fied as the scheelite type. In some of the compositions investigated in this paper, we seem to have a similar fergusonite $\rightleftharpoons$ scheelite transition at much lower temperature. It appears to be in the vicinity of room temperature and therefore is very sluggish. In the case of $LnTi_{0.5}W_{0.5}O_4$ we could detect a small portion of scheelite type oxide with $a_t = 5.10$ Å. and $c_t = 10.90$ Å., indicating that part of the compound had not completely inverted to the lower symmetry upon cooling.

With $YTi_{0.5}W_{0.5}O_4$ we also obtained samples which were sometimes free of scheelite, sometimes contained small portions thereof. In general, a decrease in cation size causes an increase in the transformation temperature. An r_B/r_A ratio of 0.57 as for the La compound is obviously too small and the ratio of 0.80 for the Sc compound is too large to allow for either the fergusonite or the scheelite structure. This establishes a rough tolerance limit for r_B/r_A of 0.62–0.76 permitting either fergusonite or scheelite structure.

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Preparation and Properties of Crystalline Gold Trifluoride

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Auric trifluoride was first prepared by Moissan[3] by heating gold wire in fluorine at dull red heat. Treatment of gold powder with BrF_3 has been successfully employed to prepare essentially pure AuF_3 contaminated with a small amount of bromine.[4,5]

The only gold trihalide for which crystallographic data have been reported is $AuCl_3$. The crystal structure analysis[6] showed that auric trichloride is composed of Au_2Cl_6 dimers in square-planar configuration as predicted by Wells.[7] Extensive work has been done on the crystal structure of trifluorides of the transition elements preceding gold in the periodic table so that structural analogies can be drawn.[8]

In the present work the structural characterization carried out by X-ray powder methods at Newcastle has been confirmed and extended by single-crystal techniques and by density determination at Los Alamos. AuF_3 is hexagonal and is not isostructural with other known crystalline trifluorides.

Experimental

Synthesis of AuF_3.—Two general methods which yielded pure AuF_3 on the multigram scale were used.

(a) **BrF_3.**—Gold powder, produced by reduction of an aqueous solution of gold(I), was dissolved in excess BrF_3 upon gentle warming.[4] After evaporation of Br_2, the solution was lemon-yellow. Removal of the excess BrF_3 in an inert atmosphere or by vacuum distillation gave a yellow solid, presumably $AuBrF_6$. Further heating of this salt under vacuum at temperatures up to 300° yielded nearly pure AuF_3.[5] The purity was checked by optical and X-ray methods.

(b) **Fluorine.**—A number of Au(I) salts were treated with gaseous fluorine in an unsuccessful attempt to prepare pure AuF_3; AuCN, AuI, and AuCl all reacted violently, yielding mixtures of AuF_3, Au, and an unidentified dark brown or black material. However, $AuCl_3 \cdot xH_2O$ could be converted to pure AuF_3 by the slow addition of fluorine at 200°. The purity was checked by weight change and by optical and X-ray examination. AuF_3, contaminated by unreacted gold, can also be prepared by fluorination at 250° of powdered gold made by reduction of gold salts in solution.

Preparation of Single Crystals.—In the direct fluorination of gold salts, an orange-yellow sublimate was formed in the reactor at temperatures exceeding 300°. The crystals were preserved by immersion in Fluorolube oil.[9]

Density of AuF_3.—Densities were measured on two different preparations of AuF_3. The first sample (2 g.) resulted from the reaction of BrF_3 with gold powder. The second sample (7 g.) was made by reaction of gaseous fluorine with $AuCl_3$. In each case, the freshly prepared AuF_3 was transferred in a helium atmosphere to a 10-ml. pycnometer containing Fluorolube oil. The density of the oil was 1.941 g./cm.^{3} at 25°. The occluded gas was removed from the sample by evacuating the pycnometer and contents. The density was then measured. On standing for a day or more, gradual darkening of the orange-yellow AuF_3 was noticed, but no change in the density was observed. Protection from light slowed or prevented this effect. The densities of the two different preparations were 6.722 for the BrF_3 preparation and 6.714 for the F_2 preparation. The value chosen is 6.72 g./cm.^{3} at 25°.

X-Ray Methods.—X-Ray powder photographs were taken at 18 ± 2° using a 19-cm. diameter Unicam camera with crystal-reflected Fe Kα radiation from a lithium fluoride monochromator.

