TABLE V

HEATS OF FORMATION OF HYDROGEN-BONDED COMPLEXES FROM VAPOR-PHASE STUDIES

System	Method of investigation	$-\Delta H$, kcal/mol	$\Delta\nu$,[h] cm^{-1}
$CH_3OH-N(CH_3)_3$	Ir[a]	7.1 ± 0.2	302[a]
$CH_3OH-N(CH_3)_3$	Pressure meas[a]	7.5 ± 0.3	
$CH_3OH-N(CH_3)_3$	Nmr[b]	5.8 ± 0.7	
$CH_3OH-N(C_2H_5)_3$	Ir[c]	7.6 ± 0.5	362[c]
$CH_3OH-O(C_2H_5)_2$	Ir[d]	4.7 ± 0.7	124[d]
$HCl-O(CH_3)_2$	Nmr[e]	7.1 ± 0.8	
$HCl-O(CH_3)_2$	Pressure meas[f]	7.6	
$HCl-O(CH_3)_2$	Ir[g]	5.6	316[i]
$HCl-O(C_2H_5)_2$	Ir[g]	7.5 ± 0.3	336[i]

[a] This work. [b] Reference 7. [c] Reference 2b. [d] R. G. Inskeep, F. E. Dickson, and J. M. Kelliher, *J. Mol. Spectry.*, **4**, 477 (1960). [e] Reference 8. [f] Reference 9. [g] Reference 10. [h] The shifts are calculated relative to the free OH band in methanol at 3682 cm^{-1} and the free band centered at 2886 cm^{-1} in HCl. The references to the numbers in this column refer to the frequencies for the shifted bands. [i] Reference 3.

gained. Figure 3 shows a continuous relation between the ΔH values obtained in the infrared studies and $\Delta\nu$ (Table V, column 4) in spite of the uncertainty assigned to the individual heats of formation of the complexes, if the infrared value of -5.6 kcal/mol for the hydrogen chloride–dimethyl ether complex is disregarded. The correlation indicates curvature similar to that displayed in condensed-state work, although an extrapolation to a zero value is purely arbitrary.[12] From the shift $\Delta\nu$, the implication is that the nmr value of -7.1 kcal/mol is correct for this system. On this basis the two systems requiring further attention are an nmr study of the methanol–trimethylamine system and an infrared study of the hydrogen chloride–dimethyl ether system. However, it is probably too much to expect that the hydrogen chloride and methanol systems will be represented by the same curve in Figure 3 since they represent two different acid systems. Such a correlation must await vapor-phase studies on additional hydrogen chloride–donor molecule systems.

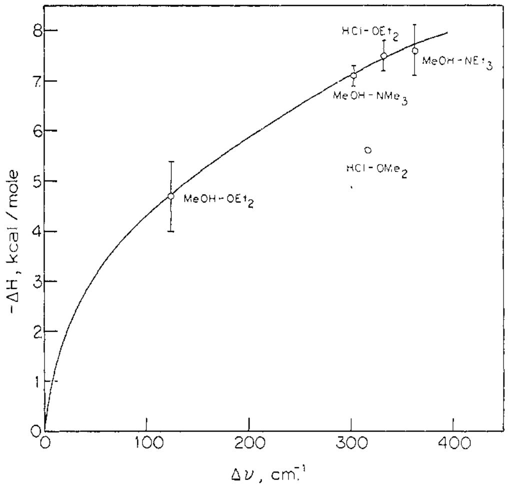

Figure 3.—Plot of the heat of formation ($^-\Delta H$) *vs.* $\Delta\nu$ for hydrogen-bonded complexes in the vapor state.

Examination of the heats of formation for the methanol complexes determined from the infrared studies shows a lower value for the complex with diethyl ether, -4.7 kcal/mol, than that with trimethylamine, -7.1 kcal/mol. This behavior is expected on the basis of the donor properties of these molecules, diethyl ether being the weaker base and probably giving rise to a weaker complex. In this regard little can be said about the relative influence of the amines, trimethylamine and triethylamine, on complex stability, since the heats of formation reported in the infrared studies are not sufficiently different compared to the uncertainties assigned to the respective values. It seems clear, however, that the difference in donor properties of the amines and ether represent an important factor governing the hydrogen-bond energy in the methanol complexes.

