Selenium Tetracysteine

To an aqueous solution of 0.01 mole of cysteine hydrochloride an aqueous solution of 0.0025 mole of sodium selenite was added. On cooling, a white granular material separated. It was removed by filtration, washed with water, and recrystallized from hot water. The yield was 80–85% of the theoretical amount. Under the microscope, the crystals had the form of clusters of small rods. The substance began to darken at 164–165° and decomposed at 195–196°. The analysis of the substance indicated that it was apparently identical with selenium tetracysteine.

	C	H	N	Se	N:Se
Found	25.41	4.38	9.87	14.00	4:1
Calcd. for $Se(SC_3O_2NH_8)_4$	25.73	4.29	10.01	14.16	

Selenium tetracysteine is moderately soluble in cold water, readily soluble in hot water. It is soluble in dilute mineral acids, but decomposes on heating the acid solution to yield what appears to be elementary selenium (brick-red in color, characteristic odor, gives intense codeine test). It readily decomposes in cold dilute alkali yielding elementary selenium. An aqueous solution of selenium tetracysteine gives a negative test for free SH— with nitroprusside and ammonia. On treatment with sodium cyanide, the nitroprusside test becomes positive.

The ready reactivity of the selenite toward cysteine is analogous to that of arsenious acid toward cysteine to give arsenious tricysteine. The latter compound was prepared by Johnson and Voegtlin[1] using arsenious trichloride. We found in unpublished studies that arsenious acid also reacts with cysteine to give the tricysteine in 90% yields.

The cysteine derivatives of selenium and arsenic are of interest in connection with the selenium poisoning in animals, and the well-known inactivation of certain enzymes by arsenious acid and the selenite.

(1) J. M. Johnson and C. Voegtlin, *J. Biol. Chem.*, **89**, 27 (1930).

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COMMUNICATION TO THE EDITOR

SOME X-RAY DIFERACTION MEASUREMENTS ON BIOTIN

Sir:

About one milligram of free biotin, $C_{10}H_{16}O_3N_2S$, was made available to the writer through the courtesy of Dr. Vincent du Vigneaud, of the Cornell Medical School. Repeated micro-recrystallizations produced a few crystals large enough for single crystal X-ray studies.

Biotin crystallizes in long thin needles. Under the polarizing microscope, the extinction is straight, the fast vibration direction, α, being along the length. The needle cross-section is approximately a rhombus, the acute angle of which is about 55°. This value could not as usual be determined accurately by the use of optical reflections, as the prism faces were not perfect enough. The intermediate vibration direction, β, is the obtuse angle bisector, and γ the acute. Optically the crystal is negative. These data suggested that the crystal was orthorhombic, a choice confirmed by the subsequent X-ray work. The a, b and c axes were taken to coincide with the corresponding principal optic directions α, β and γ.

Oscillation films about all three crystallographic axes were made as well as "a" axis Weissenberg films of the equator, first and second layers. The only systematic absences found were the extinctions of the odd orders of the (h00), (0k0), and (00l) reflections. The space group is therefore $P2_12_12_1$. This space group has four general positions.

The lengths of the a, b and c axes were found to be 5.25, 10.35 and 21.0 Å., respectively. If the molecules are asymmetric and identical, then there would be four molecules per unit cell. The density of the crystals as measured by immersion in a mixture of carbon tetrachloride and methylene dichloride was 1.41. The X-ray molecular weight, computed from these data, is 245 ± 6. The molecular weight computed from the chemical formula is 244.

Some idea as to the possible character of the molecule may be obtained from the X-ray data without making a detailed analysis. The short "a" axis and the fact that it is parallel to the fast vibration direction, α, suggests a flattish molecule lying approximately in the bc plane. The width would be approximately in the "b" direction and the length in the "c" direction. The molecules will almost certainly deviate somewhat from be-

ing parallel with the crystallographic directions but nevertheless a molecule about 5 × 5.5 × 10.5 Å. in size is indicated.

