

mentioned above gave similar analytical values, close to the theoretical, for carbon and hydrogen, and all fractions of the iodide gave copious precipitates of silver nitrate. It was therefore felt that the desired quaternary ammonium salt in varying stages of purity was in hand and that one preparation should be selected for bioassay. The preparation melting at 189.9–190.6° (darkens) cor. was available in some quantity, and this was chosen for bioassay and inclusion in Table I.

Oximes.—Samples of all the bromides in the β -naphthacyl series were warmed on the steam-bath for several hours in aqueous solution with a 15% excess of hydroxylamine hydrochloride and sodium acetate. In many instances there was evidence of decomposition of the bromide, but in several cases, pure oximes could be isolated. These are listed in Table II.

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A Crystal-Chemical Study of Cesium Trichlorocuprate¹

BY HAROLD P. KLUG² AND GEORGE W. SEARS, JR.³

During the investigation of the nature of inorganic halogen complexes with certain elements, the compound cesium trichlorocuprate, CsCuCl_3 , was studied. It was hoped that from its study information concerning the coordination of chlorine around copper, and the nature of the groups present in the crystalline trichlorocuprates might be obtained. Although such complete results have not been achieved, certain data were obtained which are reported in this communication.

The salt was prepared by the evaporation, over anhydrous calcium chloride, of a solution of the constituent salts containing cupric chloride in considerable excess, as described by Wells and Dupre.⁴

Gravimetric analysis for copper and chlorine confirmed the identity and composition of the garnet-red crystals.

Anal. Calcd. for CsCuCl_3 : Cu, 20.99; Cl, 35.12. Found: Cu, 20.68; Cl, 34.77.

Since no crystallographic data were available, other than the observation of Wells and Dupre⁴ that the crystals formed slender hexagonal prisms, a goniometric study was made.⁵

The chief habit proved to be the slender needles exhibiting the first-order hexagonal prism and terminated by one or more first-order pyramids. A few crystals of a different habit were observed, however, in which the first-order prism was missing, or nearly so, and one of the pyramids (10 $\bar{1}$ 3),

(1) From a thesis by George W. Sears, Jr., presented to the Graduate Faculty of the University of Minnesota in partial fulfillment of the requirements for the Ph.D. degree, January, 1944.

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(4) Wells and Dupre, *Am. J. Sci.*, [3] **47**, 94 (1894).

(5) The authors wish to express their thanks to Professor John W. Gruner of the Department of Mineralogy for his valuable assistance in connection with the goniometric measurements and the microscopic observations.

predominated. The average results of the measurements on six crystals are given in Table I in terms of the new notation for the hexagonal system as described by Palache, Berman and Frondel.⁶ The data of Table I lead to the axial ratio, $c = 2.522$.

TABLE I

ANGULAR DATA ON CESIUM TRICHLOROCUPRATE

Form	ϕ	ρ
c 000 $\bar{1}$...	0° 00'
m 10 $\bar{1}$ 0	30° 00'	90 00
r 10 $\bar{1}$ 1	30 00	71 03
n 10 $\bar{1}$ 2	30 00	55 32
l 10 $\bar{1}$ 3	30 00	44 08

The crystals show parallel extinction between crossed nicols. Pleochroism is strong, the color changing from a canary yellow to an orange brown in thin sections. Absorption is strongest when the direction of elongation is perpendicular to the plane of polarization. There was no evidence of twinning in the crystals examined by polarized light or on the goniometer. A good cleavage perpendicular to the needle axis was observed. Unusually detailed pyroelectric experiments by the method of Martin⁷ and also that of Orelkin and Lonsdale⁸ failed to give a positive test along either the vertical axis or the horizontal axes. The average value of the density from three pycnometric determinations at 24° was 3.644. The crystallographic study thus indicates the crystal symmetry class to be the normal or holohedral class of the hexagonal system, D_6^h .

Laue, rotating and oscillating crystal photographs, and c axis Weissenberg patterns were used in the X-ray study of the crystals. The dimensions of the unit cell were found to be $a_0 = 7.175 \pm 0.002\text{\AA}$. and $c_0 = 18.03 \pm 0.03\text{\AA}$. These lead to the axial ratio $c = 2.513$, in satisfactory agreement with the value from the goniometric study. The X-ray data indicated no absent types of reflections whatsoever in the first order. The lattice is therefore primitive, and the space group is either D_{6h}^1 , D_6^1 , C_{6v}^1 , D_{3h}^1 , or D_{3h}^3 . Since there is no evidence for the lack of a center of symmetry the correct space group appears to be D_{6h}^1-C6/mmm . The unit cell contains 6 CsCuCl_3 .

Much detailed study by the Patterson-Harker Fourier technique and other methods has failed to yield an atomic arrangement for the crystal in satisfactory agreement with the X-ray intensity data. From the dimensions of the cell it is hard to escape the conclusion that the structure is based on a close-packed arrangement of cesium and chloride ions, as in the case of $\text{Cs}_3\text{As}_2\text{Cl}_9$ and $\text{Cs}_3\text{Ti}_2\text{Cl}_9$.⁹ No reasonable packing of the Cs^+ and

(6) Palache, Berman and Frondel, "Dana's System of Mineralogy," 7th ed., Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 9, 23–31.

(7) Martin, *Min. Mag.*, **22**, 519 (1931).

