Chemistry. — *On geometric isomerism in Luteo-Cobaltic-salts.* By I. LIFSCHITZ and K. M. DIJKEMA. (Communicated by Prof. F. M. JAEGER.)

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§ 1. According to the classical co-ordination theory, it might be expected, that complex compounds of trivalent metals, such as, for instance: **I.** $[Met.^{III}A_3]$; **II.** $[Met.A\text{-}B\text{-}X_2]$; **III.** $[Met.A_2X_2]$, etc., in which A and B are co-ordinatively-bivalent asymmetrical substituents, X being a co-ordinatively-monovalent substituent, — wil occur in geometrically isomeric forms. *Luteo*-salts I, for instance, of the ion: $[Met.^{III}(pn)_3]^{\cdots}$ and *triacidotriammino*-salts *I*, for instance: $[Met.^{III}(glyc)_3]$, would be obtainable in *two*, some *diacidotetrammino*-salts *III*, for instance, of the ion: *flavo*-$[Met.^{III}(pn)_2\ (NO_2)_2]^{\cdot}$, even in *three* isomeric forms. Experimentally such isomerism has been observed only in cobaltic compounds and even there only in a few cases. In the first place geometrically isomeric forms were found in complex cobaltic compounds with 3 mol. α-amino-acid [1]. A. WERNER could prepare the isomeric forms of *flavo*-$[Co\ (en)\ (pn)\ (NO_2)]_2X$. [2]. But even *flavo*-$[Co\ (pn)_2(NO_2)_2]X$, of which three isomerides might theoretically be expected, appears only to occur in *one* single form [3].

The reasons why the geometric isomerism predicted by WERNER is so rarely observed, will not be discussed here. In the first place it must experimentally be investigated, whether a greater number of geometrically isomeric salts *can* be obtained.

Apart from this, however, the preparation of such isomerides in an optically-active form would be of interest with respect to the study of rotatory power and rotatory dispersion in general.

Since geometrically isomeric substances differ almost exclusively with respect to the *degree of symmetry* of their molecules, an investigation of

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[1]) C.f. I. LIFSCHITZ, Proc. Kon. Akad. v. Wetensch., Amsterdam **27**, 721 (1924); **39**, 1192 (1936); **42**, 173 (1939).

[2]) A. WERNER, Helv. Acta I, 5 (1918).

[3]) The statements of MIKLOSICH, who thought that he had isolated the 3 forms expected, are incorrect. MIKLOSICH in his experiments started from *commercial* propylenediamine, which nearly always contains ethylenediamine, as was proved by the experiments of one of us (LI). As a matter of fact., H. E. WATTS (Diss. Zürich 1912) and H. HÜRLIMANN (Diss. Zürich 1918) failed to obtain such isomerides in using *pure* propylenediamine.

their rotatory power may yield important data concerning the influence of differences in symmetry on rotatory power [1]).

§ 2. In an investigation of the complex-formation of *phenylated ethylenediamines,* it was found that the *luteo*-cobaltic-salts of *monophenyl-ethylenediamine* can rather easily be obtained in geometrically isomeric forms. This is the first case of geometric isomerism in the *luteo*-series having been demonstrated and of the polarimetric investigation of such isomers having become possible.

Phenyl-ethylenediamine: $C_6H_5CH(NH_2)—CH_2(NH_2)$ (*phenen*) was obtained in the racemic and in the optically-active forms by catalytic hydrogenation of *α-acetaminophenyl-acetic-acid-nitril*:

$$C_6H_5CH\,.\,(NHCOCH_3)\,.\,CN$$

according to H. REIHLEN's method [2]). In preparing the *luteo*-salts, the following prescription may be followed as well in the case of the racemic as of the optically-active bases.

