

formula for this compound has been confirmed. The substance is neutral and consumes only one mole of alkali on heating with alcoholic base. Since the hydrolysis products of pyrotenuin do not contain a volatile acid, the acetoxy group originally present in tenuin is eliminated in the pyrolysis reaction. The reaction with alkali is ascribed to the lactone grouping which is probably responsible for the absorption band at $5.65\text{--}5.70\ \mu$,^{7,10} occurring in all these compounds.

Pyrotenuin contains a double bond $R_2C=CHR$ since its infrared spectrum shows bands at 6.02 and $12.28\ \mu$.^{6b} It does not contain an α,β -unsaturated carbonyl group as evidenced by the ultraviolet spectrum and the disappearance of the absorption bands at 5.92 and $6.37\ \mu$. Permanganate oxidation of pyrotenuin yields one mole of volatile acid which has been identified as acetic acid, the unsaturated group may therefore be represented by $R_2C=CHCH_3$.

The absorption band at $5.72\text{--}5.78\ \mu$ is believed to be due to a strained ring carbonyl group^{6a,7} in pyrotenuin. While it has not been possible to prepare a pure oxime, pyrotenuin does react with hydroxylamine.

Experimental

All temperatures uncorrected. Analyses by Karl Zilch.

Anhydrotenuin, tenuinic acid, acetyltenuinic acid and pyrotenuin were prepared by the procedures of Clark.^{5,8,11}

Anhydrotenuin (II).—Anhydrotenuin (0.1 g., m. p. $171\text{--}173^\circ$) was saponified by refluxing with 10 cc. of 0.1076 *N* aqueous sodium hydroxide and 20 cc. of ethyl alcohol for one hour in an atmosphere of nitrogen. Titration with 0.1037 *N* hydrochloric acid against phenolphthalein showed a consumption of 1.86 moles of alkali.

Tenuinic Acid.—Anhydrotenuin (0.50 g.) was oxidized with alkaline 30% hydrogen peroxide according to the procedure described for tenuin by Clark.⁸ The crystalline acid melting at $338\text{--}340^\circ$ weighed 0.25 g. Further purification gave a constant melting point of $341\text{--}343^\circ$ and a mixed melting point of $341\text{--}343^\circ$ with an authentic sample.

Tenuinic acid was also obtained by permanganate oxidation of anhydrotenuin (0.9 g.), removal of the precipitated manganese dioxide, acidification of the filtrate with sulfuric acid and removal of the volatile acid by steam distillation. The non-volatile residue was extracted with benzene, dried, distilled and crystallized from aqueous methanol; yield 0.108 g.

Anal. Calcd. for $C_{15}H_{20}O_7$: C, 57.68; H, 6.46; mol. wt., 312. Found: C, 57.48; H, 7.02; neut. equiv., 316.

Saponification of tenuinic acid with aqueous alcoholic sodium hydroxide showed the consumption of 1.94 moles of base.

The volatile acid from the steam distillation was titrated with 0.02 *N* sodium hydroxide against phenolphthalein. The amount of base used corresponded to one mole of acid per mole of anhydrotenuin. The neutral solution was evaporated and the residual salt was converted to the anilide which gave a melting point and a mixed melting point of 114° (micro) with authentic acetanilide.¹²

Acetyltenuinic Acid.—Anhydrotenuin (0.7 g.) was oxidized with potassium permanganate as described for tenuin by Clark.⁶ The acid melting at $210\text{--}214^\circ$ weighed

290 mg. Further purification gave a product with a constant melting point of $232\text{--}234^\circ$ and a mixed melting point of $232\text{--}234^\circ$ with authentic acetyltenuinic acid.

Pyrotenuin.—Crude pyrotenuin, m. p. $174\text{--}194^\circ$ (dec.), was purified by two successive sublimations at 180° (2 mm.) which raised the melting point of the material to 209° (dec.). The analytically pure substance (from 300 mg. of tenuin) weighed 25 mg. It was soluble in benzene, acetone and chloroform, slightly soluble in methanol and insoluble in water and Skellysolve C.

Anal. Calcd. for $C_{15}H_{16}O_7$: C, 70.88; H, 7.32; mol. wt., 220.25. Found: C, 70.60; H, 7.70; mol. wt. (Rast), 220; sapon. value, 236.

The pH of its alcoholic solution was 6.82.