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High-Pressure Synthesis of Rare Earth Polyselenides[1]

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New rare earth polyselenides were prepared from Tm, Yb, and Lu and have the tetragonal $ErSe_2$ ($LaTe_2$ type) structure. Synthesis was accomplished at pressures of 14–70 kbars and temperatures of 400–2000°. The X-ray powder diffraction patterns are given.

Introduction

The polyselenides of the elements from lanthanum through gadolinium with the exception of europium were synthesized by Benacerraf, *et al.*[3] The polyselenides were formed principally by a sealed-tube technique. Wang[4] synthesized the compounds of La, Ce,

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(1) This research was supported by the National Science Foundation and the Army Research Office (Durham) and is part of a dissertation by A. W. W.

(2) Now an NAS-NRC Fellow at the Naval Research Laboratory, Washington, D. C.

(3) A. Benacerraf, L. Domange, and J. Flahaut, *Compt. Rend*, **248**, 1672 (1959).

(4) R. Wang, Doctoral Dissertation, University of Texas, Austin, Texas, 1967.

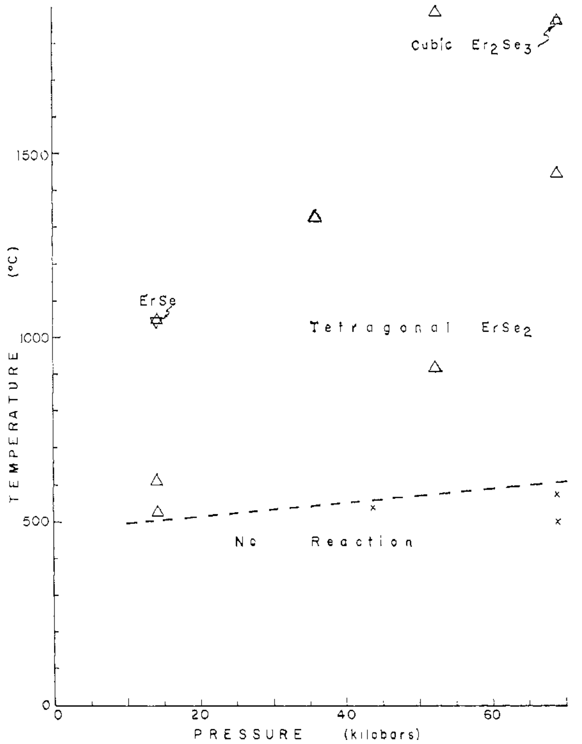

Figure 1.—Reaction product diagram for the Er + 2Se system: ×, no reaction; Δ, tetragonal $ErSe_2$; □, cubic Er_2Se_3; ∇, ErSe.

Nd, Sm, Gd, Dy, Ho, and Er, and attempted the synthesis of $YbSe_2$. Kafalas and Finn[5] reported the synthesis of samarium polyselenide of varying composition ($SmSe_{1.9}$ to $SmSe_{2.03}$) at 40 kbars and 600°. Wang attributed the failure to synthesize $YbSe_2$ to either the change in valency of Yb (+2 instead of the usual rare earth element +3) or decreasing size factors, or both. The application of high-pressure, high-temperature methods would be expected to overcome either of these problems.

We use the term "polyselenide" herein to describe compounds containing selenium in excess of the trivalent stoichiometric requirements of the rare earth.

Experimental Section

The high pressures were obtained by use of a tetrahedral press designed by Hall.[6,7] The high temperatures were generated by an internal graphite resistance heater and a controlled ac power supply which provided a low-voltage high-current source. This equipment allowed routine work to pressures of 70 kbars and temperatures of 2000°. Pressure and temperature calibrations have been described elsewhere.[8]

Powdered selenium of 99.5% purity from Fisher Scientific Co. was used. The rare earth metals were all obtained in ingot form with a purity of 99.5% or better, from either Alfa Inorganics (Tm) or Nuclear Corp. of America (Er, Yb, and Lu). The ingots were filed and sieved to −100; then a stoichiometric mix of 1:2 mole ratio of metal to chalcogen was weighed out. These were intimately mixed and stored in a desiccator for use as soon as possible. Oxygen contamination was thus minimized.