Positions of the X-ray reflections were measured with a direct reading vernier scale[10] and accurate unit-cell dimensions were calculated using the standard extrapolation method of Nelson and Riley.[11] Values of wave lengths used in the calculations were: Fe $K\alpha_1 = 1.93597$ Å. and Fe $K\alpha_2 = 1.93991$ Å. Measurements of relative intensities are in arbitrary units and were made on at least two films for each specimen with a Dobson-type microphotometer constructed from a design by Taylor.[12]

For the single-crystal studies the bladed orange crystals were immediately immersed in dry Fluorolube oil when the fluorinator was opened. A crystal was selected under the binocular micro-

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[1] Work at Los Alamos was sponsored by the U. S. Atomic Energy Commission. Requests for reprints should be directed to Los Alamos.

[2] A portion of the Ph.D. thesis submitted by R. Maitland to University of Durham, 1959.

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[9] Hooker Electrochemical Co., Niagara Falls, N. Y.

[10] J. Gibson, *J. Sci. Instr.*, **23**, 159 (1946).

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TABLE I

X-RAY DATA FOR AuF_3 (Fe Kα RADIATION)[a]

hkl	d, Å. Calcd.	$\sin^2\theta$ Calcd.	$\sin^2\theta$ Obsd.	Intensity Densitometer	Intensity Visual
100	4.46	0.0472	0.0477	424	m
101	4.30	0.0507	0.0513	868	ms
102	3.91	0.0614	0.0618	596	ms
103	3.44	0.0791	0.0799	1120	s
104	3.00	0.1040	0.1047	208	mw
006	2.709	0.1278	0.1286	100	w
105	2.628	0.1359	0.1365	238	mw
110	2.575	0.1416	0.1423	246	mw
111	2.543	0.1451	0.1459	670	m
112	2.454	0.1558	0.1565	764	ms
113	2.326	0.1735	...	...	...
106	2.315	0.1750	0.1756	122	w
200	2.230	0.1888	0.1896	284	m
201	2.209	0.1923	...	...	...
114	2.175	0.1984	0.1991	232	mw
202	2.150	0.2030	0.2040	1276	s
203	2.062	0.2207	0.2219	240	mw
107	2.060	0.2211			
115	2.018	0.2303	0.2310	982	s
204	1.954	0.2456	0.2465	900	s
116	1.866	0.2694	0.2693	29	vw
108	1.849	0.2744	0.2751	154	w
205	1.839	0.2776	...	...	...
117	1.725	0.3155	0.3167	848	ms
206	1.722	0.3166			
210, 120	1.685	0.3303	0.3311	350	mw
211, 121	1.676	0.3339	0.3349	2476	s
109	1.674	0.3347			
212, 122	1.650	0.3446	0.3452	408	mw
213, 123	1.610	0.3623	0.3627	57	vw
207	1.608	0.3627			
118	1.595	0.3688	0.3687	150	w
214, 124	1.557	0.3871	0.3878	366	mw
10.10	1.527	0.4022	0.4032	148	mw
208	1.502	0.4160	0.4161	mw	mw
215, 125	1.496	0.4191	0.4201	2076	ms
300	1.486	0.4249	0.4255	460	w
301	1.480	0.4282	...	...	...
119	1.478	0.4291	...	...	...
302	1.462	0.4389	0.4398	432	mw
303	1.434	0.4566	...	...	...
216, 126	1.431	0.4581	0.4584	2060	s
209	1.404	0.4763	0.4771	248	w
10.11	1.403	0.4767			
304	1.396	0.4815	...	...	...
11.10	1.374	0.4966	0.4968	230	w

[a] Complete data up to $\sin^2\theta = 0.985$ are available from the authors.

TABLE II

CRYSTALLOGRAPHIC DATA FOR AuF_3

Hexagonal space group, $P6_1$ or $P6_12$

$a_0 = 5.149$ Å. $c_0 = 16.26$ Å.
$Z = 6$ Density: calcd., 6.78 g./cm.^{3}
obsd., 6.72 g./cm.^{3}

scope and manipulated into a thin-walled glass capillary which was then sealed at both ends. The capillary was mounted on a goniometer head and Weissenberg X-ray photographs were taken using Cu Kα radiation (1.5418 Å.). Many of the specimens turned out to be either twinned, cracked, or decomposed. Unfortunately, the best specimens were too large to provide data of adequate quality for detailed structure determination. However, there were obtained Weissenberg photographs of five layers about c_0 (hkl, l = 0, 1, 2, 3, 4) and three layers about a_0 (hkl, h = 0, 1, 2) with data sufficient to confirm the cell dimensions and symmetry originally deduced from powder photographs.

