ured[1] by the hollow prism method. The method has proved to be useful not only for examining corrosive interhalogen compounds, but for examining highly volatile substances as well. In the present instance, an electrically heated hollow prism has been used to measure the refractive indices of the systems uranium hexafluoride–bromine trifluoride and uranium hexafluoride–bromine pentafluoride. The data obtained at 70° with the sodium-D lines are given in Tables I and II. The values of $n^{70}\text{D}$ for the pure components are averages of three or more determinations, whereas the values for the binary solutions are the results of single determinations.

TABLE I

REFRACTIVE INDICES OF URANIUM HEXAFLUORIDE–BROMINE TRIFLUORIDE SOLUTIONS

Mole fraction of uranium hexafluoride	$n^{70}\text{D}$		Mole fraction of uranium hexafluoride	$n^{70}\text{D}$	
	Expt.	Calcd.		Expt.	Calcd.
0.0000	1.4302	1.4302	0.5303	1.3836	1.3830
.0487	1.4248	1.4248	.6420	1.3758	1.3758
.0498	1.4247	1.4247	.8181	1.3656	1.3662
.1566	1.4131	1.4138	1.0000	1.3580	1.3580
.3484	1.3968	1.3968			

TABLE II

REFRACTIVE INDICES OF URANIUM HEXAFLUORIDE–BROMINE PENTAFLUORIDE SOLUTIONS

Mole fraction of uranium hexafluoride	$n^{70}\text{D}$		Mole fraction of uranium hexafluoride	$n^{70}\text{D}$	
	Expt.	Calcd.		Expt.	Calcd.
0.0000	1.3275	1.3275	0.5965	1.3477	1.3477
.1684	1.3338	1.3337	.7607	1.3522	1.3522
.3153	1.3388	1.3389	.9069	1.3560	1.3560
.4354	1.3428	1.3427	1.0000	1.3580	1.3580
.5134	1.3449	1.3452			

An empirical equation has been fitted to the data in each table, representing $n^{70}\text{D}$ as a function of N, the mole fraction of uranium hexafluoride. Equation 1, below, applies to the uranium hexafluoride–bromine trifluoride solutions, and equation 2 applies to the uranium hexafluoride–bromine pentafluoride solutions. The equations have been made to yield the experimental values of $n^{70}\text{D}$ at $N = 0$ and $N = 1$, since the data are most reliable at these points. The calculated values of $n^{70}\text{D}$ are listed in column 3 of Tables I and II.

$$n^{70}\text{D} = 1.4302 - 0.1123N + 0.0484N^2 - 0.0083N^3 \quad (1)$$

$$n^{70}\text{D} = 1.3275 + 0.0380N - 0.0065N^2 - 0.0010N^3 \quad (2)$$

The statistical probable error of $n^{70}\text{D}$ computed from equation 1 is ±0.0004, and that computed from equation 2 is ±0.0001. The smaller value is believed to be fortuitous, and a single measurement is believed to have a precision of approximately ±0.0004. Since $n^{70}\text{D}$ of bromine trifluoride differs from that of uranium hexafluoride by 0.0722, it should be possible to analyze the binary solutions to within ±0.6% by refractive index measurements. Analysis of uranium hexafluoride–bromine pentafluoride solutions within ±1.3% should be possible, since the difference in $n^{70}\text{D}$ is 0.0305.

In the present investigation, $n^{70}\text{D}$ for uranium hexafluoride was found to be 1.3580 ± 0.0004, whereas the value 1.367 has been previously reported in the literature.[2,3] The earlier value, which was obtained by measuring the critical angle of reflection at the surface of liquid uranium hexafluoride, is believed to be in error.

Experimental

The apparatus used in making these measurements and the method of purification of the bromine fluorides have been previously described.[1] In the present work, the original hollow prism was modified by the addition of electric heating coils to the top and bottom jackets, so that a temperature of 70.0 ± 0.5° could be maintained. This temperature was chosen in order to keep the uranium hexafluoride in the liquid state over the entire range of composition. The temperature was measured to ±0.1° by means of a calibrated copper–constantan thermocouple and a Leeds and Northrup model K potentiometer.

The uranium hexafluoride was obtained from Carbide and Carbon Chemicals Company. Its freezing point was found to be 64.0°, in good agreement with the value of Oliver and Grisard.[4]

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[2] J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," National Nuclear Energy Series, Div. VIII, Vol. 5, McGraw-Hill Book Co., New York, N. Y., 1951, p. 432.

