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A Study of the Lower Chlorides of Zirconium and Hafnium. The Formation of Stable Monochlorides[1]

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Reaction in a sealed tantalum tube of gaseous $HfCl_4$ from a reservoir at 450–550° with a large area of hafnium foil at 610–650° gives about an 8% yield of a metal-looking $HfCl_{1+x}$. The analogous reaction of $ZrCl_4$ with zirconium at 600° produces $ZrCl_3$ plus a smaller amount of similar metallic phase mixed with $ZrCl_2$. Equilibration of each metallic product with the respective metal at 625–650° produces the pure monochloride. The only other hafnium chlorides evident, the green $HfCl_3$ and a more reduced brown phase (Cl:Hf $\approx$ 2.5), are obtained in measurable amounts only in the presence of added $AlCl_3$ at 375°. Only the zirconium system appears to contain a dichloride. The two monochlorides are evidently isostructural, metallic conductors, and HfCl is substantially diamagnetic. An isoelectronic relationship of ZrCl and NbO is noted.

Introduction

A recent study of the Hf–HfI_4 system[2] revealed that the only stable reduced phase is the triiodide and that this phase is nonstoichiometric on the oxidized side, the upper limit composition varying from $HfI_{3.2}$ at 550° to $HfI_{3.46}$ at 475°. A scarcity of information regarding the hafnium chlorides led us to the present examination of the Hf–$HfCl_4$ system. In this case prior studies[3,4] have noted that the incomplete reaction between the metal powder and tetrachloride presented considerable difficulty and prevented the isolation or characterization of the trichloride. However, techniques developed in the recent study of the iodides[2] have been found to give a considerable advantage in such kinetically limited reactions, specifically the use of hafnium metal foil as the reductant to allow separation of products uncontaminated by metal together with the exploitation of tantalum as a strong, inert container. Once the present work established that there were indeed three lower hafnium chloride phases, including the remarkable monochloride, a similar inspection of synthetic reactions in the Zr–$ZrCl_4$ system was also carried out. Previous preparations of the zirconium(III) chloride, bromide, and iodide by reduction of the tetrachloride have generally been found to be at least kinetically considerably easier than for hafnium.[3,5–8] The isolation of a zirconium dichloride[9] and iodide[10] has also been reported, the latter from the disproportionation of the triiodide at 360–390° in a sealed tube. The dichloride was obtained from the reaction of $ZrCl_3$ with excess zirconium at 675° for 2.5–3 days in a platinum-lined silica container followed by screening to separate the unreacted metal; the yield was 50–55% with an indicated elemental recovery of 96–105% on the separated product.

Experimental Section

The techniques employed were similar to those developed in the study of the hafnium iodide system.[2] The same hafnium metal containing 3% Zr was used as a cold-rolled, 10–15-mil foil for both syntheses and final equilibrations. Available metal containing only 660 ppm of Zr was harder because of nonmetallic impurities and so was sublimed under high vacuum onto 5-mil tantalum backing to give a high surface area. Crystal bar zirconium (~0.05% Hf) was cold-rolled to a 15–20-mil foil. The tetrachlorides were each prepared by treating the metals with HCl (Precision Gas Products) beginning at 300° and increasing to 500° and thence were vacuum sublimed through a coarse frit.

The reaction rates in the Hf–$HfCl_4$ system are extremely slow and respectable yields were obtained only at 600° and above. In order to contain the 30–60-atm pressures generated by the liquid $HfCl_4$ even in hot–cold tubes, tantalum caps were welded onto the ends of the cylindrical tubing rather than using simple welded crimps which were found to expand and leak. The 0.5-in. tubes were often found to expand as much as 25% before they ruptured. The necessary silica jackets included a portion which extended outside the furnace to allow for condensation of the tetrachloride in case the tantalum container failed. This portion also allowed the introduction of either an internal thermometer or ceramic lead-throughs for two thermocouples.

