

TABLE I
ADDITION COMPOUNDS OF TETRAHYDROTHIOPYRAN

Inorg. salt	Solvent	Solubility	M. p., °C.	Formula	Metal analyses, %	
					Calcd.	Found
HgBr ₂	Alcohol	Sl. sol. hot aq. alc.	101-105	HgBr ₂ ·(CH ₂) ₆ S	43.36	43.26
CuCl ₂	Alcohol	Ins. aq., org. solv.	154.5-157	CuCl·(CH ₂) ₆ S	31.59	31.55
Cu ₂ Cl ₂	Alc. HCl	Same	154.5-160	CuCl·(CH ₂) ₆ S	31.59	31.50
CuBr ₂	Alcohol	Same	123-124	CuBr·(CH ₂) ₆ S	25.88	25.85
Cu ₂ Br ₂	Alc. KBr	Same	121.5-122.5	CuBr·(CH ₂) ₆ S	25.88	25.79
Cu ₂ I ₂	Alc. KI	Same	164-165 d.	CuI·(CH ₂) ₆ S	21.73	21.85
HAuCl ₄	Ether	Sl. sol. alc., ins. eth.	120-122 d.	AuCl ₃ ·(CH ₂) ₆ S	48.60	48.39
HAuCl ₄	Alcohol	Ins. alc. eth.	179-182 d.	AuCl·(CH ₂) ₆ S	58.89	58.66
HAuBr ₄	Ether	Sl. sol. alc. eth.	140-145 d.	AuBr ₃ ·(CH ₂) ₆ S	36.58	36.70
^a	Alcohol	Sl. sol. hot alc.	173-179 d.	AuBr·(CH ₂) ₆ S	51.99	51.83
SnCl ₄	^b	Sol. chl., dec. aq.	149-151.5	SnCl ₄ ·2(CH ₂) ₆ S	25.53	25.57
SnBr ₄	Chlorof.	Sol. chl., dec. aq.	149.5-151	SnBr ₄ ·2(CH ₂) ₆ S	18.36	18.45
H ₂ PtCl ₆ -KI ^c	Alcohol	Ins. alc.	194.5-196 d.	PtI ₂ ·2(CH ₂) ₆ S	29.88	29.98
PdCl ₂	Acetone-H ₂ O	Sl. sol. acet., ins. aq.	146.5-148.5 d.	PdCl ₂ ·2(CH ₂) ₆ S	27.93	28.07

^a AuBr₃·(CH₂)₆S boiled with alcohol and excess thiopyran. ^b Thiopyran and tin(IV) chloride mixed directly. ^c Excess potassium iodide solution added to chloroplatinic acid in alcohol, precipitate dissolved by heating, and thiopyran added till no further precipitation.

hydrothiopyran by refluxing with excess sodium sulfide in ethanol.

The addition compounds were formed by dissolving the metal salt in ethanol or ether, adding salt or acid if necessary, and adding slight excess of sulfide, sometimes dissolved in the solvent. The data on the complexes are given in Table I.

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Structures of Complex Fluorides. Rubidium Hexafluogermanate

BY W. B. VINCENT AND J. L. HOARD

In an earlier paper¹ we have reported the X-ray determination of structure for the isomorphous crystalline compounds potassium hexafluogermanate and ammonium hexafluogermanate, R₂GeF₆. Upon the basis of X-ray data obtained from a single specimen of what we supposed was rubidium fluogermanate, we stated at that time that this substance crystallizes in a more complex structural type than do the corresponding potassium and ammonium salts. This particular specimen occurred as a hexagonal prism, almost needle-like in shape, whereas we have since obtained only hexagonal tablets and plates by recrystallizing rubidium fluogermanate from aqueous solution at room temperature. X-Ray study of a number of these tabular crystals shows that they crystallize in the same structural type as do

potassium and ammonium fluogermanates. The single needle-like specimen may or may not have been rubidium fluogermanate: the values of the lattice constants indicate that it may have been a different crystalline modification of closely related and only slightly more complicated structure than that to be discussed here. In any case we must correct our earlier statement at least to the extent of asserting that the usual and presumably the stable form at room temperature of rubidium fluogermanate is fully isomorphous with the corresponding ammonium and potassium salts.

The X-ray data for Rb₂GeF₆ lead to a hexagonal unit cell with $a = 5.82$, $c = 4.79$ Å., space-group $D_{3d}^3 - C\bar{3}m$, containing one stoichiometric molecule. The atomic coordinates² are Ge in (a): 000; 2Rb in 2(d): $\frac{1}{3}$ $\frac{2}{3}$ u ; $\frac{2}{3}$ $\frac{1}{3}$ \bar{u} with $u = 0.695$; 6 F in 6(i): xxz , etc., with $x = 0.144$, $z = 0.213$.

