

Chemistry. — “*On relatively asymmetrical synthesis in the case of Complex Salts of heavy Metals.*” By Dr. J. LIFSCHITZ. (Communicated by Prof. F. M. JAEGER).

(Communicated at the meeting of September 27, 1924).

On boiling an aqueous solution of rac. Alanine with cobalt-hydroxyde LEY and WINKLER ¹⁾ obtained two complex cobaltic salts of alanine, the first of which, the red coloured β -form, appeared to be nearly insoluble in water, whilst the second or α -form, having a violet red colour, was moderately soluble in water even at 25°. According to LEY and WINKLER these complex salts are stereoisomerides, differing only in the arrangement of the three coordinated molecules of alanine. No other products of reaction were obtained, the yield of the reaction-product being a fairly good one. In a later paper LEY ²⁾ however mentions another hydrate of the violet cobaltic salt of alanine, which was obtained incidentally. The existence of such hydrates is, of course, without any direct importance for the views advanced by this author.

The properties of both complex salts are, in so far as they were investigated, in perfect harmony with LEY's views, and, up to this date, no objections have been brought forward against the stereoisomerism of these cobaltic salts. Moreover A. WERNER ³⁾ has shown, that an isomerism of a perfectly analogous character is observed in the case of the *flavo-dinitro-ethylenediamine-propylenediamine-cobaltic salts*.

In connection with my investigations ⁴⁾ on rotatory dispersion of coloured active compounds, it seemed interesting to compare firstly active triacido-triammine-cobalti-complexes with the hexammine and hexacido salts, and secondly to study the stereoisomerides of the *Trialanine-cobaltic*-type. As the main difference of these latter only consists in a relatively small variation of the symmetry of the molecule as a whole, it might be expected, that some conclusions about the influence of molecular symmetry on the rotation of such complexes could be drawn. Pure d-Alanine was prepared in relatively

¹⁾ Ber. **42**, 3894 (1909).

²⁾ Ber. **45**, 372 (1912).

³⁾ Helv. **1**, 5 (1918).

⁴⁾ Zeitschr. f. wissenschaft. Photogr. **19**, 212 (1920).

Zeitschr. f. physikal. Chem. **105**, 27 (1923).

large amounts from silk-waste, following E. FISCHER's method ¹⁾. The obtained dextrogyrate product was carefully fractionated and a fraction, showing the same rotation as indicated by this author for pure d-Alanine, was boiled with cobaltic-hydroxyde according to the method of LÉY. The hydroxyde was precipitated from pure aqueous