Analyses.—Reduced phases were dissolved in dilute HF as earlier and metal values determined by precipitation of the cupferrate followed by ignition to the dioxide. No oxide was seen during the solution of any products. (Of course, the reduction of and solution in water rather than aqueous HF produced a white precipitate because of the increase in pH.) Data given for each component usually represent the average of analyses of a pair of weighed samples of the same preparation. Occasionally, analysis for both components in the same sample was accomplished by first precipitation and filtration of the chloride, addition of chloride to remove the excess silver followed by a second filtration, and then the usual metal precipitation. The ignited oxide was off-color if complete silver removal was not attained.

The $HfCl_3$ always gave a yellow solution [maxima at 20 and 26.8 $\times$ 10^3 cm^{-1}] which faded in about 1 hr. Dilute H_2O_2 or HNO_3 hastened the decolorization. The $ZrCl_3$ solution gave a similar orange solution; the absorption maxima have been reported to be at 22 and 24.4 $\times$ 10^3 cm^{-1}.[11]

X-Ray Data.—Powder diffraction data were obtained from samples loaded into 0.2–0.3-mm Lindemann glass capillaries in the drybox. A 114.6-mm diameter camera was used with

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(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) A. W. Struss and J. D. Corbett, *Inorg. Chem.*, **8**, 227 (1969).

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

(4) L. F. Dahl, T. Chiang, P. W. Seabaugh, and E. M. Larsen, *Inorg. Chem.*, **3**, 1236 (1964).

(5) H. L. Schläfer and H. Skoludek, *Z. Anorg. Allgem. Chem.*, **316**, 15 (1962).

(6) H. L. Schläfer and H.-W. Wille, *ibid.*, **327**, 253 (1964).

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

(8) F. Gil-Arnao and E. M. Larsen, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, No. INOR 138.

(9) B. Swaroop and S. N. Flengas, *Can. J. Chem.*, **43**, 2115 (1965).

(10) F. R. Sale and R. A. Shelton, *J. Less-Common Metals*, **9**, 60 (1965).

(11) W. A. Baker and A. R. Janus, *J. Inorg. Nucl. Chem.*, **26**, 2087 (1964).

nickel-filtered Cu Kα radiation, and the data were corrected for film shrinkage. Interplanar distances corresponding to the stronger diffractions >1.4 Å, with relative intensities in parentheses, are as follows: ZrCl: 9.73 (w), 8.86 (vs), 4.45 (m), 2.96 (m), 2.72 (vs), 2.60 (w), 2.346 (w), 2.226 (s), 1.991 (w), 1.885 (w), 1.785 (w), 1.724 (s), 1.692 (m), 1.607 (w), 1.489 (m), 1.457 (m) (16 of 24 observed); HfCl: 8.85 (vs), 4.42 (w), 2.94 (m), 2.84 (s), 2.55 (vs), 2.310 (s), 2.213 (s), 1.964 (ms), 1.86 (w), 1.770 (m), 1.683 (ms), 1.654 (m), 1.591 (mw), 1.461 (mw), 1.449 (mw), 1.444 (mw), 1.405 (m) (17 of 31 observed); $ZrCl_2$: 9.0 (mw), 6.44 (vs), 3.01 (w), 2.92 (mw), 2.89 (m), 2.86 (w), 2.80 (mw), 2.77 (m), 2.51 (mw), 2.42 (m, b), 2.34 (mw), 2.257 (mw), 2.154 (m), 1.693 (ms), 1.637 (m), 1.618 (mw), 1.457 (w, b) (17 of 25 observed).

The compounds prepared in this study generally gave relatively high-quality patterns so that the components of mixtures could readily be deduced within the usual sensitivity limits of this method.