20,4 g. phenyl-ethylenediamine and 4,2 cc HCl (s.g. 1.19) are added to a solution of 11.9 g $CoCl_2\,.\,6H_2O$ in 350—400 cc methylalcohol and a current of air is blown through it by means of a gasdispersion-tube. Very soon a yellow salt crystallizes, whilst the solution becomes dark brown. After ca. 20 hours the solid salt (L_1) is sucked off, boiled three times with methyl-alcohol (each time with ca. 100 cc.) and, after complete cooling, sucked off.

The salt thus obtained is then fractionated by crystallisation from water, whilst some cc. of HCl (1,4) are added to the filtered and slightly cooled solution [3]).

Besides some luteo-salt L_1 the deep-brown methyl-alcoholic mother liquor of L_1 contains a deep-brown, occasionally somewhat greyish-coloured salt, which, after evaporation, is left as a syrupy substance, which on cooling solidifies into a crystalline mass. It probably consists of a polynuclear salt, which, however, even by re-crystallization from water [4]), could not be obtained in a pure state.

When this salt is dissolved in hot water, to which some cc hydrochloric acid (1 : 4) are added, and the solution is filtered and cooled, the colour changes to a yellowish-brown and a yellowish-brown salt (L_2) crystallizes from it; the latter can be purified by fractionated crystallisation from very dilute *HCl* in the way previously described.

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[1]) I. LIFSCHITZ, Rec. Trav. Chim. Pays-Bas **58**, 785 (1939); more extensive literature is given there.

[2]) H. REIHLEN, Ann. **493**, 20 (1932); **494**, 157 (1932).

[3]) L_1 is considerably less soluble in dilute HCl than in pure water; moreover, in this way a brown colouring matter is removed (see following pages).

[4]) After re-crystallization from water, one finds, for instance, $Cl = 14{,}80\,\%$; $14{,}75\,\%$; N (micro) $= 13{,}01\,\%$; $13{,}06\,\%$; $H_2O = 6{,}9\,\%$ so that $N : Cl = 2{,}24 : 1$.

This salt appears to be the *luteo*-salt L_2, which is geometrically isomeric with L_1. The dry solid salts differ but little in colour, — L_2 having a little darker yellow hue. Analysis yielded the following values:

	Co:	Cl:	N:	H_2O:
L_1	9.72 %; 9.78 %	17.51 %; 17.56 %	13.77 %; 13.67 %	5.0 %
L_2	9.39 %; 9.36 %	16.89 %; 16.83 %	13.44 %; 13.31 %	8.6 %; 9.2 %
calculated for	$[Co(phenen)_3]Cl_3 . 3H_2O$:	9.39	16.98	13.39	8.6 %
calculated for	$[Co(phenen)_3Cl_3] . 2H_2O$:	9.67	17.48	13.78	5.7 %.

Thus L_1 appears to be a *di*hydrate, L_2 a *tri*hydrate. A determination of the molecular weight of the dried salts in phenol, yielded the following values:

	gr. salt	gr. phenol	Δt:	M (found):	
L_1	0.293	17.25	0°.210	591	
L_1	0.290	16.23	0°.222	596	M (calculated) = 573
L_2	0.391	16.07	0°.290	607	

Both salts, therefore, are *mononuclear* ones and have *the same* molecular weight. The difference of colour of the solid salts is also noticeable in aqueous solutions: solutions of the same concentration by means of a PULFRICH-photometer proved to show an absorption of different extent. In methyl-alcohol L_1 dissolves with difficulty, L_2 rather easily.

The saturated aqueous solution of L_1 at 25° contains 1.16 gr. that of L_2 2.47 gr. of salt in 100 cc of water. In hot, boiling water both salts readily dissolve, L_2 melting under water to a brown liquid mass, whereas L_1 remains solid, until complete solution has occurred.

On heating in a drying room, the two salts become green, L_2 at ca. 140°, L_1 at 150°, under partial conversion into *praseo*-salts.