The sample charge was tamped into a small BN tube capped on both ends by BN disks. The BN tube was used to prevent formation of rare earth carbides. This was placed in the graphite tube resistance heater and the whole assembly was inserted into a pyrophyllite tetrahedron, using molybdenum strips for electrical conduction from the tetrahedron faces to the graphite tube. The tetrahedron was then painted with a slurry of red iron oxide in methanol to increase the surface friction, and the whole assembly dried at 110° for at least 1 hr. This baking increases the pressure obtained by a given ram load.[11]

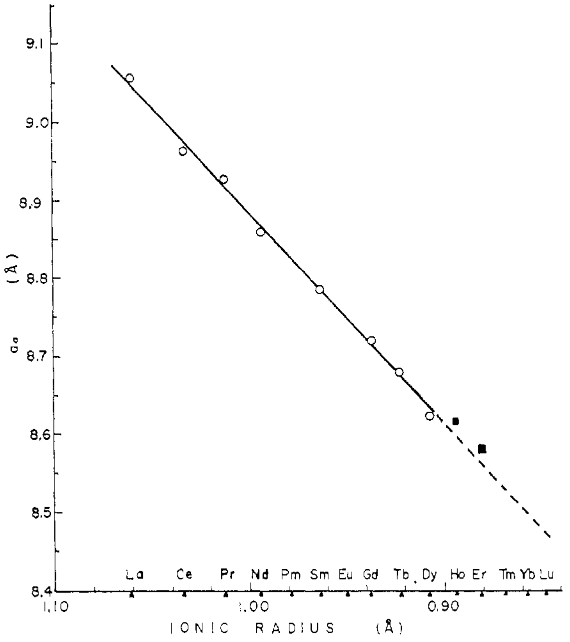

Figure 2.—Lattice constants of the cubic Th_3P_4-type R_2Se_3 compounds: ○, ref. 9; ■, this work. Ionic radii used are from ref 10.

The tetrahedron was placed in the press and the pressure was slowly increased to a load of 400 psi oil pressure and then rapidly to the pressure of interest, since experience has shown that the major part of gasket formation occurs below about 250–300 psi. The power was increased to the desired wattage over an interval of about 15 sec. The power was held at this value for a time inversely dependent upon the wattage used partially to offset expected kinetic effects and then abruptly cut to quench the sample.

The samples were broken open immediately upon removal from the press and the product slug was extracted. A fragment of the slug was then ground between two polished tungsten carbide flats, and the powder was placed in a 0.5-mm capillary for an X-ray diffraction powder pattern. The product was then identified from the X-ray film since the visual appearance of the samples varied little between runs.

The systems of interest were studied over a pressure range of 14–70 kbars and a temperature range of 400–1900°. Temperatures above 1100° were not attempted at the lower pressures. The scatter in the calibration data limited the definition of the run parameters to ±3 kbars for the pressure and about ±7% for the temperature (in centigrade degrees). From 10 to 15 runs of varying pressure and temperature conditions were made on each of the rare earth–selenium systems studied.

Figure 1 shows the reaction product diagram of the Er + 2Se system. It is not a phase diagram. It only shows the product formed by quenching after application of high pressures and elevated temperatures. The no reaction line extends from 500 to 600° (from 10 to 70 kbars, respectfully, for all the systems dis-

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[5] J. A. Kafalas and M. C. Finn, "Solid State Research," No. 3, Lincoln Laboratory, 1963, p 26.

[6] H. T. Hall, *Rev. Sci. Instr.*, **29**, 267 (1958).

[7] H. T. Hall, *ibid.*, **33**, 1278 (1962).

[8] A. W. Webb and H. T. Hall, submitted for publication.

[9] J. Flahaut, F. Laruelle, M. P. Pardo, and M. Guittard, *Bull Soc. Chim. France*, 1399 (1965).

[10] O. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.*, **76**, 5237 (1954).

[11] L. E. Millett, Doctoral Dissertation, Bringham Young University, Provo, Utah, 1969.

TABLE I

DENSITY AND LATTICE PARAMETERS OF THE RARE EARTH POLYSELENIDES

Compound	Density, g/cm³						
	Obsd	Theoret					
		RSe_2	$RSe_{1.8}$	a_0, Å	c_0, Å	Vol, Å³	Mean atomic vol, Å³
$ErSe_2$	7.0	8.35	7.94	3.973 ± 0.004	8.197 ± 0.009	129.39	21.57
$TmSe_2$	7.4	8.45	8.04	3.961 ± 0.003	8.188 ± 0.007	128.47	21.41
$YbSe_2$	7.9	8.56	8.15	3.970 ± 0.004	8.151 ± 0.008	128.47	21.41
$LuSe_2$	7.5	8.76	8.34	3.936 ± 0.007	8.147 ± 0.015	126.21	21.04

