

Zusammenfassung.

Es wurden die Extinktionskurven von $\text{Co}(\text{SCN})_2$ -Lösungen im Wasser und in absolutem Aethanol bei verschiedener $\text{Co}(\text{SCN})_2$ -Konzentration mit und ohne KSCN Zusatz ausgemessen. An Hand dieser Versuchsdaten wurden die Kurven der Verbindungen: $\text{Co}(\text{SCN})_2$ annähernd berechnet. Die periodische Extinktionsänderung von $\text{Co}(\text{SCN})_2$ -Lösungen wurde mit Polymerisation derselben erklärt.

Auch an dieser Stelle möchte ich dem Prof. A. Kiss für die Anregung an diese Arbeit bestens danken.

Schrifttum.

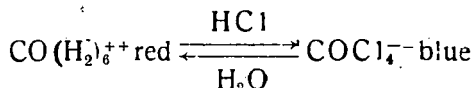
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The $\text{CoCl}_2\text{—H}_2\text{O—HCl}$ system

by P. F. VÁRADI

In the watery solution of CoCl_2 a reversible change of colour takes place, effected by the increasing or decreasing concentration of the HCl:



We can state this on basis of other investigators (2). This system (or the change of colour) was studied in the Institute (7) and herebelow we shall discuss some problems in connection with it.

1. What is the structure of the complexes with six and with four coordination numbers?

2. What is the composition of the coplexes which form themselves in the $\text{CoCl}_2\text{—H}_2\text{O—HCl}$ system?

3. What kind of bond-types are forming?
4. What effects the change of colour?

Experimental. producere. We used for our experiments the König—Martens and Grünbaum's spectralphotometer. The measuring method of the magnetic properties of this system was already published (17). The literature referring to the measuring methods are enumerated below (4, 7, 9).

Materials. The materials used in the experiments were discussed in the earlier literature (3, 17).

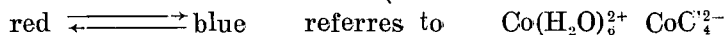
The discussion of the problems mentioned above follows below:

1. On basis of the researches carried out until now (7, 13), we suppose, that the complex with the coordination number six, is octahedral, while the complex with the coordination number four is tetrahedral.

2. In the change of colour: red \rightleftharpoons blue, referring to $\text{Co}(\text{H}_2\text{O})_6^{2+} \rightleftharpoons \text{CoCl}_4^{2-}$ it was unavoidable to take into consideration an intermediary compound. The composition of this intermediary compound is probably $\text{CoCl}_2(\text{H}_2\text{O})_4$ (17). In the paper (17) it was also shown that the central atom of the complexes may use not more than two 3d orbitals in $\text{Co}(\text{H}_2\text{O})_6^{2+}$ and $\text{CoCl}_2(\text{H}_2\text{O})_4$ for forming hybrid bonds, while three 3d orbitals in CoCl_4^{2-} .

3. The bond-types of the compounds were discussed in earlier publication (17).

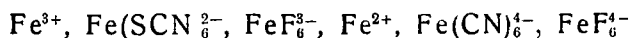
4. As mentioned above, earlier authors ascertained that the change of colour



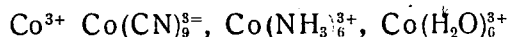
The change of colour of the compounds is not rare in chemistry. This can occur in connection with oxydation, dissociation, etc., but the bivalent cobalt is unique, because we do not know other reversible processes, when the hybridization of the bond orbitals could be changed so easy.

It is interesting to compare the compound of Fe^{3+} , Fe^{2+} , CO^{3+} , CO^{2+} , Ni^{2+} . Here we cannot observe a Co^{2+} like change of colour. Table I. represents the electron number of the ions, and illustrates the electron distribution on the 3d orbital.

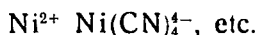
The tri-, and bivalent iron formes usually octahedral complexes:



The trivalent cobalt has the same electron-distribution than the bivalent iron, and forms similarly octahedral complexes:

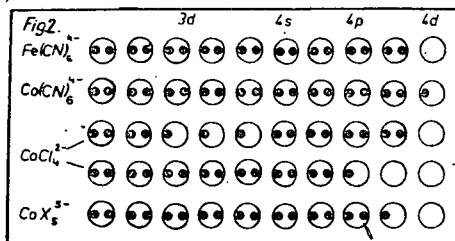
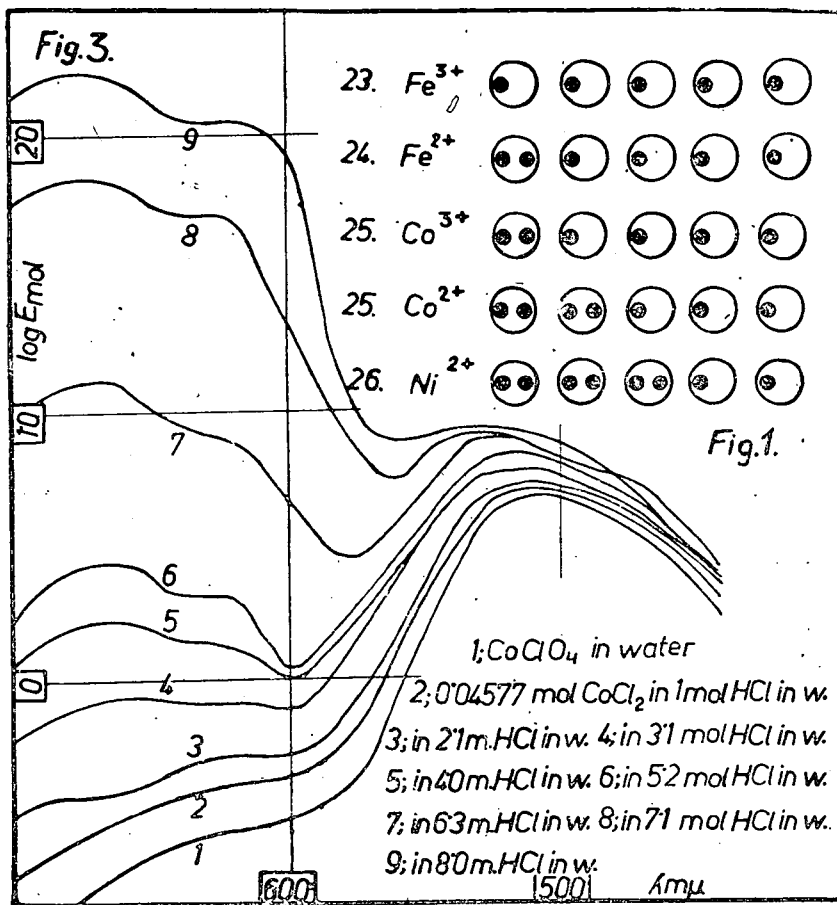


The coordination number of bivalent nickel is usually four, with a square or tetrahedral configuration:



In the periodical system between the iron and nickel cobalt is to be found. We may suppose that in case the coordination number of iron is six and that of nickel four, than the coordination number of the bivalent cobalt could be five. The carbonyls and

carbonylhydrides will present an example. The Langmuir thesis predicts (8) the stability of the carbonyls and carbonylhydrides. This thesis was extended on the polynuclear carbonylcomplexes by Sidgwick and Bailey (14). According to this thesis the molecule is stable if the effective electron-number of the central atom (with



these given by the CO molecules) reaches the electron number of the next noble gas (1). Mathematically:

$$E = \frac{xM + 2y}{x} = x - 1 \quad (A)$$

Here E means the effective electron number of the noble-gas, x the number of the central atoms of the complex and M their electron number, and y represents the number of the carbonyl radicals.

From the formula we obtain:

Ni(CO) ₄	effective electron number	36
Fe(CO) ₅	" "	36
Co(CO) ₄	" "	35 ≠ 36
Co(CO) ₆	" "	39 ≠ 36

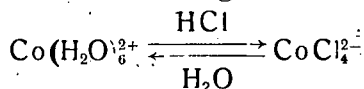
Cobalt cannot form mono-nuclear carbonyls, because the noble gas configuration is not yet or it is overcompensated. Therefore, the complex is unstable. Using the formula (A) in case of polynuclear cobalt carbonyls, we shall find that only those complexes are stable, which give a correct equation. The experimental data verified the thesis (1). This example has shown that the stability of a complex depends only on the central atom's *valence field* and the way how it is compensated by the surrounding molecules. It is interesting to note, that the carbonylhydrides are verifying the Langmuir thesis too.

The compounds Fe(CO)₄H₂, Ni(CO)₄ and Co(CO)₄H are known (5). Applying the formula (A) to these compounds, we obtain an equation. In these compounds the valence-fields of the central atoms are compensated.