Trial and error methods were used to deduce the unit-cell type from the powder photographs. In Table I X-ray data (values of d to 1.37 Å.) are listed which are indexed satisfactorily on the basis of a hexagonal cell of the dimensions given in Table II. No reflections were observed which could not be accounted for, and the only systematic absences are $00l$ when $l \neq 6n$. In principle, the two enantiomorphic pairs of space groups, $P6_1$, $P6_5$, and $P6_12$, $P6_52$, could be distinguished by comparing the intensities of (hkl) and (khl) reflections (which must be the same in the latter but not in the former). An unequivocal selection of space groups was not possible although intensities of (hkl) and (khl) reflections did appear to be nearly the same.

Suspensions of auric trifluoride in Fluorolube oil were examined with a petrographic microscope. The crystals are uniaxial positive. Indices of refraction were not measurable owing to chemical reaction between the crystals and the immersion oils.

Discussion of the Probable Structure

Gold trifluoride is apparently not isostructural with any known trifluoride. The unit-cell dimensions and density of AuF_3 are compared in Table III with those of some pseudo-hexagonal transition element trifluorides, the true bimolecular structural units of which are rhombohedral. It is notable that the c_0 parameters of these compounds are much smaller than that of AuF_3, while the a_0 parameters are very similar. The sudden increase in molecular volume of AuF_3 arising from the difference in cell dimension suggests that the coordination number of Au(III) in AuF_3 is not six as in the other listed transition element trifluorides. Other compounds of Au(III) have the square-planar configuration with the gold having a coordination number of four.

TABLE III

HEXAGONAL UNIT-CELL DIMENSIONS AND DENSITIES OF SOME TRIFLUORIDES[7]

	a_0, Å.	c_0, Å.	ρ, g./cm.^{3}	Molecular vol., Å.^{3}
AuF_3[a]	5.149	16.26	6.78	37.5
FeF_3	5.198	13.331	3.60	31.3
CoF_3	5.035	13.218	3.98	29.1
RuF_3	4.967	13.756	5.38	29.4
RhF_3	4.874	13.579	5.70	28.1
PdF_3	5.009	14.118	5.20	31.5
IrF_3	4.940	13.819	8.53	29.2

[a] This work.

Nyholm and Sharpe[13] reported magnetic susceptibility measurements on AuF_3, observing weak paramagnetism, $\chi_g = 0.30 \times 10^{-6}$. Bartlett and Rao[5] state: "AuF_3 prepared by decomposition of $BrAuF_6$ at ~200° was paramagnetic and still contained small amounts of bromine. Fluorination of this material at ~250° gave diamagnetic ($\chi_g = -0.36 \times 10^{-6}$ c.g.s. unit at 25°) orange-yellow material." The suggestion by Nyholm and Sharpe[13] that there are no unpaired electrons appears established and the square-planar configuration is given additional support. Four coordinated Au(III) would have eight 5d-electrons in

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[13] R. S. Nyholm and A. G. Sharpe, *J. Chem. Soc.*, 3579 (1952).

the d_{z^2}, d_{xz}, d_{yz}, and d_{xy} orbitals, with a square-planar configuration.

Gold trifluoride belongs to the space group $P6_1$ or $P6_12$. Accordingly, the gold atoms must all be equivalent in the crystal and also must be related by the 6_1-screw axis. The structure probably consists of either monomeric AuF_3 (which we believe unlikely) or infinite spiral chains parallel to the *c* axis. The space group rules out the possibility of dimers.