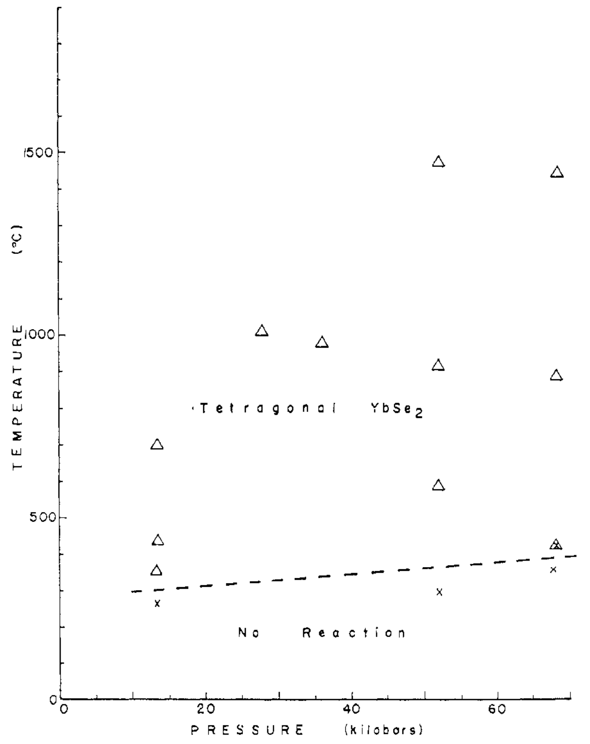

Figure 3.—Reaction product diagram for the Yb + 2Se System. Symbols have the same relative meaning as in Figure 1.

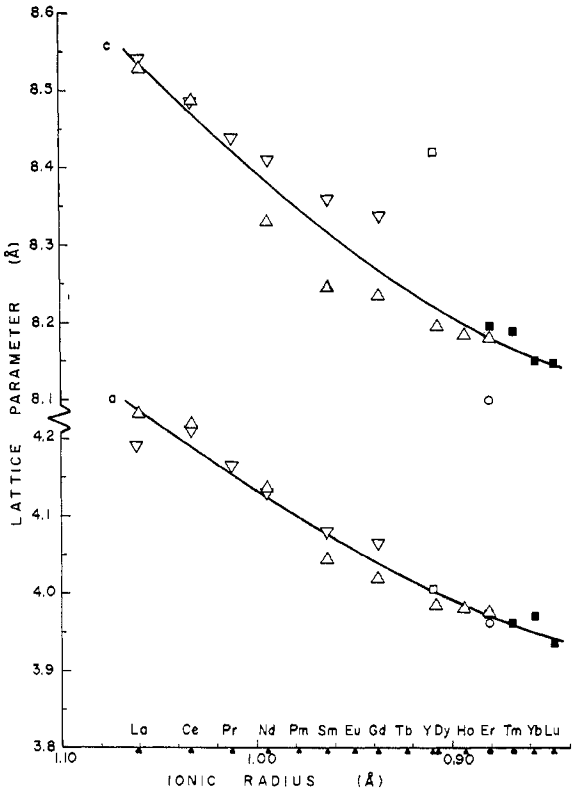

Figure 4.—Lattice parameters of the rare earth polyselenides: △, ref 14: ○, ref 12; ▽, ref 3; □, ref 15; ■, this work. Ionic radii used are from ref 10, except that for Y, which comes from ref 16.

cussed below). Above the no-reaction temperature, tetragonal $ErSe_2$ was formed at all points investigated. The product was identified by comparison of the X-ray diffraction powder pattern with data from Haase, *et al.*[12] Above 1000° at 15 kbars ErSe (NaCl structure) was also formed. At 1800° and 70 kbars cubic Er_2Se_3–Er_3Se_4 was also formed. This material had the cubic Th_3P_4 structure and may be γ-Er_2Se_3 which was previously unknown. Figure 2 shows that the lattice constant fits well with those of the known γ-R_2Se_3 compounds. Also included in Figure 2 is the value for γ-Ho_2Se_3 which was produced for the first time from a stoichiometric mixture of the elements at the same conditions as above. The lighter R_2Se_3 and R_3Se_4 compounds have the same lattice constants, however, and the products might have either of these stoichiometries or an intermediate composition as X-ray diffraction techniques cannot differentiate between the compositions. This work has been reported more fully elsewhere.[13]

The diagram for the system Tm + 2Se is similar to Figure 3. The no-reaction line runs from 600 to 500°. Above this temperature tetragonal $TmSe_2$ was formed at all points investigated except 600° and 45 kbars where a very complex X-ray diffraction pattern was obtained for the product. An unknown product was also produced at 900° and 50 kbars. The tetragonal $TmSe_2$ was identified by comparison of its X-ray diffraction pattern with that obtained for $ErSe_2$.