(8) Orelkin and Lonsdale, *Proc. Roy. Soc. (London)*, **A144**, 633 (1934).

(9) Hoard and Goldstein, *J. Chem. Phys.*, **3**, 117 and 199 (1935).

Cl^- ions seems possible on the basis of D_{6h}^1 , chiefly because of the 6-fold axis which forces cesium and chlorine, whose diameters are approximately equal to half the cell edge, to lie either directly on the axis or at a distance of half a lattice length away. The non-centrosymmetrical space groups, D_6^1 and C_{6v}^1 , because of their 6-fold axes, are subject to the same difficulty. Only on the basis of D_{3h}^1 could chemically reasonable packings of the cesium and chloride ions be obtained. For at least two of these arrangements, positions could be found for the copper atoms which explained the intensities of the various orders of (0001) fairly satisfactorily. For other types of planes agreement with the observed intensities was unsatisfactory.

It seems probable that the difficulties encountered in this structure study may arise from some unknown and very perfect twinning. Hoard and Goldstein observed a case of this kind in their study of $\text{Cs}_2\text{Tl}_2\text{Cl}_6$,⁵ and were fortunate in finding untwinned individuals. In this study no crystals were found whose diffraction effects showed different symmetry. In view of these results it has seemed unprofitable to pursue the study further at this time.

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Structure of Polyvinyl Alcohol

BY A. D. McLAREN AND R. J. DAVIS

In connection with certain analytical procedures, it was necessary to look for possible existence of a small amount of 1,2-glycol structure in polyvinyl alcohol. Several investigators^{1,2,3} have advanced evidence for a preponderance of 1,3-glycol structure in polyvinyl alcohol. The existence of some 1,2-glycol structure is indicated by the work of Staudinger² and of Nord,⁴ but is doubted by Marvel and Denoon.³ Reduction of periodic acid is considered specific for 1,2-glycol configuration. The latter authors found that polyvinyl alcohol was not appreciably oxidized by periodic acid at 0° in thirteen hours. We have reinvestigated the action of periodic acid upon polyvinyl alcohol.

Using polyvinyl alcohol⁵ containing 0.31% residual vinyl acetate and yielding 0.39% of ash, oxidations with periodic acid were carried out as described previously³ and at 25°. Results of a typical case using 25-cc. aliquots from a mixture of 150 cc. of 0.511% polyvinyl alcohol in water and 30 cc. of 1.2% periodic acid, at 25°, are given in Table I.

(1) Staudinger, *Ber.*, **59**, 3019 (1926).

(2) Staudinger, Frey and Stark, *ibid.*, **60**, 1782 (1927).

(3) Marvel and Denoon, *THIS JOURNAL*, **60**, 1045 (1938).

(4) Nord, *Naturwissenschaften*, **24**, 763 (1936).

(5) Osmotic molecular weight 30,000, courtesy of Dr. G. F. Lanzl.

TABLE I

OXIDATION OF POLYVINYL ALCOHOL WITH PERIODIC ACID

Time, hours	Cc. 0.1 N $\text{Na}_2\text{S}_2\text{O}_8$ (for 0.511% alcohol)	Specific viscosity (for 0.4% alcohol)
0	0	0.065
1.0	0.1	.062
3.25	.15	.055
6.0	.17	...
18.0	.35	...
24.0	..	.051
48.0	.36	...

Viscosity data for a similar run, utilizing 10 cc. of 0.4% polyvinyl alcohol and 2 cc. of aqueous periodic acid, are also given in Table I.

These results indicate that oxidation takes place at an appreciable rate at 25° and is essentially complete in from six to eighteen hours for low concentrations of the polymer (up to 1%). The reaction proceeds at a very slow rate at 0° and is only about half complete in forty-eight hours. Execution of the periodic acid oxidation at 25° is not considered to modify the specificity of this test.⁵

For polyvinyl alcohol solutions ranging in concentration from 0.1–1.0%, the average titer corresponding to the periodic acid reaction with twenty-five cc. of 0.1% solution of the alcohol was 0.11 cc. of 0.1 N thiosulfate solution. This figure indicates that the fraction of vinyl alcohol residues united in 1,2-glycol configuration is $0.019 \approx 0.007$.

For some unknown reason, polymer solutions in the range of 2% or greater continue to react with periodic acid at room temperature, even after forty-eight hours have elapsed. This may, in part, be the result of cross-linkage with the periodic acid or oxidative side reactions.⁶

If actual cleavage of the polyvinyl alcohol molecule is expected to take place between 1,2-glycol carbon atoms,⁵ a decrease in viscosity of aqueous solutions would be expected. Viscosity measurements were conducted with polyvinyl alcohol solutions containing periodic acid and it was observed that the specific viscosity of these mixtures fell off to a constant value after eight to twelve hours had elapsed. This approach to constancy of specific viscosity with time was anticipated since, for solutions of comparable concentration, the periodic acid uptake also ceases at about this time interval. In order to be certain that these viscosity decreases had probably no connection with acetal formation, similar observations were made with polymer solutions containing an equivalent normality of hydrochloric acid. The addition of hydrochloric acid caused an immediate rise in viscosity in accordance with previous findings.⁷

It is interesting to note that the small amount

(6) A general discussion of this test is presented by Jackson, "Organic Reactions," Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1944, p. 341.

(7) Marvel and Inskeep, *THIS JOURNAL*, **65**, 1710 (1943).