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The Fluorides of Titanium: X-Ray Powder Data and Some Other Observations

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Titanium trifluoride, prepared from the tetrachloride by reduction with aluminum in the presence of AlCl_3 ² and subsequent conversion with HF, was oxidized with chlorine. The resulting TiF_3Cl is a yellow powder which sublimes more readily than TiF_4 , reacts with water to form a clear acid solution, and dissolves slightly in chloroform but neither in benzene nor in carbon tetrachloride. It hydrolyzes readily, and the air-stable product obtained by atmospheric hydrolysis and subsequent drying, both from it and from TiF_4 , appears to be TiOF_2 . The material so obtained and the oven-dried (100°) product of treating TiO_2 with 50% aqueous HF gave identical powder diffraction patterns. TiF_4 was prepared from the tetrachloride and anhydrous HF following Ruff³ and others, and was purified by sublimation.

X-Ray powder diffraction data (Table I) were obtained for all the fluorides except TiF_3Cl , which was very finely divided and gave unsatisfactory patterns. Our data for TiF_4 disagree with the ASTM data⁴; these have previously been reported

to be unreliable,⁵ and comparison with the TiOF_2 pattern (see Table I) now shows that the original sample must have been predominantly TiOF_2 . Except for $d = 2.18$ and $d = 1.20$, all the TiOF_2 lines of $d > 0.900$ appear in the ASTM data in proper position and sequence of intensity, and the three strongest TiOF_2 lines are the three strongest ASTM TiF_4 lines.

The TiOF_2 lines may be given simple-cubic indices, and the report of a complete structural investigation is in press.⁶

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Metal-Amine Coördination Compounds. IV. Copper(I) Complexes

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The copper(I) coördination compounds described are formed in the reaction of the copper(I) ion with 1,10-phenanthroline, 2,2'-bipyridine, 2,2',2''-terpyridine and 2,2'-biquinoline. Compounds of the first two chelating agents have received considerable attention in the past. Since the first observations on the color reaction,² many investigators have examined the absorption characteristics and the application of the complexes to the analytical determination of copper.³⁻⁵ The formula of the 1,10-phenanthroline complex⁴ and the stability of the 2,2'-bipyridine compound⁶ have been determined, whereas the stability of the copper(I)-1,10-phenanthroline complex has not been evaluated.

The selectivity of 2,2'-biquinoline for the copper(I) ion accounts for the interest in it. This selectivity and the characteristics of the 2,2'-biquinoline complex in various non-aqueous solvents have been studied by several investigators.^{4,7-9} Studies on substituted 1,10-phenanthroline reagents, which also exhibit selectivity for the copper(I) ion, have been carried out.¹⁰⁻¹² Most of the work has been done in immiscible alcoholic media with the emphasis toward application of the complexes to the determination of the copper.

No work has been reported on the copper(I)-2,2',2''-terpyridine complex. An examination of

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TABLE I

X-RAY POWDER DIFFRACTION DATA							
TiF_3		TiF_4				TiOF_2	
d	I/I_0	Obsd. d	Obsd. I/I_0	ASTM d	ASTM I/I_0	d	I/I_0
4.23	1	8.5	12	6.50	10	3.76	100 ^b
3.84	100	6.0	8	5.45	3	2.67	13
3.57 ^a	45	4.00	85	4.75	2	2.18	<1
3.11	10	3.79	1	4.35	2	1.89	31 ^b
2.71 ^a	25	3.68	100	3.80	100 ^b	1.69	32 ^b
2.31	6	3.09	35	3.56	2	1.54	7
2.08	100	2.68	10	3.40	2	1.34	13
1.92 ^a	45	2.35	2	3.22	20	1.26	11
1.80	85	2.22	4	2.68	12.5	1.20	1
1.72 ^a	45	2.01	10	2.35	3	..	<1
1.62	1	1.89	70	2.18	6	1.09	3
1.57	1	1.72	20	1.90	40 ^b	1.050	3
1.36 ^a	4	1.69	20	1.70	40 ^b	1.012	3
1.28	50	1.63	30	1.61	4	.949	<1
1.089	45	1.50	2	1.55	6	.921	4
1.042	20	1.39	17	1.485	1	.895	1
0.9033	6	1.34	17	1.345	12.5	..	<1
.8287	20	1.28	20	1.266	10	.850	4
.8074	15	1.25	2	1.098	2	.829	4
		1.04	1	1.054	2	..	<1
		1.00	1	1.015	2		
				0.921	2		

^a Diffuse line. ^b Strongest lines.

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