*Specific Rotation
in Grades.*

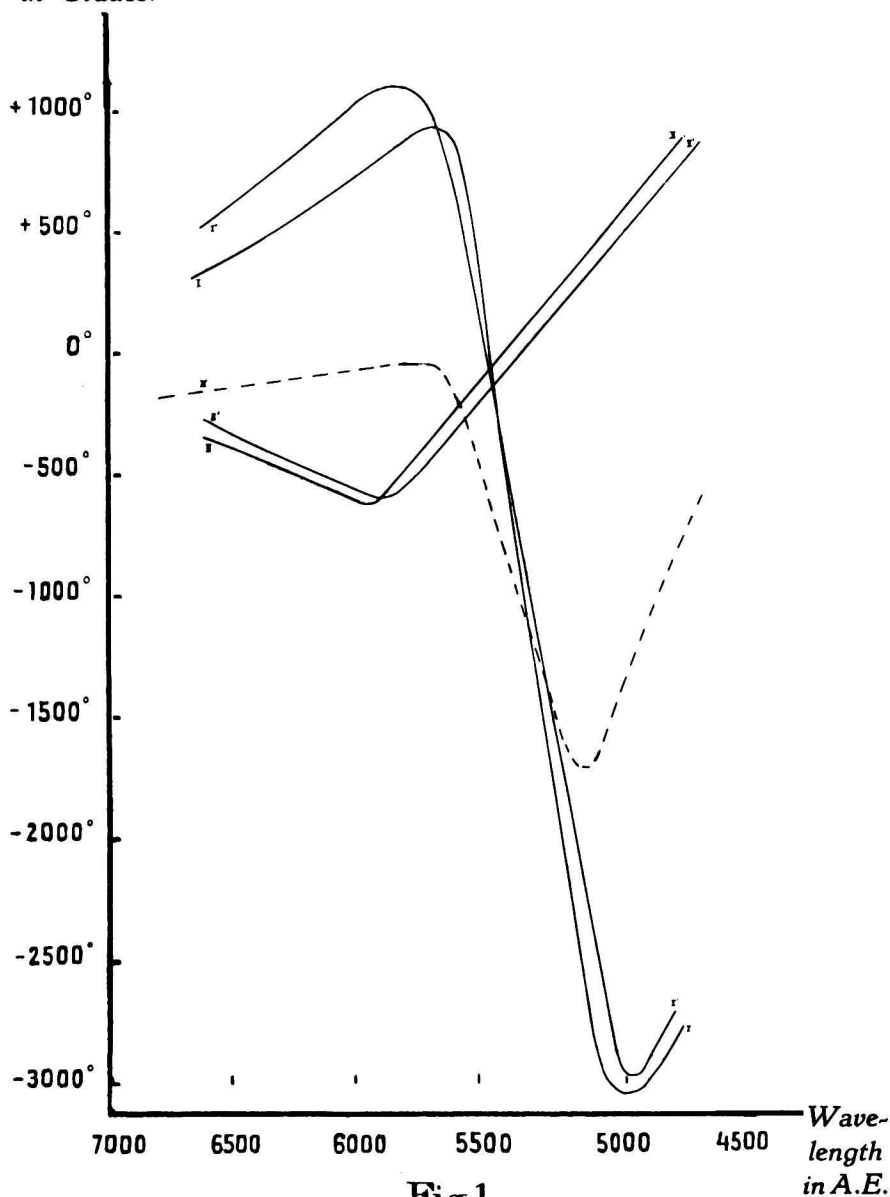


Fig.1

¹⁾ Ber. 39, 462.

cobaltochloride or -sulphate by an alkali-solution of bromine, the precipitate was filtered and thoroughly washed with hot water.

The red coloured isomeride of the *tri-d-alanine-cobaltic* salt obtained is perfectly insoluble in water. It is freed from cobaltic-oxyde and obtained in a pure state by repeatedly suspending it in aqueous solutions of sulphurous acid. A fairly good quantity was obtained by repeating this procedure. The substance readily dissolves, like the inactive compound, in 50 % H_2SO_4 aq. without any change; the rotation of this solution is shown by the curve III of fig. 1.

The mother-liquors from the (crude) red *tri-d-alanine-cobaltic* salt are deep violet in colour. On fractional crystallization, first a violet salt was obtained, which in all points corresponded to the violet inactive isomeride of LEY. It was carefully recrystallized from boiling water, and beautiful small needles were obtained, containing 1 molecule of water. The rotations of this α -salt in aqueous and 50 % H_2SO_4 aq. solutions, are shown by the curves I and I' of fig. 1.

The mother-liquors of the α -salt contain, besides further quantities of this, a second, extremely soluble and more purple coloured salt, α' , which can be isolated with some difficulty. It is firstly freed from greater quantities of the α' -salt by fractional crystallization, and finally freed from the last traces of this and of d-Alanine, by repeated precipitation from a fairly concentrated solution by 97 % alcohol. A great deal of α' -compound remains in the aqueous-alcoholic liquid, from which it is isolated by evaporation; it was washed with 97 % alcohol, and purified, until no alteration of the rotation is any more observed. The rotation of the somewhat hygroscopic salt is shown by the curves II and II' in water and 50 % H_2SO_4 aq. respectively.

In order to establish the constitution of the α' -salt, both the α - and the α' -complexes were analysed, and the following data obtained:

Theoretical for	(Co-d-alanine ₂)	Co-d-alanine ₂). H_2O
Co	18,27 %	17,30 %
N	13,00 %	12,32 %
H_2O		5,28 %
Observed: α -salt: 17,73 % Co; 12,04 % N; 12,09 % N; 5,34 % H_2O .		
,, α' -salt: 18,66 % Co; 12,64 % N; 12,67 %; for dried salt		
(constant at 145°—150°).		

From these data, of which the estimation of nitrogen is especially a very delicate test in this case, it is seen, that both salts are trialanine-complexes, differing only in degree of hydration. Cryo-

scopic measurements of the molecular weight of the α' -salt, which is in fact the only new, as it were anomalous product gave values, which are in accordance with mononuclear constitution, viz. theoretical value for (Co-d-alanine₂) 323; observed: 295, 293, 291.

