different. Hence, it is very important to obtain evidence of a rate-determining isotope exchange reaction between Fe^{+2} and FeX$_n^{+3-nq}$. In the work reported here we have obtained excellent evidence that the

(1) On leave from Osaka University, Osaka, Japan.
(2) (a) J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952); (b) J. Hudis and A. C. Wahl, *J. Am. Chem. Soc.*, **75**, 4153 (1953); (c) G. S. Laurence, *Trans. Faraday Soc.*, **53**, 1326 (1957); (d) D. Bunn, F. S. Dainton, and S. Duckworth, *ibid.*, **55**, 1267 (1959); *ibid.*, **57**, 1131 (1961); (e) R. A. Horne, *J. Phys. Chem.*, **64**, 1512 (1960); (f) N. Sutin, J. K. Rowley, and R. W. Dodson, *ibid.*, **65**, 1248 (1961); (g) W. L. Reynolds and S. Fukushima, *Inorg. Chem.*, **2**, 176 (1963); (h) K. Bachman and K. H. Lieser, *Z. physik. Chem.* (Frankfurt), **36**, 236 (1963).