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[4] G. D. Oliver and J. Grisard, THIS JOURNAL, **75**, 2827 (1953).

Yttrium Chromium Oxide, a New Compound of the Perowskite Type

BY JOHN T. LOOBY AND LEWIS KATZ

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The search for suitable systems in which to study the distribution of trace ions between a molten salt and a solid led us to consider the possibility of the replacement of lanthanum in $LaCrO_3$ with yttrium using sodium chloride as the liquid phase. This appeared to be a convenient system since suitable radioactive isotopes of both yttrium and lanthanum are available. In the course of this work a finely divided green solid was prepared from the oxides Cr_2O_3 and Y_2O_3. Casual inspection of the X-ray diffraction pattern suggested that the structure was similar to that of perowskite. This result is perhaps not surprising in view of the fact that the tolerance factor t in the Goldschmidt relationship $R_A + R_O = t\sqrt{2}(R_B + R_O)$ has the value of 0.86. According to Náray-Szabó,[1] this would lead one to expect a monoclinic distortion of the perowskite structure or according to Megaw[2] an orthorhombic distortion.

Experimental

Chromic oxide was prepared by ignition of reagent grade chromic nitrate until there was no further loss of weight. The yttrium oxide was obtained from Fisher Scientific Company and was labeled 99% pure. Mixtures of the two oxides, with the yttrium oxide to chromic oxide molar ratio always greater than one, were heated in a sodium chloride flux at 900° in a hydrogen atmosphere. The flux was removed from the water-insoluble product by leaching with water; excess yttrium oxide was removed by leaching with very dilute hydrochloric acid. In all cases the X-ray diffraction patterns appeared the same. The density of the com-

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[1] I. Náray-Szabó, *Muegyetemi Közlemenyek*, **1**, 30 (1947).

[2] H. D. Megaw, *Proc. Phys. Soc.*, **58**, 133 (1946).

pound was determined pycnometrically by water displacement and an average value of 5.78 ± 0.05 g./cc. was obtained.

Chromium was determined by dissolving the sample in boiling, concentrated perchloric acid and titrating the resulting chromium(VI) in potassium iodide solution with sodium thiosulfate. Yttrium was determined as the oxalate. For the sample for which the X-ray data are given in Table I, analysis showed: chromium, 28.75 ± 0.05%; yttrium, 46.1 ± 0.1%. Theoretical percentages for $YCrO_3$ are: chromium, 27.54%; yttrium, 47.06%. If one accepts the formula $YCrO_3$ for the reaction product, the above figures would indicate an excess of about 2.5% Cr_2O_3.

All but two lines of the X-ray powder pattern were indexed on the basis of a monoclinic cell (Table) with dimensions $a = c = 7.61 \pm 0.01$ Å.; $b = 7.54 \pm 0.01$ Å.; $\beta = 92° 56' \pm 6'$. One of the two very weak extra lines matched a medium reflection of the chromic oxide pattern. The remaining chromic oxide lines were effectively covered by the yttrium chromium oxide pattern. Thus a small excess of chromium oxide was indicated by the X-ray evidence and also could be implied from the chemical analysis.

