ing density along a spike in reciprocal space, $\mathfrak{D}$, depends on the structure amplitude of the relp F_{hkl} and the distance from the relp, R, according to the expression,

$$\mathfrak{D} \sim |F_{hkl}|^2 R^{-n}$$

where $n = 2{\cdot}2 \pm 0{\cdot}1$. The same value of n was obtained for all the spikes of all the relps investigated, namely, 111, 220, 311, and 331. The results concerning the occurrence and relative intensities of the spikes are contained in the following Table.

Indices of relp	Zone indices of spike			X-radiation used
	[100]	[010]	[001]	
111	87	87	87	Cu Kα
220	76	76	absent	Cu Kα
113	100	100	absent	Cu Kα
222	~75	~75	~75	Cu Kα
004	< 5	< 5	~30	Cu Kα monochr.
331	7	7	104	Cu Kα
224	72	72	30	Cu Kβ
115	present	present	absent	Mo Kα monochr.
333	absent	absent	absent	Mo Kα monochr.

The numbers given in the Table were obtained by dividing $\mathfrak{D}$ at unit distance from the corresponding relp by the $|F_{hkl}|^2$ values given by BRILL *et al.*[1] The photographs were taken so that there appeared on the same film the spikes associated with different relps. In this way a comparison between the intensities of the spikes could readily be made. The spikes obtained only with Mo Kα radiation were too weak to express numerically. The accuracy of the Figures is about 10%.

It will be seen from the Table that a simple relation exists between the indices of the relps and $\mathfrak{D}/|F_{hkl}|^2$. Thus when h has a given value, no matter what the values of k and l may be, the value of $\mathfrak{D}/|F_{hkl}|^2$ for the spike [100] is the same. For instance, when h has the values 0, 1, 2, 3, and 4, these values are $<$ 5, 100, 74, 5, and 30 respectively. The only significant departure from this statement occurs for the relp 111, but this may not be a true exception because the value of F_{111} given by BRILL *et al.* is possibly too high. The symmetry of the crystal requires that similar statements can be made about the relations between indices h, l and the spikes parallel to [010] and [001].

The absolute measurements can only relate to a particular crystal since the spikes occur with varying strengths in different crystals. The crystal used in this work was nearly spherical, of diameter about 0·5 mm and showed strong spikes. The absolute measurement was made by comparing the spike with the thermal diffuse spot. Taking the known values for the elastic constants of diamond it is possible to calculate from the usual formulae the absolute intensity of the thermal diffuse scattering for any given line passing through any relp. A comparison of the spike with the diffuse spot then puts the spike intensity on an absolute scale. The diffuse beam corresponding to the spike parallel to [100] passing through the relp 113 was studied. At a distance of $a^*/10$ from the relp the ratio of the diffuse and incident beams was 7×10^{-7}.

The above information expresses in quantitative form what previous authors have largely given in qualitative form. The relation between the value of the index h and the intensity of the corresponding spike determines certain features of a stratification parallel to the cube faces. The inverse square law which we have found to be approximately valid would be expected to hold if this stratification is subject to random variations. Further work is in progress on the interpretation of these results.

One of us (J. HOERNI) acknowledges the award of a scholarship by the Swiss Commission for Post-doctoral Studies in Mathematics and Physics. We gratefully acknowledge the loan of a number of diamonds by Dr. H. GRENVILLE WELLS and by Mr. P. GRODZINSKI.

J. HOERNI and W. A. WOOSTER

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, April 24, 1952.

Résumé

La diffraction des rayons X par certains diamants présente des réflexions anormales que nous avons étudiées quantitativement. Elles correspondent, dans l'espace réciproque, à l'intersection de la sphère d'EWALD par des zones de diffusion passant par les points du réseau réciproque du cristal, et sont dirigées selon les axes quaternaires. Les résultats obtenus fournissent une relation simple entre les intensités des diverses zones de réflexion diffuse.

[1] R. BRILL, H. G. GRIMM, C. HERMANN, and C. PETERS, Ann. Phys., Leipzig *34*, No. 5, 393 (1939).