The data concerning the rotation-curves of the two isomerides are to be found in Fig. 1, (curves *I* and *II*). It is noteworthy that, — in contradistinction to the case of *l*-stilbenediamine, — *l*-phenylethylenediamine yields *levo*-rotating *luteo*- and *praseo*-salts. The rotation-curves of the two isomerides show the same qualitative course, but they strongly differ in regard to the *absolute* magnitude of their rotations. Both isomerides possess a considerably higher maximal rotatory power than $[Co(l\text{-}stien)_3]Cl$. As the curve shows, the *l*-base gives a *positive* contribution to the rotation [1]; the partial racemic complexes: $[Co(rac.\ phenen)_3]X_3$ therefore, ought to possess a much higher rotatory power. The polarimetric investigation of the geometrically isomeric *luteo*-salts fully confirms the rules [2] previously stated by one of the authors (LI) with other geometrically isomeric series:

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[1]) In the red part of the spectrum, where the luteo-complexes practically have *no* rotation, the said contribution is very evident, see curve II.

[2]) I. LIFSCHITZ, l.c. Proc. Ned. Akad. v. Wetensch. Amsterdam, l.c.

1. Geometrically isomeric substances show a rotation which is *qualitatively quite analogous*, but *quantitatively very different*.

2. A *lower* degree of symmetry of the molecule causes a *higher* rotation: $[Co(l\text{-}stien)_3]X_3$ rotates much less than $[Co(l\text{-}phenen)_3]X_3$ and practically as much as $[Co(en)_3]\ X_3$ [1]).

3. From this, the working hypothesis obtains fresh support [2]), that of two geometric isomerides the *less symmetrical* one shows the *higher* rotation.

§ 3. Besides *luteo*-salts, we also prepared the *praseo*-compounds; theoretically these might also occur in *two* isomeric forms, namely in a *cis*- and a *trans*-form. We, indeed, got the impression that *two* praseo-chlorides $[Co(phenen)_2Cl_2]Cl$ are formed; but they were only little stable and, therefore, they could up till now not be isolated in the pure state with complete certainty.

For their preparation the following prescription is recommended:

7.8 gr. of $CoCl_2 . 6\,H_2O$ are dissolved in 300 cc alcohol, 8.1 gr. base and then 10 cc HCl (s.g. 1.19) are added and the mixture then is oxydized with a current of air during about 20 hours. A green salt soon begins to crystallize, the solution assuming a blackish-green colour.

The crystallized *praseo*-salt (P_1) is sucked off and the mother liquor strongly concentrated; on cooling, a considerably darker salt (P_2) then begins to crystallize. Both salts, after recrystallizing them from alcoholic hydrochloric acid and drying at 130°, are, however, still impure. A pure *praseo-nitrate* could finally be obtained by mixing a solution of P_1 in methyl-alcohol with an aqueous solution of KNO_3. This salt, which dissolves in water with great difficulty and slightly better in alcohol, gave the following values:

$[Co(phenen)_2Cl_2]NO_3$ Calc.: $Cl = 15{,}31\ \%$; $N = 15{,}09\ \%$; found: $Cl = 15{,}44\ \%$; 15,54 %; 15,26 %; $N = 14{,}83\ \%$; 14,88 %. The values for nitrogen, which are a little too low, are caused by the presence of *Cl* in the molecule [3]). The data concerning the rotation-curve of the *praseo*-salt, which shows a course perfectly analogous to that of the curves of other *prasea*-compounds [4]), is given in Fig. 1 by curve *III*. By treating the *praseo-chlorides* with potassium- or silver-oxalate, an *oxalo-salt*: $[Co(phenen)_2C_2O_4)]Cl$ finally also could be obtained. The salt crystallizes from water in red little prisms, containing 2 molecules of water: Calc.: $N = 11{,}42\ \%$; $Cl = 7{,}2\ \%$; found: $N = 11{,}33\ \%$ and 11,40 %; *Cl* 7,2 and 7,0 %. Curve *IV* in Fig. 1 graphically represents the rotation of this salt. It can be remarked, that the *oxalo*-salt:

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[1]) I. LIFSCHITZ and J. G. BOS; this paper will soon appear in Rec. trav. chim. d. Pays-Bas, **59**, (1940).