Results

Hafnium Chlorides.—The reaction between metal and liquid $HfCl_4$ was found to be substantially less than the limited reaction observed earlier with HfI_4, for example, in an isothermal reaction at about 500° where the $HfCl_4$ pressures approach the capability limit of the tantalum container. Reactions were therefore carried out under a temperature gradient so that higher temperatures could be maintained on the foil while the liquid tetrachloride in the lower and cooler end exerted a manageable pressure. Even so, a reaction at 550/450° for several days gave only traces of a brown product overlying a thin blue-gray layer. Successful preparations were finally achieved on a regular basis by going to smaller ($^1/_2$–$^3/_8$-in. diameter) and hence stronger tubing in longer (12–18 in.) lengths so that a higher reaction temperature and a larger gradient could be maintained. Reactions at 610/450° up to 650/560° for 15–28 days then yielded up to 1 g of metallic gray material from 400 cm^2 of metal foil and 9–12 g of $HfCl_4$. Reaction tubes held with the upper temperature at 700° always leaked.

The product of such a reaction had a Cl:Hf ratio of 1.27–1.30 at 600° (with 3% Zr), less at higher temperatures where the yield was better. Equilibration of this product with clean foil for 4–6 days at 650° then produced the monochloride, whereas the same reaction for 9 days at 500° was without effect. Some typical analytical data are collected in Table I for all compounds investigated. Emission spectroscopy results suggested that the generally slightly low recoveries for the HfCl phase resulted in good part from the presence of about 1% tantalum, which probably derived mainly from the use of tantalum backing for the metal reductant.

TABLE I

ANALYTICAL DATA FOR REPRESENTATIVE HAFNIUM AND ZIRCONIUM CHLORIDES

Compound	% Cl		% M		Cl:M		Remarks
	Calcd	Found	Calcd	Found	Calcd	Found	
HfCl	16.57	15.86	83.43	83.00	1.00	0.96	0.14% Zr
		16.72		83.12		1.01	
$HfCl_3$	38.17	38.67	61.83	...	3.00	3.06	7.1% Zr
ZrCl	27.97	27.80	72.03	70.63	1.00	1.01	0.1% Hf
		...		70.72		1.06	0.1% Hf
$ZrCl_2$	43.74	44.19	56.26	55.33	2.00	2.06	
$ZrCl_3$	53.83	53.33	46.17	46.68	3.00	2.94	

The monochloride as prepared on foil could easily be mistaken for hafnium metal itself save for the fact it slowly dissolved in water with hydrogen evolution. The monochloride is about as soft as lead, and the total (dc) resistance of a 1-mil layer as formed on the foil is only a few ohms. Magnetic measurements on a sample of $HfCl_{1.01}$ by the Faraday method gave a χ_M value of only $(53 \pm 12) \times 10^{-6}$ emu mol^{-1} at room temperature (from a Honda–Owen extrapolation and with a diamagnetic correction of 42×10^{-6}). The temperature dependence was not well established because of difficulties with the apparatus, but the results appeared to be roughly temperature independent to at least −150°.

The X-ray data of the monochloride may be indexed on the basis of a hexagonal cell, $a = 10.24$, $c = 10.01$ Å; this symmetry was confirmed by preliminary single-crystal examination. X-Ray evidence suggests there is a homogeneity range on the oxidized side of the monochloride, with a small increase in lattice spacings relative to HfCl. The monochloride is evidently the only reduced product (other than metal) obtained on reaction of sodium metal with $HfCl_4$, but synthesis by this method was abandoned when separation from the other product Na_2HfCl_6 could not be achieved.

Subsequent to work published earlier on hafnium triiodide, it was determined that the amount of triiodide obtained from the analogous Hf–HfI_4 reaction at 500° was approximately doubled by the addition of AlI_3. Synthesis of two other reduced hafnium chlorides in amounts sufficient for analysis was achieved *only* in the presence of $AlCl_3$. The green trichloride was so obtained in no more than 0.2-g amounts from reaction of $HfCl_4$ plus $AlCl_3$ (12 g total, 40 mol % $AlCl_3$) with metal foil at 375° for 10 days followed by sublimation of the unreacted chlorides at 225°. The product occurred mainly on the foil, but some had been dissolved or suspended in the salt phase. The use of substantially larger $AlCl_3$ proportions produced $HfAl_3$ on the foil, and this did not react significantly with $HfCl_4$ under these conditions.