Zur Kenntnis des Isonikotinsäurehydrazid-Cu-Komplexes

Metallionen und biologische Wirkung, 9. Mitteilung [1]

Das für die Chemotherapie wichtig gewordene Isonikotinsäurehydrazid bildet, wie bereits berichtet wurde[2], mit $Cu^{\cdot\cdot}$ einen Komplex, der in Gegenwart von SO_4'' als schwerlösliches Salz isoliert werden kann. Da, wie wir fanden, die Wirkung des Isonikotinsäurehydrazids auf Tbc-Kulturen im Kirchner-Milieu durch Zusatz von $Cu^{\cdot\cdot}$ bis auf das zehnfache gesteigert werden kann, und andererseits die Verhältnisse im isolierbaren Festkörper nicht für die Deutung der in der Lösung vorhandenen Komplexe verwertbar sind, war es von Interesse, die Reaktion zwischen Isonikotinsäurehydrazid und $Cu^{\cdot\cdot}$ in verdünnter wässriger Lösung näher zu charakterisieren.

Wir haben durch spektrophotometrische Absorptionsmessungen bei 760μ von Isonikotinsäurehydrazid-$CuSO_4$-Mischlösungen die Komplexbildung untersucht. Bei Variation des Konzentrationsverhältnisses, so dass

$$[Cu^{\cdot\cdot}] + [R\mathrm{H}] = 0{,}01 = \text{const},$$

zeigte es sich, dass ein Komplex gebildet wird, in dem 2 Mol Isonikotinsäurehydrazid auf 1 Mol $Cu^{\cdot\cdot}$ enthalten sind.

Die Frage, ob es sich hier um einen einfachen Ion-Dipolkomplex handelt oder ob Isonikotinsäurehydrazid in der tautomeren Form als Pseudosäure reagiert:

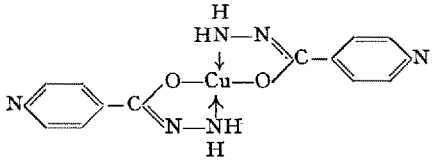
$$2\ R\mathrm{H} + Cu^{\cdot\cdot} = R_2Cu + 2\mathrm{H}^{\cdot}$$

konnte durch Ermittlung der die Reaktion begleitenden Änderung der $[\mathrm{H}^{\cdot}]$ entschieden werden. Die Messungen zeigen, dass $\mathrm{H}^{\cdot}$-Ionen frei werden, so dass ein Komplex von der Formel (I) in der Lösung anzunehmen ist.

[1] 8. Mitteilung: V. KOCHER und E. SORKIN, Helv. chim. acta *35*, Fasc. 5 (1952).

[2] E. SORKIN, H. ROTH und H. ERLENMEYER, Helv. chim. acta *35*, Fasc. 5 (1952).

Aus den Versuchen, die zur Ermittlung der Beständigkeitskonstanten dieses Komplexes bei pH 4 durchgeführt wurden, geht hervor, dass die Beständigkeit in der Grössenordnung der Beständigkeit des Oxin-Cu-Komplexes[1] entspricht.



(I)

Ausführliche Angaben über Messungen und Berechnungen erfolgen in einer späteren Mitteilung in den Helv. chim. Acta.

S. FALLAB und H. ERLENMEYER

Anstalt für anorganische Chemie der Universität Basel, 29. Juni 1952.

Summary

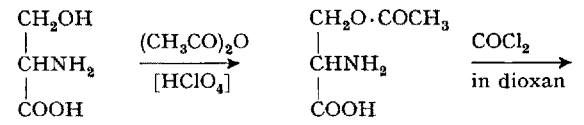
The complex formation between Isonicotinic acid hydrazide and Cu^{++} in aqueous solution has been investigated by a spectrophotometric method.

[1] S. D. RUBBO, A. ALBERT und M. I. GIBSON, Brit. J. exp. Path. *31*, 425 (1950).

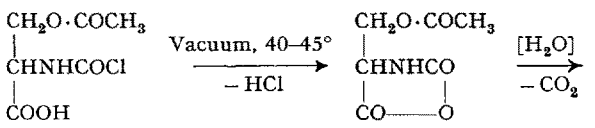
Synthesis of Poly-O-acetylserine and of Polyserine

In a previous publication we have reported on the preparation of the N-carboxy anhydrides of O-acetylserine and of O-carbobenzoxyserine[1], starting from O-acetyl-N-carbobenzyloxyserine, and from O,N-dicarbobenzyloxyserine respectively. With the aid of these compounds, polyacetylserine and polyserine are in principle accessible, but the fact that the polymerisation products obtained were of comparatively short chain length, and the interference of certain preparative difficulties, made it desirable to work out a different route for the synthesis of polyacetylserine and of polyserine.