[2]) I. LIFSCHITZ, Rec. trav. chim. d. Pays-Bas, **58**, 785 (1939).

[3]) I. LIFSCHITZ and J. G. BOS, Rec. trav. chim. **58**, 795 (1939).

[4]) F. M. JAEGER and H. BLUMENDAL, Z. anorg. allg. chem. **175**, 191 (1928).

$[Co(phenen)_2C_2O_4]Cl$ may occur in *three* geometrically isomeric forms. An isomeric salt, however, was in our experiments only found once, in a

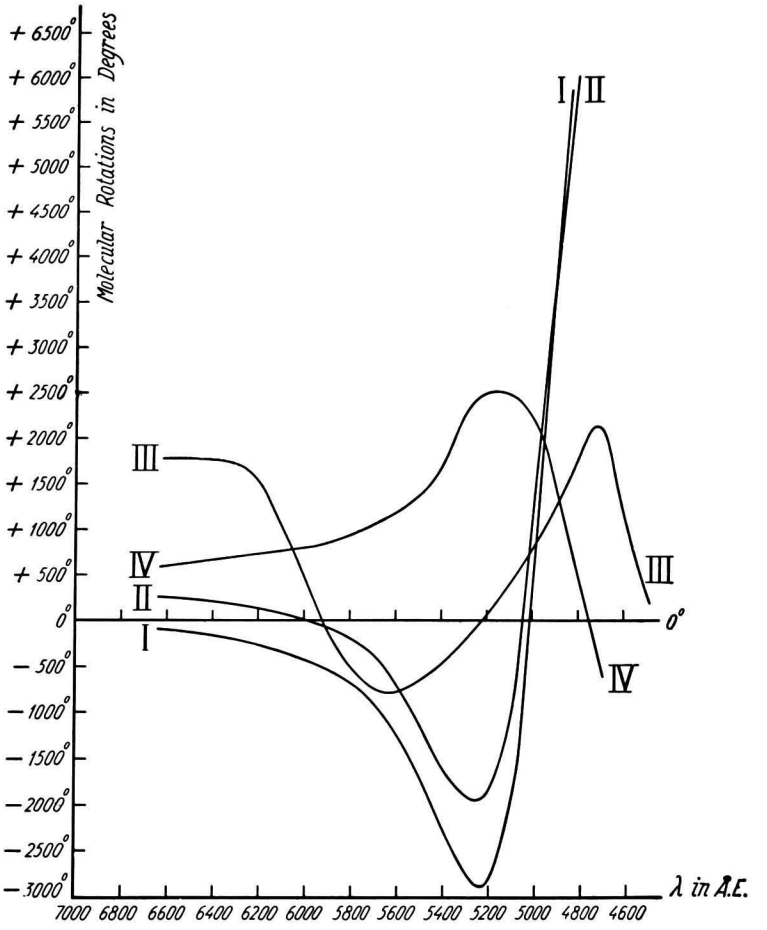

Fig. 1. Rotatory Dispersion of:

I. Luteo-salt L_1 in water, ($c = 0{,}2252$ gr. in 100 cc).
II. Luteo-salt L_2 in water, ($c = 0{,}2244$ gr. in 100 cc).
III. Praseo-salt: $[Co(phenen)_2Cl_2]NO_3$ in alcohol + 5% conc. HCl ($c = 0{,}1300$ gr. in 100 cc).
IV. Oxalo-salt: $[Co(phenen)_2C_2O_4]Cl$ in water ($c = 0{,}1180$ gr. in 100 cc).

minimal quantity. Because of the lack of material, for the present we have abstained from more extensive investigations. The determination of N of this salt yielded: 11,40 and 11,50 % N; calculated for the compound: $[Co(phenen)_2C_2O_4]Cl \,.\, 2\,H_2O$: 11,42 %.

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