TABLE I

COMPARISON OF OBSERVED AND CALCULATED INTERPLANAR SPACINGS

I	$d_{obs.}$	$d_{calcd.}$	hkl
vvw	5.59	5.52	$\bar{1}01$
vvw	5.21	5.24	101
w	4.31	4.29	111
m	3.775	3.770	020
		3.801	200
vw	3.624	(3.62)	Cr_2O_3
s	3.387	3.393	210
		3.377	120
vw	3.054	3.059	121
		3.047	211
vw	2.972	2.961	220 β
s	2.756	2.759	$\bar{2}02$
vvs	2.674	2.677	220
s	2.621	2.619	202
m	2.587	2.591	$\bar{2}12$
w	2.472	2.474	212
vw	2.365	2.368	301
vw	2.312	2.323	$\bar{3}11$
m	2.263	2.259	311
		2.266	131
m^-	2.223	2.227	$\bar{2}22$
m	2.152	2.152	222
m	2.095	2.097	230
w^+	2.049	2.050	$\bar{3}21$
w	2.005	2.005	321
		2.007	231
s	1.902	1.901	400
m^+	1.883	1.885	040
m^-	1.858	1.859	$\bar{2}32$
m	1.842	1.843	410
		1.839	$\bar{3}03$
vw	1.815	1.813	232
		1.812	$\bar{4}11$
vvw	1.737	1.736	$\bar{4}02$
vvw	1.722	1.723	331
s	1.690	1.689	240
		1.692	$\bar{4}12$
w	1.670	1.672	$\bar{4}21$
		1.666	402
w^+	1.626	1.627	412
vvw	1.607	?	?
vw	1.593	1.594	332
m^+	1.577	1.577	$\bar{4}22$
m^+	1.555	1.557	$\bar{2}42$
s	1.525	1.524	422
		1.527	$\bar{4}13$
m^+	1.428	1.429	$\bar{4}32$
vw	1.404	1.402	250
vw	1.380	1.380	$\bar{4}04$
		1.382	423
w^+	1.357	1.357	$\bar{4}14$
m^+	1.339	1.339	440
vvw	1.325	1.325	$\bar{4}33$
		1.326	$\bar{4}41$
		1.324	252
w	1.310	1.310	441
		1.311	404
w	1.293	1.292	414
		1.292	531
vw	1.273	1.272	351
		1.273	531
w	1.249	1.249	442
		1.248	532
		1.250	610
w	1.206	1.205	$\bar{6}12$
w^+	1.193	1.193	260
w	1.183	1.183	540
		1.182	$\bar{2}61$
		1.184	602
vw	1.171	1.170	612
vw	1.159	1.159	$\bar{5}24$
		1.159	504
w	1.137	1.137	533
		1.139	$\bar{4}52$
w	1.132	1.132	630
vw	1.117	1.117	542
		1.118	$\bar{3}61$
		1.118	452
w	1.098	1.098	$\bar{6}32$
		1.099	613
w	1.077	1.076	444
		1.077	070
w	1.070	1.069	$\bar{6}14$
w	1.018	1.018	$\bar{4}62$
		1.018	$\bar{4}54$
		1.017	$\bar{7}03$
m^-	1.002	1.003	642
m^-	0.9936	0.9938	624
		0.9940	722

The monoclinic cell has each of its axes doubled as compared to the fundamental perowskite unit and thus corresponds to eight molecules. Using the density of 5.78 g./cc., the calculated X-ray molecular weight is 190 ± 2 molecular weight units as compared to the formula weight for $YCrO_3$ of 188.9. In itself, this agreement is not conclusive proof for the simple formula, because the molecular weight is not a sensitive test of formula. As examples, $Y_{1.08}Cr_{0.92}O_3$ has a formula weight of 192; $Y_{0.97}Cr_{1.03}O_3$ has a formula weight of 188. When we consider the X-ray and chemical evidence together, however, the simple formula seems well established.

It cannot be stated with certainty that the a and c axes are exactly equal although they are not likely to differ by more than 0.015 Å. If they are exactly equal, then choosing the diagonals of the a,c face as new a and c axes gives a cell for which all the angles are 90°. This cell would imply that the crystal is orthorhombic, rather than monoclinic.

Discussion

The reason for the distortion from cubic symmetry, as indicated by the tolerance factor, is the inadequate size of the yttrium ion. The ratio of yttrium to oxygen univalent radii would indicate a coördination number of eight[3] for yttrium rather than the twelve of the undistorted perowskite structure. The atomic positions have not as yet been determined. However, simply shortening one axis of the cubic cell could reduce the number of nearest neighbors about yttrium from twelve to eight. The attendant adjustment of atomic positions to give the most satisfactory coördination polyhedra could then result in a puckering of the structure as evidenced by the doubled cell.[4]

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Some Observations on the 8-Quinolinol and 5,7-Dihalo-8-quinolinol Chelates of Scandium

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Reaction between scandium ion and 8-quinolinol has been shown[1] to yield the 1 to 4 chelate, $Sc(C_9H_6NO)_3 \cdot C_9H_6NOH$, a compound which is useful for the gravimetric determination of scandium[2] but one which, unlike the comparable thorium and uranium(VI) compounds,[3] cannot be converted to the normal chelate by heating.[1] The absorption spectrum of this compound in toluene amounts to an intense peak at 317 mμ (same wave length as is characteristic of 8-quinolinol) and a much less intense peak at 375 mμ.[4] Absorption spectra data are interpreted in terms of bonding of the extra mole of 8-quinolinol in the solid by lattice forces.[4]

The similarity of the reported absorption spectrum[4] to the spectra of the partially hydrolytically

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