The oxidation of 0.00305 mole of pyrotenuin with aqueous permanganate (1.5 g.) in acetone gave 0.0031 mole of volatile acid as determined by titration of the steam distillate. The anilide of the acid (0.00079 mole) melted at 113° and did not depress the melting point of acetanilide.

Absorption Spectra.—Ultraviolet and infrared absorption spectra were determined by Dr. E. E. Pickett, University of Missouri.

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Crystal Structure of Cesium Pentachloromono-aquothallate, $Cs_2TiCl_5H_2O$

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As an extension of our research on trivalent thallium complexes, we have investigated the crystal structure of cesium pentachloromono-aquothallate, $Cs_2TiCl_5H_2O$. In the course of the research, two papers, the one on the crystal structure of ammonium pentachloromonoaquoferate, $(NH_4)_2FeCl_5H_2O$,¹ and the other on ammonium pentachloromonoaquoindate, $(NH_4)_2InCl_5H_2O$,² were published. It was found that the crystal structure of cesium pentachloromonoaquothallate is isomorphous with the two crystals mentioned above, and a brief account of our research will be given below.

Crystals of cesium pentachloromonoaquothallate were prepared by slow evaporation from aqueous solutions containing thallic chloride and a large excess of cesium chloride (gravimetric ratio, $CsCl:TiCl_3 = 10:1$). According to Wallace,³ the crystal belongs to the orthorhombic bipyramidal class with the axial ratios $a':b':c' = 0.9690:1:1.4321$, and its density is 3.879 g./cc. at 20° .

Crystals selected for the present study were $0.8 \times 0.8 \times 0.4$ mm. in dimensions and showed no remarkable cleavage.

Laue, oscillation and powder photographs were taken using $Cu\text{-}K\alpha$ radiation. The identity periods obtained from oscillation photographs around the *a*-, *b*- and *c*-axes were refined by the powder photographic method and are listed in Table I, together with those of the two crystals,

(1) I. Lindqvist, *Arkiv Kemi, Mineral. Geol.*, **24A**, 1 (1946).

(2) H. P. Klug, E. Kummer and L. Alexander, *This Journal*, **70**, 3064 (1948).

(3) R. C. Wallace, *Z. Krist.*, **49**, 427 (1911).

(10) Rasmussen and Brattain, *This Journal*, **71**, 1076 (1949).

(11) Clark, *ibid.*, **62**, 600 (1940).

(12) The acetic acid was undoubtedly formed in the hydrolysis of acetyltenuinic acid during the steam distillation.

ammonium pentachloromonoquo-ferrate and -indate. The axial ratios of the thallate are found to be $a':b':c' = a/2:c:b = 0.9729:1:1.4377$, in agreement with the values reported by Wallace. The possible space group is $D_{2h}^{16}-Pnma$. There are four formula units in the unit cell, calculated density being 3.904.

TABLE I

Chemical formulas	$(NH_4)_2FeCl_5H_2O$	$(NH_4)_2InCl_5H_2O$	$Cs_2TiCl_5H_2O$
Axial lengths (in kX)	<i>a</i> 13.68 <i>b</i> 9.88 <i>c</i> 7.02	14.10 10.17 7.16	14.36 10.61 7.38
Axial ratios	1.385:1:0.711	1.387:1:0.704	1.352:1:0.695

The relative intensities of reflections were visually estimated with the aid of calibrated scales. These were corrected for polarization, Lorentz and absorption factors.

The cell dimensions, the corresponding space group, and the general features of the reflection intensities suggested that the structure would be quite close to those of the two crystals, ammonium pentachloromonoquo-ferrate and -indate. Referring to the structures of the two crystals and making use of Patterson diagrams, we have made a detailed survey of the atomic parameters. Special care was paid to the structure factors $F(hk0)$ (obtained from excellent oscillation photographs) used in synthesizing a Patterson diagram $p(xy)$. Structure amplitudes calculated using the atomic coordinates given in Table II were found to be in good agreement with those derived from the observed intensities. Using the well-known criterion

$$R_1 = \Sigma(|F_{obsd.}| - |F_{calcd.}|) / \Sigma|F_{obsd.}|$$

R_1 has the satisfactory value 0.248 for data from the pinacoids, $(hk0)$, and $(0kl)$ planes.⁴