Although not a primary purpose of this study, a brown hafnium chloride which was evidently pure according to X-rays was obtained from the same reaction mixture under more stringent conditions (*e.g.*, 15 days at 450°). One approximate analysis gave Cl:Hf ≈ 2.5. Traces of the phase observed after monochloride synthesis reactions evidently participated in a transport reaction. A brown, nonstoichiometric *zirconium* chloride phase with 2.5 < Cl:Zr < 2.88 has been obtained elsewhere in the presence of $AlCl_3$.[8,12]

Zirconium Chlorides.—Relative to hafnium, the reduction of $ZrCl_4$ by excess zirconium is quite facile. A hot–cold reaction of 45 g of metal foil in the hot (600°) and middle zone with 12 g of $ZrCl_4$ for 12 days gave a 2–3-mil layer of gray metallic product at the hot end overlaid by a trace of brown. A few crystal flakes (later shown to be $ZrCl_2$) were found in the middle portion along with green overlaying a gray layer on

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[12] E. M. Larsen, private communication.

the foil. A large amount (~9 g) of green $ZrCl_3$ which had in part obviously sublimed or transported was found in the cooler (500°) end. The trichloride gave a powder pattern in excellent agreement with that reported by Dahl, *et al.*,[4] and by Watts;[13] on the other hand, the pattern obtained for $HfCl_3$ is considerably more complex.

The above gray material as prepared usually had a composition where $Cl:Zr \approx 1.3–1.4$ and consisted of ZrCl and $ZrCl_2$. Equilibration with about 10 times as much metal foil for 5 days or more at 625° gave quantitative conversion to ZrCl (Table I), whereas a temperature of 575° in the last step was not adequate. X-Ray powder data indicate that there is again a homogeneity range for the monochloride on the high chloride side, with $Cl:Zr \geq 1.14$ at 675°. The monochloride disproportionated to metal and gaseous $ZrCl_4$ at an observable rate under high vacuum at 610°; the corresponding temperature for HfCl was found to be 690°.

The zirconium monochloride appears to be isostructural with the hafnium analog on the basis of the powder patterns, with hexagonal cell dimensions of $a = 10.31$ and $c = 10.14$ Å or ~0.07 Å *larger* than each of the values obtained for HfCl.

The fact that total recoveries on analysis of samples in the neighborhood of the zirconium monochloride were often about 0.5–1% low gave rise to some concern that the samples under study were actually chlorohydrides. This worry was dispelled by helium-fusion analysis (in graphite) which yielded on the order of 0.6% oxygen and 0.04% nitrogen but no detectable hydrogen. Emission spectrographic examination indicated $\leq 0.05\%$ tantalum and no more than trace amounts of the principal other elements Si, Al, Mg, Fe, Ni, and Co.

A pure phase substantially equal to the dichloride in composition was obtained by isothermal equilibration (*via* the vapor phase) of a sample of higher composition with one of lower composition, a process which requires that one of the samples end up single phase. For this 1.2 g of a composition $ZrCl_{1.4}$ in a 0.25-in. tantalum tube open at the upper end was in turn contained in a sealed 0.5-in. diameter tube together with an excess of $ZrCl_3$ and the assembly was equilibrated 4 days at 600° followed by 3 days at 650°. The portion in the outer tube was found by X-rays to be a mixture of $ZrCl_3$ and $ZrCl_2$ while that in the inner tube appeared single phase and analyzed as $ZrCl_{2.06}$. Similar equilibrations at 560° for even 13 days did not attain equilibrium. Actually, the same phase with slightly smaller diffraction spacings and somewhat altered intensities was first recognized during Hf–$HfCl_4$ reactions at 500–575° for times shorter than necessary to give good yields of HfCl. However, in these cases the phase was found *only* when the starting materials contained 3–4% zirconium and never when this impurity was only 600 ppm. The very small amounts of dichloride obtained in this way were found to contain (qualitatively) major amounts of zirconium, so it would appear that the pure hafnium dichloride phase is not stable. This dichloride sometimes appeared to have participated in a relatively slow transport reaction during synthesis, and equilibration of it with $HfCl_4$ gave the aforementioned brown phase. Only traces of a brown zirconium chloride were encountered under the conditions used.

