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COMPLEX FORMATION IN THE SYSTEM $CoCl_2$–HCl–H_2O

(Presented by Academician I. I. Chernyaev, 5 V 1960)

Despite the large number of works devoted to the study of complex formation in aqueous solutions of $CoCl_2$ ([1–12]), information on the composition and structure of the complex compounds formed in these solutions is contradictory. Data on the quantitative content of complex compounds in the system $CoCl_2$–HCl–H_2O are absent from the literature.

In the present work an attempt is made to establish the composition and quantitative content of complex ions of Co(II) in the system $CoCl_2$–HCl–H_2O at varying concentrations of the components. The identification of the complexes formed in these solutions was carried out by us by comparing the electronic absorption spectra of the solutions with the spectra of crystalline complex compounds of Co(II).

Figure 1 shows the nearest environment of the cobalt ion in crystalline Co(II) complexes, as established by X-ray structural analysis. From regular octahedra $[Co(H_2O)_6]^{+2}$ is built the crystal lattice of the crystalline hydrate $[Co(H_2O)_6](ClO_4)_2$ ([13]); the complexes $[Co(H_2O)_4(ClH_2O)_2]$ form the crystal lattice of $CoCl_2 \cdot 6H_2O$ ([14]); from the complexes $[CoCl_4(H_2O)_2]$ and $[CoCl_6]$ are composed the chain and layered lattices of the crystals $CoCl_2 \cdot 2H_2O$ ([15]) and $CoCl_2$ ([16]). The tetrahedral complexes $[CoCl_4]^{-2}$ and Cs^+ ions form the crystal lattice of Cs_2CoCl_4 ([17]).

(Figure: Fig. 1. Structure of the inner sphere of Co(II) complex compounds in crystals: a –$Co(ClO_4)_2 \cdot 6H_2O$, –$CoCl_2 \cdot 6H_2O$, –$CoCl_2 \cdot 2H_2O$, –$CoCl_2$, –Cs_2CoCl_4)

Fig. 1. Structure of the inner sphere of Co(II) complex compounds in crystals: *a* –$Co(ClO_4)_2 \cdot 6H_2O$, *b* –$CoCl_2 \cdot 6H_2O$, *c* –$CoCl_2 \cdot 2H_2O$, *d* –$CoCl_2$, *e* – Cs_2CoCl_4

The data on the electronic absorption spectra of $CoCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 2H_2O$, $CoCl_2$, and Cs_2CoCl_4, presented in the article by S. V. Grum-Grzhimailo and I. I. Plyusnina ([18]), were obtained mainly for powder preparations and do not allow calculation of the values of the absorption coefficient of Co(II) complexes. In addition, when working with finely crystalline samples of crystalline hydrates,

one cannot be certain of the homogeneity of the chemical composition of such preparations.

In this connection, we measured the absorption spectra, in natural and polarized light, of thin plates (1 mm–0.01 mm) cut from large crystals of $Co(ClO_4)_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 2H_2O$, and Cs_2CoCl_4. The measurements were carried out on an SF-11 spectrophotometer. A Frank-Ritter prism was used as the polarizer. The absorption spectrum

Table 1

Wavelengths corresponding to the maxima of the absorption curves of complex compounds of Co(II), and values of the absorption coefficient $-\chi_\lambda$, at the maxima of the absorption curves. Experimental temperature 20°

Crystal	Inner sphere of the complex	λ_{max}, mμ; χ_λ, cm^2/g-ion
$Co(ClO_4)_2 \cdot 6H_2O$	$[Co(H_2O)_6]$	$\frac{512^*}{4.2}$
$CoCl_2 \cdot 6H_2O$	$[Co(H_2O)_4(ClH_2O)_2]$	$\frac{470}{1.3}$; $\frac{505}{3}$; $\frac{550}{5.2}$
$CoCl_2 \cdot 2H_2O$	$[Co(H_2O)_2Cl_4]$	$\frac{516}{6.5}$; $\frac{620}{4}$
$CoCl_2$	$[CoCl]_6$	530; 580
Cs_2CoCl_4	$[CoCl]_4$	$\frac{306}{2.4}$; $\frac{320}{1}$; $\frac{380}{0.8}$; $\frac{412}{1}$; $\frac{450}{2.2}$; $\frac{535}{8}$; $\frac{625}{170}$; $\frac{660}{190}$; $\frac{685}{240}$
1 M solution of $CoCl_2 C_{HCl} < 5$ mole/l		512–520
1 M solution of $CoCl_2 C_{HCl} > 5$ mole/l		304; 320; 380; 414; 450; 535; 625; 660; 685

* The numbers above the line denote λ_{max}; those below the line denote the corresponding χ_λ.

of small crystals of $CoCl_2$ was measured on a microspectrophotometer kindly made available to us by M. V. Savost' yanova.

Table 1 gives the wavelengths corresponding to the maxima in the absorption curves of the crystalline Co(II) complexes studied, as well as the values of the absorption coefficient χ_λ, calculated per 1 gram-ion of Co^{+2} for natural radiation. Measurements carried out by us in polarized radiation showed that the pleochroism of the crystals considered is reduced to the case of "absorption" (19) –a change in the orientation of the crystal is not accompanied by the appearance of new frequencies in its absorption spectrum.

The absorption spectra of aqueous $CoCl_2$ solutions in the presence of HCl were studied at $CoCl_2$ concentrations of 1 mole/l, 0.1 mole/l, 0.01 mole/l, and 0.001 mole/l; the HCl concentration in each series of experiments was varied from 0 to 11 mole/l, $t = 20$°C.