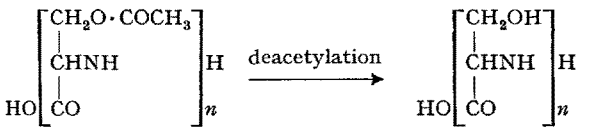
The following scheme represents the steps involved in it:



(I) D,L-Serine (II) O-acetylserine



(III) O-acetyl-N-chloroformylserine (IV) O-acetyl-N-carboxyserine anhydride



(V) Poly-O-acetylserine (VI) Polyserine

[1] M. FRANKEL and M. HALMAN, J. Chem. Soc., London (in press).

The differential acetylation of the hydroxyl group of D,L-serine, leading to O-acetylserine, is possible according to the technique of SAKAMI and TOENNIES[1] under the influence of perchloric acid, making use of the fact that in acetylation with acetic acid anhydride in glacial acetic acid, the acetylation of α-amino groups is increasingly suppressed, while that of the hydroxyl group is promoted catalytically with increasing concentration of perchloric acid.

On suspending the finely powdered O-acetylserine (II) in dry dioxan and passing gaseous phosgene with stirring through the suspension at a temperature of 35–40°, the acetylserine dissolved within about two hours. Removal of excess phosgene and of solvent in vacuo and subsequent heating in vacuo at 40 to 45°, leads directly to O-acetyl-N-carboxyserine anhydride (IV), through loss of hydrogen chloride from the intermediate O-acetyl-N-chloroformylserine (III). A similar procedure has been used by several authors for the preparation of other N-carboxy anhydrides of α-amino acids ("Leuchs" anhydrides[2]). The polymerization was carried out either by heating near the decomposition point of (IV) in high vacuum, or in indifferent solvents (pyridine, dioxan, nitrobenzene), mostly with the addition of initiators. Water, sodium hydroxide or glycine dimethyl amide were used as such.

The poly-O-acetylserine (V) thus obtained was soluble in hot glacial acetic acid and was precipitated from this solution by dry ether. Biuret and ninhydrin reactions were positive. According to analyses the average chain length was about fifty units. In order to obtain polyserine (VI) from polyacetylserine, experiments on deacetylation were carried out, using either lithium hydroxide, barium hydroxide or ammonia as saponification agents. Some difficulties were encountered in obtaining complete deacetylation without splitting the polymer peptide chain.

The polyserine preparations eventually obtained, on evaporating their aqueous solutions in vacuo, constituted hard films; polyserine is hygroscopic, easily soluble in water and gives both biuret and ninhydrin reactions. The average chain length was found by analyses to correspond to the parent acetyl derivatives.

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Department of Organic Chemistry, The Hebrew University, Jerusalem, Israel, April 12, 1952.

Zusammenfassung

Eine befriedigende Methode für die Synthese von Polyazetylserin und von Polyserin geht von O-Azetylserin (II) aus, das aus D,L-Serin durch selektive Azetylierung mittels Essigsäureanhydrid in Eisessig unter katalytischer Mitwirkung von Perchlorsäure erhältlich ist[3]. (II) wird in Dioxansuspension durch Phosgen in O-Azetyl-N-chloroformylserin (III) übergeführt, das im Vakuum bei 40 bis 45° Chlorwasserstoff abspaltet und in O-Azetyl-N-carboxyserinanhydrid (IV) übergeht. Polymerisation von (IV), in der Hitze im Hochvakuum oder in inerten Lösungsmitteln unter Zusatz von Initiatoren, liefert Poly-O-azetylserin (V). Die durchschnittliche Ketten-

[1] W. SAKAMI and G. TOENNIES, J. Biol. Chem. *144*, 203 (1942).

[2] F. FUCHS, Ber. Dtsch. chem. Ges. *55*, 2943 (1922). – A. L. LEVY, Nature *165*, 152 (1950). – A. C. FARTHING and R. J. W. REYNOLDS, Nature *165*, 647 (1950) (cf. Patentliterature cited there). – A. C. FARTHING, J. Chem. Soc. 3213 (1950).

[3] W. SAKAMI and G. TOENNIES, J. Biol. Chem. *144*, 203 (1942). FARTHING, J. Chem. Soc. 3213 (1950).