TABLE II
ATOMIC PARAMETERS

	<i>x</i>	<i>y</i>	<i>z</i>
4Ti ³⁺ in 4(<i>c</i>)	0.123	0.250	0.300
(Fe ³⁺ in $(NH_4)_2FeCl_5H_2O$)	.114	.250	.309 ^a)
(In ³⁺ in $(NH_4)_2InCl_5H_2O$)	.110	.250	.313 ^a)
4Cl ₁ ⁻ in 4(<i>c</i>)	.002	.250	.049
4Cl ₂ ⁻ in 4(<i>c</i>)	.250	.250	.065
4Cl ₃ ⁻ in 4(<i>c</i>)	.238	.250	.554
4H ₂ O in 4(<i>c</i>)	.01	.250	.50
8Cl ₄ ⁻ in 8(<i>d</i>)	.120	.010	.300
8Cs ⁺ in 8(<i>d</i>)	.365	.000	.300
(N in $(NH_4)_2FeCl_5H_2O$)	.36	.002	.33 ^a)
(N in $(NH_4)_2InCl_5H_2O$)	.366	.000	.349 ^a)

^a The parameters of important atoms in $(NH_4)_2FeCl_5H_2O$ and $(NH_4)_2InCl_5H_2O$ are given for comparison.

The isomorphism between $Cs_2TiCl_5H_2O$, $(NH_4)_2FeCl_5H_2O$ and $(NH_4)_2InCl_5H_2O$ is thus established.

(4) At the editor's request one of the referees has made certain revisions of the manuscript. This calculation was made and inserted by the referee on the basis of a table of structure amplitude data for 122 planes submitted for the referees' use, but not for publication as a part of the manuscript because of its length.

They belong to the $J1_3$ -type in the classification of the "Strukturbericht." The parameters of the cesium atoms are, however, believed to be more accurate than those of the ammonium nitrogen atoms in the two ammonium salts. This may afford useful data for the discussion of the rôle of water molecules in hydrated salt crystals.^{5,6,7}

Interatomic distances are given in Table III. The average distance between the thallium and chlorine atoms is found to be 2.53 ± 0.02 kX which is in good agreement with the value 2.55 kX reported for those in $K_3TiCl_6 \cdot 2H_2O$.⁹ Other interatomic distances are also found to be reasonable. It must be mentioned here that all the typical compounds found in the ternary system TiX_3-MX-H_2O , where X stands for halogen and M for ammonium or alkali ions, are now determined in detail (see Table IV).

TABLE III

INTERATOMIC DISTANCES (IN kX.)

Tl-Cl ₁	2.54	Cl ₁ -Cl ₂	3.56	Cs-H ₂ O	4.16
Tl-Cl ₂	2.52	Cl ₁ -2Cl ₄	3.58	Cs-H ₂ O	4.02
Tl-Cl ₃	2.51	Cl ₂ -Cl ₃	3.61	Average	4.09
Tl-2Cl ₄	2.55	Cl ₂ -2Cl ₄	3.60	Cs-Cl ₁	3.42
Average	2.53	Cl ₃ -2Cl ₄	3.59	Cs-Cl ₁	3.65
Tl-H ₂ O	2.19	Average	3.59	Cs-Cl ₂	3.69
H ₂ O-Cl ₁	3.33			Cs-Cl ₂	3.57
H ₂ O-Cl ₂	3.30			Cs-Cl ₃	3.62
H ₂ O-2Cl ₄	3.34			Cs-Cl ₃	3.66
Average	3.33			Cs-Cl ₄	3.53
				Cs-Cl ₄	3.95
				Cs-2Cl ₄	3.48
				Average	3.61

TABLE IV

TERNARY SYSTEM TiX_3-MX-H_2O

Molar ratio of components $TiX_3:MX$	Chemical formulas of substances whose crystal structures have been determined
1:1	$NH_4TiBr_4 \cdot 2H_2O$, $KTiBr_4 \cdot 2H_2O$, $RbTiBr_4 \cdot H_2O$, $CsTiBr_4$, $KTiI_4 \cdot 2H_2O$, $RbTiI_4 \cdot 2H_2O$, $CsTiI_4$ ⁸
1:2	$Cs_2TiCl_5H_2O$
1:3	$K_3TiCl_6 \cdot 2H_2O$, $Rb_3TiBr_6 \cdot 8/7H_2O$ ⁹
2:3	$Cs_2Ti_2Cl_5$ ¹⁰

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