Figure 3 shows the reaction product diagram for Yb + 2Se. The no-reaction line runs from 300 to 400°. At higher temperatures tetragonal $YbSe_2$ was formed at all points investigated.

The system Lu + 2Se gave results similar to those shown in Figure 1. The no-reaction line runs from 450 to 500°. Above this region the new tetragonal $LuSe_2$ was formed. Also formed at 1000° and 15 kbars was LuSe which had the NaCl structure. No sesquiselenide was found.

An attempt was made to measure the densities of a number of the samples using the pycnometric method with anisole as the displacement fluid. Only 0.1–0.2 g of product was available for each determination so a precision of only ±10% is expected. Theoretical densities were calculated assuming both RSe_2 and $RSe_{1.8}$ stoichiometries. These values are given in Table I.

Chemical analysis was not attempted due to (1) the small sample size, (2) the difficulty of producing the products of interest, and (3) the lack of suitable techniques for separating the product from either other products or from unused reactants which might be left in the closed reaction system.

The four rare earth polyselenides studied were all metallic gray, crushing readily to give a black powder. They all showed a moderately high electrical resistance before powdering. All the polyselenides reacted with aqueous solutions of HCl, HNO_3,

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(12) D. J. Haase, H. Steinfink, and E. J. Weiss, *Inorg. Chem.*, **4**, 538 (1965).

(13) N. Eatough, H. T. Hall, and A. W. Webb, *ibid.*, **8**, 2069 (1969).

(14) R. Wang and H. Steinfink, *ibid*, **6**, 1685 (1967).

(15) L. D. Norman, Jr., U. S. Bureau of Mines, Report of Investigations, No. 6851, Mines Bureau, Pittsburgh, Pa., 1966.

(16) A. Iandelli in "Rare Earth Research," E. V. Kleber, Ed., The Macmillan Co., New York, N. Y., 1961, p 140.

TABLE II
X-RAY DIFFRACTION DATA FOR THE RARE EARTH POLYSELENIDES (Å)