The powder pattern reported in the literature[9] for $ZrCl_2$ (from the reaction of metal and $ZrCl_3$ at 675° in a platinum-lined silica container) shows a very poor correspondence with that obtained in the present work. A reaction was also carried out under conditions close to those previously reported[9] but with an open-ended tantalum tube as the reaction container within a sealed silica tube. X-Ray diffraction data indicated the product both on the foil and as a separate powder was a mixture of $ZrCl_2$ and $ZrCl_3$. Larger quantities of the same reactants held at 675° in the usual sealed tantalum tube for a longer time yielded ZrCl on the foil and ZrCl plus $ZrCl_2$ as a separate powder.

Discussion

Most other reports in the literature concerning lower chlorides of zirconium and hafnium correlate poorly with present findings. Two studies have involved measurement of $ZrCl_4$ pressures above Zr–$ZrCl_4$ mixtures in silica. In one,[14] the inference that $ZrCl_3$ and $ZrCl_2$ are the reduced phases is basically conjectural since the effects observed appear to have been determined more by kinetic limitations. In a second,[15] the presence of $ZrCl_3$, $ZrCl_2$, and ZrCl solids was *assumed* in interpretation of the data although three reduced phases seem to be indicated; the upper limits of stability given for disproportionation of $ZrCl_3$, $ZrCl_2$, and ZrCl—~400, ~600, and ~800°, respectively—depend on the volume of the system and are not directly related to properties reported here. Formation and disproportionation studies of $HfCl_3$[16] give no quantitative support for the reported $HfCl_2$ and refer to HfCl only as a gaseous product.

The patent literature[17] describes an interesting product called "Zirklor" which was made by electrolytic reduction of an $SrCl_2$–NaCl–$ZrCl_4$ melt (63:34:3) onto graphite. The material's analysis (25–28% Cl; balance substantially Zr), softness, and graphitic character are similar to those of ZrCl, but the powder pattern data given in the patent agree very poorly with those reported here. However, a sample of the material "Zirklor" was found to be poorly crystalline but to have substantially the same pattern as that for ZrCl.

The monochlorides reported here appear to possess a substantial and perhaps even surprising stability (with respect to disproportionation). The lack of any earlier recognition of them has probably resulted mainly from kinetic limitations in synthesis attempts under less drastic conditions.

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[13] J. A. Watts, *Inorg. Chem.*, **5**, 281 (1966).

[14] S. I. Troyanov, V. I. Tsirel'nikov, L. N. Komissarova, and V. I. Spitsyn, *At. Energ.* (USSR), **24**, 52 (1968).

[15] K. Uchimura and K. Furanki, *Denki Kagaku*, **33**, 163 (1965); translation LA-TR-67-62 available from CFSTI, U. S. Department of Commerce, Springfield, Va.

[16] S. I. Troyanov, A. S. Izmailovich, V. I. Tsirel'nikov, and L. N. Komissarova, *Zh. Neorgan. Khim.*, **14**, 869 (1969).

[17] R. S. Dean, U. S. Patent 2,941,931, June 21, 1960.

The zirconium and hafnium monochlorides are further remarkable in that they are the first evidently metallic halides prepared which are not iodides (other than Ag_2F).[18] The small net paramagnetism of HfCl, 53×10^{-6} emu mol^{-1}, is typical of (but not conclusive evidence for) a Pauli contribution in a metallic salt; for example, compare 104×10^{-6} and 50×10^{-6} for LaI_2 and ThI_2, respectively.[18,19] Qualitative evidence suggests that the two monochloride phases near the oxidized limit of their homogeniety ranges are more paramagnetic.