The spiral model would include two distinct kinds of fluorine atom, one in a special position of sixfold symmetry and the other in a general position. The former could be in a position (a) of $P6_12$ and would be "bridging fluorines," linking AuF_2 groups in infinite spirals about the sixfold screw axis. Four fluorines would be bonded to each gold atom, and the configuration of these four fluorines about the gold atoms could be approximately planar and square. The intensities of reflections in the Weissenberg photographs suggest that the gold atoms might lie in special positions (b) of space group $P6_12$. An estimate of the single-position parameter of the gold atom could be made from (h00) intensities. A preliminary calculation of relative powder pattern line intensities was made with Au only, $x_{(\mathrm{Au})} = 0.24$. Satisfactory agreement between most observed and calculated intensities was obtained, and, though these Au parameters give no direct indication of F positions, a spiral chain model could be developed from the Au skeleton in the symmetry framework of $P6_12$. However, a more complete and accurate set of single-crystal data is needed for further calculations.

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A π-Cyclopropenyl Derivative of Nickel Carbonyl

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There are two reports in the literature[1,2] of unsuccessful attempts to stabilize the triphenylcyclopropenyl radical by forming a π-complex with a transition metal atom.[3] We now report that triphenylcyclopropenyl bromide or chloride[4] reacts with nickel carbonyl forming a complex which gives strong evidence for the presence of this radical.

Nickel carbonyl added to a methanolic solution of triphenylcyclopropenyl bromide at room temperature under nitrogen gave a two-phase system of which the upper layer, essentially methanolic triphenylcyclopropenyl bromide, soon became red. Carbon monoxide was evolved. After several minutes brick-red crystals formed at the interface.[5] The reaction was complete within 1 hr. at room temperature or within a few minutes if the reaction mixture was gently warmed. The product was triphenylcyclopropenyl nickel carbonyl bromide. *Anal.* Calcd. for $NiCOBr(C_6H_5)_3C_3$: C, 60.9; H, 3.5; Ni, 13.5; CO, 6.5; Br, 18.4. Found: C, 59.2; H, 3.5; Ni, 12.1; CO, 6.6; Br, 19.2. The chloride was similarly prepared. *Anal.* Calcd. for $NiCOCl(C_6H_5)_3C_3$: C, 67.8; H, 3.9; Cl, 9.1. Found: C, 67.9; H, 4.3; Cl, 9.2.

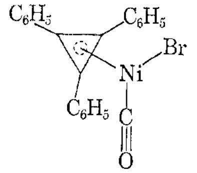
Triphenylcyclopropenyl nickel carbonyl bromide is sparingly soluble in both tetrahydrofuran and methanol to give pale red solutions instantly oxidized on exposure to air. The solid, in contrast, is fairly air stable, only decomposing completely after several weeks exposure. Under vacuum the solid appears stable indefinitely.

Attempts to purify the reaction product failed because of its low solubility and oxygen sensitivity in solution. It decomposes at *ca.* 120° under vacuum without subliming.

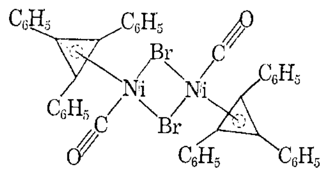
The infrared spectrum in the carbonyl region shows a sharp peak at 2039 $cm.^{-1}$ but no strong absorption at either 1710 or 1400 $cm.^{-1}$, eliminating structures analogous to those found by Coffey[1] or Chatt and Guy,[2] although the analysis is consistent with the former if only the terminal carbonyl is liberated during the analysis for CO. *Anal.* Calcd. for $C_{23}H_{15}BrNiO_2$: C, 59.8; H, 3.3; Ni, 12.7; CO, 6.1; Br, 17.3.

The solid is weakly paramagnetic (about 0.2 unpaired electron) at room temperature, but this may be due to an impurity.

The simplest formulation of the compound is as I but a more plausible structure is II. The infrared spectrum suggests that the latter has a center of symmetry.



I



II

Higher polymers are also possible formulations but the sharpness of the 2039 $cm.^{-1}$ infrared peak and its failure to split in either a mull or potassium bromide disk make these unlikely. Structure II, which is similar to that found for tetramethylcyclobutadiene nickel dichloride,[6] satisfies the "inert gas rule" if the $A_2''(\pi)$ of each cyclopropenyl radical donates two

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(3) R. B. King, *Inorg. Chem.*, **2**, 642 (1963), reports that the reaction between triirondodecacarbonyl and 1,3,3-trimethylcyclopropene does not yield a complex with the triangular moiety π-bonded to the transition metal.

(4) R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, **83**, 2367 (1961).

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