		$ErSe_2$		$TmSe_2$		$YbSe_2$		$LuSe_2$	
hkl	Intens	d_{obsd}	d_{calcd}	d_{obsd}	d_{calcd}	d_{obsd}	d_{calcd}	d_{obsd}	d_{calcd}
002	w	4.06	4.10	4.07	4.09	4.04	4.08	4.05	4.07
101	m	3.56	3.58	3.55	3.57	3.55	3.57	3.53	3.54
...	vvw	2.935	...	2.931	...	...	...	2.913	...
102	vvw	...	2.853	...	2.847	2.844	2.843	...	2.832
110	m	2.809	2.809	2.789	2.801	2.792	2.807	2.769	2.783
003	vs	2.707	2.732	2.719	2.721	2.707	2.717	2.713	2.716
111	m	2.651	2.658	2.638	2.650	2.639	2.654	2.627	2.634
...	vvw	2.511	...	2.526	...	...	...	...	...
112	vvs	2.314	2.317	2.306	2.312	2.307	2.312	2.288	2.298
103	vvs	2.241	2.251	2.240	2.247	2.237	2.242	2.232	2.235
004	vw	2.036	2.049	2.043	2.047	2.034	2.038	2.034	2.037
200	m	1.992	1.987	1.979	1.981	1.982	1.985	1.959	1.968
113	vvw	1.953	1.959	1.948	1.955	1.946	1.952	1.940	1.944
...	vvw	1.898	...	1.890	...	...	...	...	...
104	vvw	1.817	1.821	1.813	1.819	1.809	1.813	1.806	1.809
202	vw	1.790	1.788	1.781	1.783	1.780	1.785	1.767	1.772
211	vw	1.740	1.736	1.731	1.731	1.732	1.735	1.716	1.721
114	vvw	1.653	1.656	1.650	1.653	1.645	1.649	...	1.644
212	vvw	1.629	1.630	...	1.626	1.626	1.628	1.615	1.616
203	w	1.610	1.607	1.602	1.603	1.602	1.603	1.591	1.594
105	m	1.512	1.515	1.512	1.513	1.507	1.508	1.505	1.506
213	s	1.492	1.490	1.485	1.486	1.485	1.486	1.474	1.477
...	vvw	1.449	...	1.444	...	...	...	1.428	...
204	vvw	1.426	1.426	1.422	1.423	1.420	1.422	1.404	1.415
115	vw	1.411	1.416	1.410	1.414	1.405	1.407	1.387	1.399
220	w		1.405	1.399	1.400	...	1.404		1.392
214	vvw	1.345	1.342	1.337	1.340	1.337	1.339	1.331	1.332
222	vvw	1.331	1.329	1.324	1.325	1.327	1.327	1.314	1.317
301	vvw	1.311	1.307	1.302	1.304	1.305	1.306	...	1.295
106	m	1.289	1.292	1.289	1.290	1.284	1.285	1.284	1.284
310	w	1.263	1.256	...	1.253	1.256	1.255	...	1.245
223	vw	1.251	1.249	1.246	1.246	1.244	1.247	1.240	1.239
311	vw		1.242	1.239	1.238		1.241		1.231
116	vw	1.228	1.229	1.226	1.227	1.222	1.223	1.220	1.220
215, 312	vs	1.205	1.203	1.199	1.200	1.200	1.200	1.196	1.193
303	vvw	1.195	1.192	1.188	1.189	1.189	1.190	1.178	1.181
007	vvw	1.168	1.171	...	1.170	1.164	1.164	1.164	1.164
224	vvw		1.159	...	1.156	...	1.156	1.148	1.149
313	vvw	1.147	1.141	1.139	1.138	1.138	1.140	1.129	1.131
321	vvw	1.097	1.092	1.089	1.089	1.090	1.091	...	1.082
216	m	1.083	1.083	1.080	1.081	1.078	1.079	1.075	1.075
305	vvw	...	1.030	1.027	1.028	1.027	1.027	1.020	1.020
323	w	1.026	1.022	1.019	1.019	1.020	1.020	1.012	1.013
		+21 other lines		+27 other lines					

and H_2SO_4 to produce gas with dissolution of the compound. Reaction with KOH solution produced first red selenium and then later the gray form. Water produced a small amount of H_2Se gas and some red selenium but did not disintegrate the sample slug. Anisole caused no apparent change.

The stability of the rare earth polyselenides in air was determined by reexamining them by X-ray diffraction. $TmSe_2$ and $LuSe_2$ were checked after 1 month, $ErSe_2$ after 3 months, and $YbSe_2$ after 6 months. No change was noted in the X-ray diffraction patterns.

X-Ray Diffraction Studies

Several different studies have been made of the X-ray crystallography of the rare earth polyselenides. Single-crystal work has been done with some of them. Eliseev and Kuznetsov[17] reported that $NdSe_{1.9}$ was isostructural with $LaTe_2$ which has the tetragonal space group P4/nmm. Wang and Steinfink[14] studied $ErSe_2$ and found it to have a tetragonal subcell of the P4/nmm space group from the strong reflections, but a number of weak reflections were also found which did not occur for $LaSe_2$ and $CeSe_2$. The indexing of these weak reflections was accomplished on the basis of an orthorhombic supercell composed of 24 of the tetragonal subcells. Refinement of the structure was accomplished for the subcell but could not be achieved for the supercell. Guittard and Flahaut[18] reported that $ErSe_{1.75}$ had the Fe_2As ($LaTe_2$) structure. Recently Marcon and Pascard[19] reported that $CeSe_2$ is in fact monoclinic with the $P2_1/a$ space group and a pseudotetragonal structure.

Due to the lack of a supercell refinement for $ErSe_2$ and the lack of the weak supercell reflections in $CeSe_2$, the P4/nmm tetragonal subcell indexing is considered the most meaningful for the rare earth polyselenides at the present time. This is in agreement with Guittard's findings on $ErSe_2$.

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[17] A. A. Eliseev and V. G. Kuznetsov, *Izv. Akad. Nauk SSSR, Neorgan. Materialy*, **2**, 1157 (1966); *Chem. Abstr.*, **65**, 14544*c* (1966).

