tively. Val-Val bonds are extremely resistant to hydrolysis and low yields would be anticipated after hydrolysis in 6 N HCl at 108° for only 18 h. Their results with carboxypeptidase A digestion of Pa-5 do not really distinguish between a Val-Val-Ala and a Val-Ala-Val sequence. In any event, our finding of a tripeptide N-1 (Table 2) which has the sequence Val-Ala-Asp would appear to be conclusive.

Several structural features of the leghemoglobin-1 sequences are common to those of animal hemoglobins. In particular, Leu and His (residues 88 and 92 in the human β chain) appear invariant. This leucine makes an important contact with the heme and His 92 is linked to the iron atom. Comparison of the sequences in terms of base changes is given in Table 2. Leghemoglobin-1 may be homologous with animal hemoglobins; both may have arisen from a common ancestor. The sequences also suggest that the heme in leghemoglobin may be partially buried in a hydrophobic pocket as it is in animal hemoglobins.

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1. Ellfolk, N. and Sievers, G. *Acta Chem. Scand.* **23** (1969) 2994.
2. Koch, B., Evans, H. J. and Russell, S. *Plant Physiol.* **13** (1967) 466.
3. Anson, M. L. and Mirsky, A. E. *J. Gen. Physiol.* **13** (1930) 469.
4. Gray, W. R. In Colowick, S. P. and Kaplan, N. O. *Methods in Enzymology*, Academic, New York 1967, Vol. 11, p. 469.
5. Whitfield, R. E. *Science* **142** (1963) 577.
6. Braunitzer, G., Gehring-Müller, R., Hilschmann, N., Hilse, K., Hobom, G., Rudolff, V. and Wittman-Liebold, B. *Z. Physiol. Chem.* **325** (1961) 283.
7. Fitch, W. M. and Margoliash, E. *Science* **155** (1967) 279.
8. Braunitzer, G. and Fujiki, H. *Naturwiss.* **56** (1969) 322.

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Djurleite Synthesis in Low Temperature Aqueous Solution

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A synthetic phase, corresponding to the mineral djurleite,[1,2] $Cu_{1.97}S$, has been identified as the major product of the reaction between cuprous oxide and aqueous sodium sulphide solution at 25°C and 1 atm pressure.

100 mg analytical grade Cu_2O, suspended in 10 ml oxygen-free deionized water, was placed in a 500 ml Kilner jar. 23.4 ml analytical grade Na_2S solution (100 g/l) was made up to 300 ml with O_2-free deionized water and 10 % analytical grade HCl to the required pH. The poised sulphide solutions were added to the Cu_2O suspension, and the Kilner jar sealed under nitrogen. 10 runs with Na_2S solutions of pH = 6.81 to 8.91 (E_h = −129 to −192 mV) were made.

The precipitates were aged for 14 days at 25°C with intermittent agitation. The pH and E_h of the solutions were measured. The pH values found varied from 7.03 to 10.71 (E_h = −185 to −247 mV). Samples of the precipitates were sealed in 0.3 mm bore Lindemann glass capillaries and analysed, wet, by X-ray powder diffraction analysis in an 11 cm Debye-Scherrer camera with Cu$K\alpha$ radiation. The remainder of the products were filtered through sintered glass filters, washed in O_2-free deionized water and alcohol, and dried at room temperature in a vacuum desiccator. X-Ray powder diffraction photographs were obtained from a Guinier focussing camera with Cu$K\alpha_1$ radiation and a KCl internal standard.

X-Ray data for the products of run C201 are shown in Table 1. In this run the pH of the sodium sulphide solution was 7.96 (E_h = −136) and the final pH of the reaction mixture 10.30 (E_h = −162). The products were identified as major djurleite admixed with minor covellite. The djurleite reflections were extracted and indexed by desk calculation according to an orthorhombic cell [3] with cell dimensions of a = 26.9, b = 15.5, c = 13.3 Å. Further mathematical refinements were not attempted with these data because the reflections were too diffuse to give greater

Table 1. X-Ray powder data for specimen C201 (djurleite and covellite).

Debye-Scherrer camera[a]		Guinier camera[b]		Djurleite	
d Å	I_{obs}[c]	d Å[d]	I_{obs}[c]	d Å$_{calc.}$[e]	hkl[f]
4.210	w			4.237	331
3.583	w	3.603	w	3.612	612
3.363	m	3.357	w	3.358	800
				3.353	440
3.084	vw			3.057	314
2.998	w	2.998	w	2.998	802
				2.997	151
				2.994	442
2.866	m	2.863	m	2.863	911
				2.857	351
2.747	vw	2.753	vw		
2.629	m	2.623	m	2.614	551
2.529	w	2.532	w	2.534	260
				2.532	061
				2.530	025
				2.527	153
2.458	vw	2.451	vw	2.460	10, 1, 2
2.368	vs	2.374	vs	2.374	11, 1, 1
				2.370	842
2.298	vw				
2.238	vw			2.230	063
2.176	vw				
				(164)	
2.118	vw				
1.935	vs	1.937	vs	1.934	080
				1.924	046
1.897vt	m	1.914 vt[g]	w		
		1.894			
1.859	vs	1.857	vs	1.861	12, 4, 2
				1.857	12, 0, 4
1.791	vw				
1.759	vw				
		1.738	w		
1.679	w				
1.626	w	1.625	w		
		1.537	w		
		1.497	w		