On considering the comparison between the complexes of tri- and bivalent iron, tri- and bivalent cobalt, and bivalent nickel, and also table I., which represents the electron-distributions of the complexes, it can be said: bivalent cobalt has no stable complex, neither with a coordination number four, nor with six (12). Probably a complex, with a coordination number five will be the stable one. The example of the carbonylhydrides showed that a cobalt complex Co(CO)₄H with a coordination number five is stable. But, on the basis of literary data it can be stated, that there exists no stable cobalt complex, with a coordination number five. Table II. shows a hypothesis of the electron distribution of the bivalent cobalt, with a coordination number five. The complex cannot be stable, because the central atom valence-field would be overcompensated.

The valence-field of the bivalent cobalt with four, five, or six bonds is not yet, or it is over compensated. If we still can speak about compounds with a coordination number four or six, we can do to only by introduction of *constraint forces*.

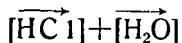
Stanworth (15) and Millner (10) introduced such forces in the case of cobalt glasses. In the change



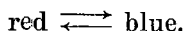
the H₂O or HCl causes such forces, and changing the conditions of the constraints, the system changes too. With the introducing of such forces, we can explain the properties of the CoCl₂, also the following experiment: CoCl₂(H₂O)₆ crystals lose their red colour

and get a lilacred one, in a vacuum exsiccator which contains CaCl_2 and P_2O_5 . On air the red colour recovers again. Accordingly in a vacuum exsiccator which contains, KOH , H_2CoCl_4 crystals lose their deep blue colour and get a light blue one. In an atmosphere containing some percentage of HCl gas, the deep blue colour recovers again. This experiment demonstrates, that both of the configurations six and four, is stable under pressure only. In the first case the pressure of the water-vapour of the air, in the second case the pressure of the HCl produced the constraint force. If there is no HCl or H_2O pressure, the crystal decomposes itself. Both structures are instable and they remain stable only above a certain pressure, that means, under some constraint condition.

The first result, on basis of researches, that the change of colour in the $\text{CoCl}_2 - \text{H}_2\text{O} - \text{HCl}$ system is caused by the changing of the constraint conditions. $[\overrightarrow{\text{HCl}}]$ should mean the constraint force of the hydrochloric acid, and $[\overrightarrow{\text{H}_2\text{O}}]$ of the water. The constraint force has a magnitude and a direction too. We get information of the magnitude of the forces by taking into consideration, that the change of colour is produced by different concentrations of the different materials. The change of colour is a function of the concentration. The direction of the force means the direction of the change red \rightarrow blue, or the opposite one red \leftarrow blue. Therefore we use the symbols: $[\overrightarrow{\text{HCl}}]$ and $[\overrightarrow{\text{H}_2\text{O}}]$. Since this forces have a magnitude and also a direction, the vector sum of the constraint conditions:



will determine the process



This hypothesis is not in contradiction with the existence of the intermediary compound. It states only, that the intermediary compound can be stable only on a certain constraint condition.

We shall give a detailed discussion of the problem of the valence-field in a following paper.

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The structure of the complexes formed by cobaltous chloride with absolute organic solvents, according to an analysis of light-absorption curves plotted in the visible spectrum

By GEORGE VARSÁNYI

Introduction.

According to Hantzsch, also Donnan and Basett, as well as Dirking, the blue colour of cobalt complexes is related to a coördination number of four, viz., there is no blue cobalt complex with a coördination number of six. The two complexes can be described by the formulae CoCl_2L_2 and CoCl_2L_4 respectively, as chlorine is situated in the coördination belt of the complex.

On the basis of research performed earlier in the Institute of Inorganic Chemistry of the University of Szeged, the view expressed above had to be rejected. My own research appears to substantiate this rejection, as the existence of blue cobaltous chloride complexes with a coördination number of six can be regarded as proven, on the basis of spectrophotometric analysis of anhydrous cobaltous chloride in various organic solvents and the application of suitable methods of calculation.

In order to investigate the problem, I have observed the visible-light absorption of anhydrous cobaltous chloride in methyl-, ethyl-, propyl-, butyl-, and amylalcohol, as well as pyridine. A considerable part of my investigation consists of the measurements performed on cobaltous chloride dissolved in a mixture of pyridine and ethylalcohol, the alcohol of the highest dipolemoment, and those performed in the two latter solvents both pure and mixed in the presence of excess chlorine.

In obtaining my data I have used the König—Martens—Grünbaum photometer.

I have plotted the absorption spectrum of the solution of anhydrous cobaltous chloride in ethylalcohol at a con-