[18] M. Guittard and J. Flahaut, *Compt. Rend.*, **C264**, 1951 (1967).

[19] J. P. Marcon and R. Pascard, *ibid.*, **C266**, 270 (1968).

The X-ray diffraction spectr awere obtained by the Debye–Scherrer method with a 143.2-mm diameter camera. Nickel-filtered copper radiation was used. The *d* values were calculated using the values $\lambda(K\alpha)$ 1.5418 Å and $\lambda(K\alpha_1)$ 1.54050 Å.

A preliminary indexing of the patterns was accomplished by comparison with previously published indexing of related systems. The lattice parameters were then calculated on an IBM 7040 computer using the least-squares program LSRSTR.[20]

The indexing of the rest of the observed reflections was accomplished by the use of the FORTRAN IV program POWDER.[21] This program calculates the expected powder pattern intensities for all *d* values of interest using atomic scattering factor tables, the general positions, the special extinctions, and the atomic positions of the atoms in the asymmetric unit. For this work the atomic positions determined by Wang for $ErSe_2$[14] were used. It was assumed that the positions could be used for the polyselenides of Tm, Yb, and Lu to calculate the approximate reference powder patterns. These calculated patterns were then used to assign indices to the observed diffraction lines on the basis of the calculated and observed intensities.

The lattice parameters obtained from the indexed patterns were used to generate reference patterns with which to index the full films. These indexings were then intercompared for consistency and the final lattice parameter refinements were made. The lattice parameters are given in Table I and compared with other work in Figure 4. X-Ray diffraction powder patterns are given in Table II.

Discussion

Tetragonal polyselenides of Tm, Yb, and Lu have been made for the first time. From the data collected in this work it is improbable that the change in valency accounts for Wang's inability to synthesize $YbSe_2$.[14] All of the new polyselenides were formed at pressures as low as 15 kbars. Ytterbium is known to undergo an electronic transition from the divalent to the trivalent state at 39.5 kbars and room temperature. At 400° this transition is lowered to about 30 kbars.[22] Thus, unless the polyselenide also tends to favor the trivalent state, this is not the limiting factor for the formation of $YbSe_2$. Decreasing size factors was the second restriction postulated by Wang. If a minimum pressure of formation does exist as has been recently found for the cubic RS_2 compounds,[8] it is below 15 kbars for lutetium, the smallest of the lanthanides studied, and apparently does not increase with increasing atomic number (or decreasing ionic radius) as rapidly as was found for the polysulfides.[8]

Acknowledgments.—We thank Norman L. Eatough, Jim Hoen, John F. Cannon, Karl Miller, M. D. Horton, Fred D. Childs, and Leo Merrill for their assistance in various phases of this work.

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The Kinetics of the Chromium(VI)–Arsenic(III) Reaction. II. Dihydrogen Phosphate–Hydrogen Phosphate Buffer Solutions[1,2]

BY JOHN G. MASON, ALBERT D. KOWALAK,[3] AND R. MICHAEL TUGGLE

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The kinetics of the Cr(VI)–As(III) reaction have been investigated in H_2PO_4–HPO_4^{2-} buffers. Complex kinetics have been obtained. The rate law found is first order in total Cr(VI) and As(III) with a complex dependence upon buffer composition. The data point to the reaction proceeding *via* two activated complexes $H_2PO_4^-\cdot HCrO_4^-\cdot$As(III) and $HPO_4^{2-}\cdot HCrO_4^-\cdot$As(III).

Introduction

In part I,[2] kinetic evidence for the formation of a complex between As(III) and Cr(VI) was presented. It was noted at that time that although the reaction appeared to be pH independent over the pH range 4.3–5.5, a path dependence upon the concentration of acetic acid was found to be present. This is in support of the analysis of Edwards,[4] who presented evidence for general-acid catalysis in Cr(VI) oxidations. Kolthoff and Fineman[5] suggested that the rate of the Cr(VI)–As(III) should increase with increasing acidity in solutions of pH less than 9. Preliminary

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(1) Research sponsored by AFOSR(SRC)-OAR, USAF, Grants AF-AFOSR-210-63 and AF-AFOSR-210-65.

(2) Part I: J. G. Mason and A. D. Kowalak, *Inorg. Chem.*, **3**, 1248 (1964).

(3) Taken in part from the Ph.D. dissertation of A. D. Kowalak, Virginia Polytechnic Institute, 1965.

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