[a] 11 cm Debye-Scherrer camera, Cu$K\alpha$ radiation, wet precipitate in 0.3 mm Lindemann glass capillary. [b] Guinier fine focussing camera, Cu$K\alpha_1$ radiation, vacuum-dried precipitate with KCl internal standard. [c] Estimated relative intensity, decreasing according to the order vs, s, ms, m, w, vw. [d] Corrected values: $a_{KCl}=6.29194\pm9$ Å at 20°C. [e] Calculated for orthorhombic cell, $a=26.9$, $b=15.5$, $c=13.3$ Å. Covellite reflections not considered. [f] Only hkl values coincident with observed single crystal data (Takeda *et al.*[3]) included apart from 612 and 10, 1, 2 reflections. (164) indicates 164 possible reflections in this area, not observed on single crystal analysis. [g] Extremely thick (covellite) reflection, d values are for limits of broad band.

real accuracy with these large cell dimensions.

The cell dimensions are similar to those previously published for djurleite:[3] $a=26.90$, $b=15.72$, $c=13.57$ Å. Djurleite was identified as the major product of 6 runs (final pH = 7.65 to 10.71, $E_h=-190$ to -491) and tentatively identified as a

minor product in 2 further runs (final pH = 7.03 and 7.43, $E_h = -186$ and -193). In all cases djurleite was admixed with either covellite or chalcocite. In the 6 runs where djurleite was a major product, it was consistently indexable on the orthorhombic cell with $a = 26.9$, $b = 15.5$, $c = 13.3$ Å.

The X-ray powder data obtained were similar to those shown in Table 1 for C201. No consistent evidence was found for any change in the nature of the product on drying. The Guinier films showed generally weaker and broader reflections than the 11 cm films, and reflections absent from the Guinier films were generally very weak on the 11 cm film. A very broad band about 4 Å on the Guinier films was caused by the tape in sample holder, and masked possible reflections in this region. Inconsistencies in relative intensities between the films are possibly caused by some degree of sample orientation in the Guinier camera.

The very strong 046 reflection [3] ($d = 1.924$ Å) was not observed as a discrete line on any film. It is thought that the $d = 1.935$ (C201) line, which is relatively broad on all films, includes both the 080 and 046 reflections. That this line was the strongest discrete djurleite line on all films, is consistent with this interpretation.

The chemical implications of the results will be discussed in detail in a further paper.[4] However, the identification of djurleite, rather than chalcocite, as the primary product of the aqueous reaction between Cu_2O and Na_2S is consistent with observed data on natural minerals [2,5] which indicate that djurleite is rather more abundant than chalcocite, especially in the supergene enrichment zones of copper ore deposits. The reason for the formation of djurleite, in place of the apparently more reduced chalcocite is unknown. It seems to have a relatively stable structure with, possibly, little deviation from the $Cu_{1.97}S$ formula. The admixture of covellite or chalcocite with the synthetic material may indicate that Cu^{2+} or Cu^{+} ions, present in excess of that required for the $Cu_{1.97}S$ formula, are rigorously excluded from the structure, and form the end-member phases.

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1. Morimoto, N. *Mineral J. Tokyo* **3** (1962) 338.
2. Roseboom, E. H. *Am. Mineralogist* **47** (1962) 1181.
3. Takeda H., Donnay, J. D. H., Roseboom, E. H. and Appleman, D. E. *Z. Krist.* **125** (1967) 404.
4. *In preparation.*
5. Sillitoe, R. H. *Unpublished Ph. D. Thesis*, London University 1969.

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The Molecular and Crystal Structure of Dehydroascorbic Acid

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The molecular structure of the biologically important dehydroascorbic acid with the empirical formula $C_6H_6O_6$ has been disputed for some time. Several structural formulae have been proposed, including monomers, dimers [1-3] and polymers.[4]

We have studied crystals grown from dimethyl sulfoxide and from a mixture of 5 % 0.2 N hydrochloric acid in glacial acetic acid as recommended by Staudinger and Weis.[5]

The soft crystals grown from dimethyl sulfoxide give an X-ray pattern typical of a polymer.

The commercially available dehydroascorbic acid is, however, crystalline, and gives very small, but well developed crystals when recrystallized from the mixture mentioned above.

We wish to give a preliminary report on the structural analysis of crystalline dehydroascorbic acid. It crystallizes in the monoclinic system with the space group