In all cases, at an HCl concentration in solution from 0 to 4 mole/l, only an absorption band at 515 mμ is observed in the spectra of the solutions, identical with the absorption band of the ion $[Co(H_2O)_6]^{+2}$ in the spectrum of crystalline hydrate $Co(ClO_4)_2 \cdot 6H_2O$. At an HCl concentration of 4 mole/l, numerous absorption bands appear in the spectrum of the $CoCl_2$ solution, exactly coinciding with the absorption bands of the complex $[CoCl_4]^{-2}$ in the Cs_2CoCl_4 crystal. With increasing HCl concentration, the 515 mμ absorption band shifts toward 535 mμ, which is entirely explainable by the overlap of the absorption bands of the ions $[CoCl_4]^{-2}$ and $[Co(H_2O)_6]^{+2}$. Frequencies corresponding to the complexes $[Co(H_2O)_4(ClH_2O)_2]$ and $[CoCl_6]$ are not observed in the spectra of $CoCl_2$ solutions in HCl.

The absorption bands of the ion $[CoCl_4(H_2O)_2]^{-2}$, located at 516 mμ and 620 mμ, are overlapped by the corresponding absorption bands of the complexes $[Co(H_2O)_6]^{+2}$ and $[CoCl_4]^{-2}$. At the same time, crystalline hydrate $CoCl_2 \cdot 2H_2O$, in which the immediate environment of the Co^{+2} ion consists of four Cl^- ions and two H_2O molecules, has a strongly pronounced absorption at $\lambda = 280$–290 mμ. The absorption coefficient of this crystalline hydrate at

$\lambda = 280$ mμ is 10-15 times greater than the values of the absorption coefficient of crystals of $Co(ClO_4)_2 \cdot 6H_2O$ and Cs_2CoCl_4. Our measurement of the optical density of $CoCl_2$ solutions in concentrated HCl, with varying concentration of the latter, showed the absence of appreciable amounts of the complexes $[CoCl_4(H_2O)_2]^{-2}$.

As a first approximation it may be assumed that, upon transfer of the ions $[Co(H_2O)_6]^{+2}$ and $[CoCl_4]^{-2}$ from the crystalline phase into solution, the values of the absorption coefficient of these ions do not undergo significant changes.

A comparison of the absorption curves of the crystalline hydrate $Co(ClO_4)_2 \cdot 6H_2O$ and dilute aqueous solutions of Co(II) salts supports this assumption.

Since the values of the absorption coefficient of the ions $[Co(H_2O)_6]^{+2}$ and $[CoCl_4]^{-2}$ in the crystalline phase had been measured by us, it seemed reasonable to calculate, from the optical-density values of $CoCl_2$ solutions, approximate values of the concentrations of the listed ions. The data obtained by us in these calculations are approximate in character and are given in Table 2.

Table 2

Distribution of Co^{+2} ions among complex compounds in the $CoCl_2$–HCl–H_2O system at varying concentrations of $CoCl_2$ and HCl, $t = 20^\circ$ (in percent)

HCl concentration, g-mol/L	$CoCl_2$ concentration in solution, g-mol/L: 1		$CoCl_2$ concentration in solution, g-mol/L: 0.1		$CoCl_2$ concentration in solution, g-mol/L: 0.01		$CoCl_2$ concentration in solution, g-mol/L: 0.001	
	$[Co(H_2O)_6]^{+2}$	$[CoCl_4]^{-2}$	$[Co(H_2O)_6]^{+2}$	$[CoCl_4]^{-2}$	$[Co(H_2O)_6]^{+2}$	$[CoCl_4]^{-2}$	$[Co(H_2O)_6]^{+2}$	$[CoCl_4]^{-2}$
0	100	0	100	0	100	0	100	0
4	95	5	100	0	100	0	100	0
5	80	20	98	2	99	1	100	0
6	60	40	90	10	90	10	92	8
7	45	55	65	35	70	30	80	20
8	30	70	35	65	40	60	55	45
9	10	90	20	80	25	75	35	65
10			15	85	20	80	25	75
11			10	90	15	85	20	80

The substitution of H_2O molecules in the hydrate shell of the Co^{+2} ion by Cl^- ions proceeds to an appreciable extent only at high concentrations of HCl in solution. The degree of dissociation of HCl at such concentrations is small. This gives grounds to consider that the process

$$[Co(H_2O)_6]^{+2} + 4Cl^- = [CoCl_4]^{-2} + 6H_2O$$

proceeds only in the case when there is a considerable amount of undissociated HCl molecules in the solution, acting as a dehydrating agent.

A similar assumption is confirmed by the fact that the concentration of $[CoCl_4]^{-2}$ ions in the $CoCl_2$–HCl–H_2O system increases when acetone or sulfuric acid is introduced into the solution.

In connection with the above, one may suppose a high strength of the bond of the Co^{+2} ion with the H_2O molecules that form its immediate environment in aqueous solutions, which agrees with literature data on the energy of attachment of water to the Co^{+2} cation ([20, 21]).

The circumstance that, in the electronic absorption spectrum of the $CoCl_2$–HCl–H_2O system, only the frequencies of the complex ions $[Co(H_2O)_6]^{+2}$ and $[CoCl_4]^{-2}$ are observed may be explained as follows: either the process of substitution of H_2O molecules in the ion $[Co(H_2O)_6]^{+2}$ by Cl^- anions, accompanied

by a change in the coordination number of Co(II), proceeds abruptly, without the formation of intermediate complex compounds, or this same pro-

the process proceeds in several stages, but the concentration of the intermediate complexes is very small.

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Note: Figure translations are in progress. See original paper for figures.