The equatorial "*a*" axis Weissenberg shows an interesting pseudo-halving of the (0*kl*) reflections; *i. e.*, the (0*kl*) reflections for *k* odd are generally weak. A possible explanation can be given in terms of a pseudo-symmetry of the biotin molecule. A molecule which in projection is approximately symmetrical to a plane normal to the "*c*" axis could result in such an intensity distribution.

Another interesting systematic pseudo-halving exists which was not noticed until a Patterson synthesis of the (0*kl*) reflections was made. The two largest peaks (excluding of course the identity peak at 0,0) were found at $^1/_2$, 0 and $^1/_4$,$^1/_2$. The first of these peaks is merely the expression of the first mentioned pseudo-halving. The peak at $^1/_4$,$^1/_2$ can be traced to the second pseudo-halving; (0*kl*) reflections, where *k* is even and $k/2 + l$ is odd, were generally weak. This suggests that the flattish molecules are packed approximately side by side, neighbors being related to one another by a two-fold screw axis. In the direction of their lengths the packing would be imbricated. The one sulfur atom per molecule of biotin should be fairly near the central bisecting pseudo-plane of symmetry.

It should be emphasized that much of the foregoing note is highly speculative; indeed only the great interest in biotin could warrant its publication in its present form. The actual X-ray cell determinations are probably accurate to within about 1%. The picture of the molecular size and shape, however, is merely a reasonably plausible explanation of some of the X-ray and optic data. A more complete study of the X-ray data is now under way.

Much of the experimental work was done while the writer was National Research Fellow in Protein Chemistry at the Massachusetts Institute of Technology.

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NEW BOOKS

Anhydrous Aluminum Chloride in Organic Chemistry. By CHARLES ALLEN THOMAS, Central Research Director, Monsanto Chemical Company, in collaboration with MARY BALUK MOSHIER, HERBERT E. MORRIS and ROSS W. MOSHIER, Thomas and Hochwalt Laboratories, Monsanto Chemical Company. (A. C. S. Monograph Series.) Reinhold Publishing Corporation, 330 West 42nd St., New York, N. Y., 1941. xiii + 972 pp. 15.5 × 23.5 cm. Price, $15.00.

This is truly a monumental work, 878 pages of text, an author index of some 7000 names, a subject index of over 20,000 entries and a patent index with 594 U. S. patents and more from other countries.

The book opens with an historical sketch of Friedel and Crafts. This is followed by a chapter on the physical and chemical properties of aluminum chloride and its many combinations and one on the mechanisms of the reactions catalyzed by it. The manufacture, handling and storage of this material are also cared for. The main portion of the book, 656 pp., is a well-ordered, comprehensive and detailed presentation of the reactions of aromatics with alkyl halides, olefins, acyl halides, anhydrides and the like, with their numerous modifications. This is what every organic chemist knows, only a great deal more of it. Three chapters, 107 pages, are given to the new, tremendously important applications of aluminum chloride to aliphatic compounds. This section with its thousand references, largely patents, covers among other things the isomerization of hydrocarbons and the addition of olefins to paraffins to make high octane gasoline, the production of ethyl chloride from ethylene and hydrogen chloride, the polymerization of olefins to lubricants, high molecular weight, semi-solid products and resins and the cracking and refining of petroleum products.

The enormous amount of information is concisely yet clearly presented and should be of great service to organic chemists whether interested in pure chemistry or in its applications.

E. EMMET REID

A Treatise on Physical Chemistry. Third Edition—In Five Volumes. Volume One. **Atomistics and Thermodynamics.** Edited by HUGH S. TAYLOR, David B. Jones Professor of Chemistry, Princeton University, and SAMUEL GLASSTONE, Professor of Chemistry, The University of Oklahoma. D. Van Nostrand Company, Inc., 250 Fourth Avenue, New York, N. Y., 1942. vii + 679 pp. Illustrated. 15.5 × 23.5 cm. Net price, $7.50; $6.50 on order for set.

If Mr. Gallup were to poll the country's middle-aged physical chemists for the book that had the greatest in-