

On the magnetic properties of the $\text{CoCl}_2\text{—H}_2\text{O—HCl}$ system.

(Preliminary communication)

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The change in colour of the watery solution of CoCl_2 effected by different materials, is a problem several times discussed. The elements of the transition group (Fe, Co, Ni) are occupying an interesting place in the periodical system because of their magnetic properties. Several authors determined the magnetic properties, of their compounds, in solution too (1a). Meanwhile they found only a qualitative connection between colour and magnetic data. Fahlenbrach (2) searched the magnetic susceptibility of CoCl_2 in pure water, pyridin and aethylacohol, he found, that red colour and high susceptibility belong to low temperature, while to high temperature blue colour and low susceptibility. Here the change in colour has taken place by the increasing of the temperature.

I determined during my experiments the magnetic susceptibility of CoCl_2 in $\text{H}_2\text{O—HCl}$ solution. I kept constant the CoCl_2 (0.04577 mol) and changed the HCl concentration, so I could vary on constant temperature — depending only on the HCl amount — the colour of the solution, from red to dark blue. To the measuring of the magnetic susceptibility of the different coloured solutions I used the cylindrical method, what Klemm (4) recommended (and which they call also the method of Plücker (8) or of Gouy (3)). I enlarged it with the varying of the field-force recommended by McLennan, Ruedy; Cohen (5). Then I altered only a few things on the method. I counted the susceptibility of the solution according to the advice of Klemm (4) applied to this method. And with the Wiedemann (9) thesis the susceptibility of the solved salt:

$$x_{SO} = p x_s + (1-p) x_{SV}$$

Where x_{SO} means the gr. susceptibility of the solution, x_s of the salt, x_{SV} of the solvent, and p means the mass concentration of the salt. From this

$$x_s = \frac{100}{p'} \sigma (x_{SO} - x_{SV}) + x_{SV}$$

here σ means the density of the liquid, and p' the gr-s of the salt in 100 ccm.

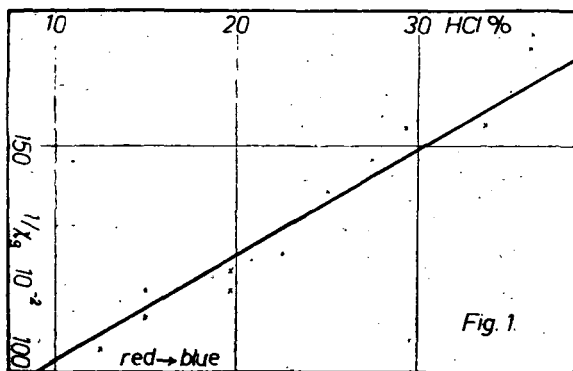
Materials: pro anal. (Ni free) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ Merck fabrication, twice distilled water from Jenaer glass, and pro anal. (free from iron) HCl. I prepared the solutions always in the same manner. I let it stand for a day. I determined the CoCl_2 concentration

by the method of Brode (1). I carried out my experiments always at a constant temperature ($17^{\circ}\text{C} \pm 1^{\circ}\text{C}$):

Fig. 1. represents my results. Here the concentration of the CoCl_2 and temperature of the solutions is always constant, and the HCl concentration in % is plotted against the $1/x \cdot 10^{-2}$ values. The colour of the solution is changing from left to right, from red to dark blue. The values of the pure watery solution are in conformity with the results of different authors, while the results of the dark blue solution are giving back the susceptibilities of other blue as concentrated CoCl_2 solutions (2). In my values — out of my experimental arrangement — the fault is $\pm 5\%$.

The evaluation of my results led in two directions. The first is the behavior of the cobalto complexes, which are forming in the $\text{CoCl}_2 - \text{H}_2\text{O} - \text{HCl}$ system in magnetic field, the second is the composition of these complexes.

On the base of my experiments for all we can state, that the CoCl_2 solvled in $\text{H}_2\text{O} - \text{HCl}$ behaves always paramagnetic,



and the susceptibilities of those between the measuring limits (4900—5700 gauss) are independent from the field-force. It could be stated also from my results, that the magnetic susceptibility of the CoCl_2 is decreasing by increasing the HCl concentration. Its reason is that by increasing the amount of HCl is developing such a paramagnetic cobalto complex, whose susceptibility is smaller, and independent from the field-force between the measuring limits.

On the base of the researches made up to the present (4a, 10) in watery and not watery blue solution of the CoCl_2 , we have to suggest the presence of CoCl_4^- complex ion whose structure however could not be cleared up alone with spectroscopy. Therefore I attempted to clear up the structure and electron distribution of the cobalto complexes developing in the $\text{CoCl}_2 - \text{H}_2\text{O} - \text{HCl}$ system, with magnetic experiments. Klemm's work (4) says only generality about the relation between magnetic properties and molecule structure of solvled materials. He remarks that to clear up such a problem in every case some other physico-chemical (spectroscopical!) experiments are needed. Pauling worked out a theory (6, 7) between the magnetic properties and electron

distribution of the compounds. By the interpretation of my results I am to rely on Pauling's works. On the base of his works I can state from my results that by increasing the HCl concentration there is beginning the hegemony of the tetrahedral cobalto complexes with a coordination number of four. It can also be said, that in the CoCl_4^{--} complex rather electronpair bonds are forming than electrostatical. To the $\text{Co}(\text{H}_2\text{O})_6^{++}$ complex, developing in the red coloured solution, I obtained the result, that the water molecules are producing a strong ion-dipol or a bond type between the ion-dipol and semipolar. Other intermediary compounds and their structure could not be cleared up by measuring the magnetic properties. To solve this problem too, I shall determine the absorption spectrum of the solution in the visible spectrum whose magnetochemical properties I have already measured.

With temperature and with the spectroscopical measuring I am the temperature and with the spectroscopical measuring I am continuing my work.

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Szeged 10 2 1949.

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