The methods used in establishing this structure closely paralleled those previously described.¹ A comparison of calculated with observed reflection amplitudes for over one hundred forms in rubidium fluogermanate led to generally excellent agreement. Having presented¹ the corresponding data in detail for potassium fluogermanate, and ammonium hexafluogermanate, it seems unnecessary to reproduce the rather extensive tables³ for rubidium hexafluogermanate in this note. In addition we find that a Fourier projec-

(2) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Gebrüder-Borntraeger, Berlin, 1935, Vol. I, p. 258.

(3) The amplitude data for rubidium hexafluogermanate are available in the Thesis of W. B. Vincent, "The Structures of Some Fluosilicates and Fluogermanates," Cornell University Library, 1940.

(1) J. L. Hoard and W. B. Vincent, THIS JOURNAL, 61, 2849 (1939).

tion of relative electron density along a using experimental ($0kl$) amplitude data is in satisfactory agreement with the parameter values given above.

Rubidium fluogermanate is an aggregate of K^+ and practically regular octahedral GeF_6^- ions (for diagrams of the structural type see ref. 1). The lattice constants and parameter values are only very slightly different from those found for ammonium fluogermanate, so that corresponding interatomic separations are virtually identical

in the two cases. The near identity in the effective radii of rubidium and ammonium ions appearing in corresponding compounds has been repeatedly observed excepting in cases where ammonium ion is restricted to a small coordination number (usually four) through the formation of strong hydrogen bonds. We may conclude again¹ that hydrogen bonding plays a relatively minor role in ammonium fluogermanate.

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COMMUNICATIONS TO THE EDITOR

ELECTRON MICROSCOPE OBSERVATIONS OF COLLAGEN

Sir:

Electron micrographs have been made of collagen fibers from a variety of sources, including rat tail tendon, beef tendons and ligaments, and human skin. Fibers were obtained either by teasing small bits of tendon in water or by dissolving the material in acetic acid and reprecipitating the fibers by neutralization.

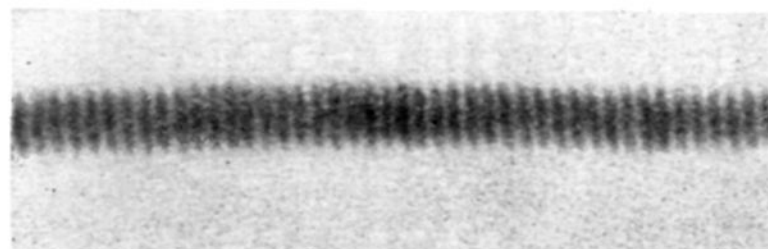


Fig. 1.—Electron micrograph of collagen fibers from beef tendon, magnification 25,000 \times .

Under appropriate conditions the fibers appear characteristically cross-striated, the relatively opaque and transparent bands extending uniformly across the fiber (see Fig. 1). The average distance between like bands can be measured with an accuracy of about 3%. The interband distance is independent of fiber width and varies considerably from one fiber to another; the extremes thus far measured are 902 and 522 \AA ., though the range shown in the fibers of any single preparation is more restricted.

Recent X-ray diffraction investigations in this

Laboratory [R. S. Bear, *THIS JOURNAL*, **64**, 727 (1942)] have demonstrated the presence in collagen of a fiber-axis periodicity of approximately 640 \AA . This spacing was obtained from all the types of collagen mentioned above and appears to be characteristic of this protein in intact tissues. There seems little doubt that the periodicities observed in the electron micrographs represent a manifestation of the X-ray diffraction periodicity in intact tendon and that the phenomenon is a consequence of the structure and arrangement of the collagen molecules in the fibers. The range of spacings observed in the electron micrographs is doubtless due to the special conditions required for the preparation of the material, chief among which are the isolation and vacuum drying of individual fibers. It is reasonable to expect individual fibers to behave differently when isolated than when present in compact bundles as in normal tendon where lateral restraints, possibly by enclosing membranes and cement substance, restrict their behavior mechanically. This interpretation is being tested by an X-ray diffraction study of teased fibers similar to those observed with the electron microscope. In addition, the effect of various physical and chemical conditions on the appearance of the fibers in the electron micrographs is being further investigated in an effort to get more information concerning the molecular architecture of collagen.

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