

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 ₂ O ₂ NH ₂) 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 test¹

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 Voegtlin¹ 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 We found in unpublished studies that arsenious acid also reacts with cysteine to give the tricysteine in 90% yields.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 DIFFRACTION MEASUREMENTS ON BIOTIN

Sir:

About one milligram of free biotin, C₁₀H₁₆O₃N₂S, 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 P2₁2₁2₁. 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-