It is significant to note that ZrCl is nominally isoelectronic with NbO which is also metallic but which possesses a simple cubic structure.[20] However, the greater size of the chloride atom in ZrCl would likely prevent or distort the square coordination of metal about the nonmetal which is found in the NbO structure if maintenance of metal–metal distances of 2.9–3.0 Å is essential for stable bonding.

The nonexistence of a dichloride of hafnium is consistent with the absence of a diiodide as well.[2] On the other hand, diverse attempts to prepare a hafnium monoiodide were unsuccessful, and, judging from conditions necessary to form HfCl, the compound should probably have formed in earlier studies were it stable. The results are, of course, in contrast with the usual guideline that compounds of the heavier halides are more stable with respect to disproportionation, but this generality disregards specific electronic effects.

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(18) J. D. Corbett, R. A. Sallach, and D. A. Lokken, Advances in Chemistry Series, No. 71, American Chemical Society, Washington, D. C., 1967, p 56.

(19) R. J. Clark and J. D. Corbett, *Inorg. Chem.*, **2**, 460 (1963).

(20) H. Schäfer and H. G. Schnering, *Angew. Chem.*, **76**, 845 (1964).

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Vibrational Spectra of Single-Crystal Sodium Nitroprusside. II. Polarized Infrared Spectra and Normal-Coordinate Analysis[1a]

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The polarized infrared spectra of a single crystal of sodium nitroprusside ($Na_2Fe(CN)_5NO \cdot 2H_2O$) were measured from 300 to 4000 cm^{-1} at 300°K. The results of these measurements along with the results of a normal-coordinate analysis provide sufficient data for a complete interpretation of the vibrational spectra of the $Fe(CN)_5NO^{2-}$ ion in the solid state. The observed splitting of the vibrational modes of HDO (included as water of hydration in crystalline sodium nitroprusside) is interpreted as due to an orientational effect.

Introduction

In a previous report by R. K. K., *et al.*,[2] the results of investigations of the Raman spectra of an oriented single crystal and the infrared spectra of a polycrystalline sample of sodium nitroprusside were described. On the basis of the observed relative intensities of the Raman-active phonons in the spectra with different polarizability (derivative) components and a comparison with the infrared spectra, an attempt was made to obtain the frequencies of the normal modes of the $Fe(CN)_5NO^{2-}$ ion. Some of the assignments, particularly in the region 600–300 cm^{-1}, remained tentative in ref 2 because of the lack of polarization data in the infrared spectra and because of extreme weakness of the Raman-active phonons in this region. Also, the fine structure of the H_2O bands in the infrared spectra (reported in ref 2) was tentatively interpreted as due to correlation field splitting. An interesting feature of the infrared spectra of the partially deuterated sample of sodium nitroprusside is the fine structure observed for each of the HDO vibrational modes. This fine structure cannot be due to correlation field splitting, and its interpretation was omitted in ref 2.

We have now completed the study of the polarized infrared spectra of sodium nitroprusside in the region 4000–300 cm^{-1}. The assignments proposed in ref 2 will be considered in view of these results and a normal-coordinate analysis of the $Fe(CN)_5NO^{2-}$ ion. In addition, we shall also provide an explanation for the splitting of the HDO vibrational modes observed in ref 2.

Experimental Section

Single crystals of sodium nitroprusside were grown as described in ref 2. Because of strong infrared absorptions by the $Fe(CN)_5NO^{2-}$ ion, the crystal face perpendicular to the radiation beam required polishing to a very thin section. Thus, two crystal specimens were prepared, one having the *ab* face perpendicular to the beam and the other having the *bc* face perpen-

(1) (a) Supported by a grant from ARPA, Department of Defense. (b) Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

(2) R. K. Khanna, C. W. Brown, and L. H. Jones, *Inorg. Chem.*, **8**, 2195 (1969).