In addition it may be pointed out, that the colours of the α - and α' -salts, as well as their stability with respect to sulphuric acid, would neither for the α -, nor for the α' -complex justify the assumption of bi- or polynuclear structures e. g. of the type:



or some analogous formulae.

It may be observed, that α' is not changed into α -salt by drying, corresponding to an equation:



It must, therefore, be concluded that the α and α' -compounds are no other than the partially asymmetrical antipodes: d-[Co-d-Alan₂] and l-[Co-d-Alan₂], a relatively asymmetrical synthesis of such inorganic complexes thus being realized in this case. We shall in this paper only make some short remarks to support this view.

As long ago as 1920¹⁾ the author has pointed out, that when an inorganic complex is synthesized from a coloured inactive metal-salt and a colourless active molecule as the coordinated component, a relatively asymmetrical synthesis may be expected. Indirectly in that and a following paper²⁾ this view was proved by measurements of the rotatory dispersion. The same conclusion was drawn independently by A. P. SMIRNOFF³⁾. A direct proof could only be offered by the isolation of the two partially asymmetrical antipodes, though, of course, it is not necessary, that both should be formed to an appreciable amount. When a compound $d\text{---}A$ reacts with, say $d\text{---}B$, a priori the compounds $d\text{---}A\text{---}d\text{---}B$ and $l\text{---}A\text{---}d\text{---}B$ may be expected, the ratio of $d\text{---}A\text{---}d\text{---}B/l\text{---}A\text{---}d\text{---}B$ depending firstly on the velocity of the reactions and secondly on the possibility of inversion of $d\text{---}A$ into $l\text{---}A$, and vice versa. Active compounds, which for some reasons, exhibit a strong tendency to racemisation, and therefore to inversion, may, solely for this reason, react to give exclusively $d\text{---}A\text{---}d\text{---}B$, or $l\text{---}A\text{---}d\text{---}B$. With organic compounds these phenomena are perhaps more familiar. It is, therefore, only a matter of pure chance, to find reactions leading to both

¹⁾ Zeitschr. f. wiss. Photogr. I.c.

²⁾ Zeitschr. f. physikal. Chem. 105, 27 (1923).

³⁾ Helv. 3, 177 (1920).

$d-A-d-B$ and $l-A-d-B$ at the same time. In the case of our complex salts, the very great stability of the trialanine-cobaltic salts may be the cause for this way of the reaction. But even under these favourable conditions, the isolation of both the partially asymmetrical antipodes would remain impossible if they were both perfectly or practically insoluble in the solvent used. Now this must be the case with the β -cobaltitrialanine, which has been obtained in one form only. The correctness of this view can directly be recognized from the curves on fig. 1.

In the first place it will be seen, that the rotation curves of the α - and β - d -trialanine-cobaltic salts are of so different a type, as by no means could be expected in the case of purely geometrical stereoisomerides. As the absorption-curves of both isomerides, though by no means identical, are commonly very much analogous, it might be expected, that the rotation-curves would be different only or chiefly in a quantitative way. Moreover, the β -curve is clearly the superposition of two curves of the type discovered by COTTON. If one of these two is supposed to be really analogous to the α -curve, then it might be expected that the second curve should exhibit a relatively strong laevo-rotation in the red and a relatively small dextro-rotation in the blue part of the spectrum. That is to say, this curve would be of precisely the same type as the α' -curve, which is in remarkable accordance with our views.

With respect to the α - and α' -salts, it must be borne in mind, that also two racemic α -trialanine-cobaltic salts must exist, viz. d -alanine- d -cobaltic + l -alanine- l -cobaltic salt, and d -alanine- l -cobaltic + l -alanine- d -cobaltic salt, one of these being probably much more soluble in water than the other. Perhaps LEY succeeded to isolate both of them in the form of his different hydrates, without understanding the reason of their occurrence. At any case, it is worth while, to investigate the rac. complex salts of alanine with cobalt, from the view point mentioned above.

Summarizing, the results communicated in this paper seem to indicate a direct proof of a relatively asymmetrical synthesis of complex cobaltic salts, occurring if they are prepared from an inactive metal-salt and active coordinating molecules. Full discussion of the curves of rotatory dispersion, as well of the importance of the possibility of getting active complex salts, will be given in a separate paper on rotatory dispersion.

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