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Complex Formation in the System $CoBr_2$–HBr–H_2O

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The formation of complexes of Co(II) with Br^- ions has been investigated mainly in organic solvents ([1–4]). Information on complex formation in aqueous solutions of Co^{+2} is scarce ([1,2,5–7]) and requires further experimental verification. In studying the composition and structure of complex compounds formed in the system $CoBr_2$–HBr–H_2O, we, as in our previous works ([8]), assumed that the most reliable information about the complexes formed in solution can be obtained by comparing the frequencies observed in the electronic absorption spectra of these solutions with the frequencies in the spectra of crystalline complexes.

In the present study we measured the electronic absorption spectra of the following crystalline complexes of Co(II): $Co(ClO_4)_2 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$, $CoBr_2 \cdot 6H_2O$, $CoBr_2 \cdot 2H_2O$, $CoBr_2$, Cs_3CoBr_5. The spectra of these crystals have been little studied ([8–13]); their structures are either known or can be predicted with considerable reliability.

In the crystal $Co(ClO_4)_2 \cdot 6H_2O$, the Co^{2+} ion is surrounded by six water molecules oriented at the vertices of a regular octahedron ([14]). It is very probable that in the crystal $CoBr_2 \cdot 6H_2O$ the nearest environment of the Co^{2+} ion is built according to the same principle as in the crystal $CoCl_2 \cdot 6H_2O$: the coordination number of the cobalt ion is six, but two coordination positions are occupied by halogen ions ([15,16]).

The chain structure and the habit of the $CoBr_2 \cdot 2H_2O$ crystal, similar to those of the $CoCl_2 \cdot 2H_2O$ crystal, give grounds to suppose that in the former crystal the inner sphere of the Co^{2+} ion, as in $CoCl_2 \cdot 2H_2O$, is formed by two H_2O molecules and four halogen ions ([17]).

In anhydrous $CoBr_2$, the nearest environment of Co^{2+} consists of six Br^- ions oriented at the vertices of an octahedron ([18]). The crystal Cs_3CoBr_5, by its formula and external habit, is analogous to the crystal Cs_3CoCl_5. It may be assumed that in the former crystal the Co^{+2} ion, as in the crystal Cs_3CoCl_5 ([19]), is surrounded by four halogen ions located at the vertices of a regular tetrahedron.

The electronic absorption spectra of the listed preparations were measured by us in the region 240 mμ–1500 mμ on an SF-11 spectrophotometer. In the

Figure 1

Figure 1: Figure 1

region 400 mμ–750 mμ, measurements were also carried out on a recording SF-10 spectrophotometer. The spectra of all complexes, except $CoBr_2$, were investigated on plates cut from large single crystals, which made it possible to calculate the values of the absorption coefficient. The spectrum of small $CoBr_2$ crystals was measured on a microspectrophotometer kindly placed at our disposal by M. V. Savostyanova, and also on an SF-10 spectrophotometer. The absorption curves of the crystalline complexes, measured in natural radiation, are shown in Figs. 1 and 2.

The spectra of the same crystals were also measured by us in polarized radiation, for which a Frank–Ritter prism was mounted in the SF-11 spectrophotometer. It was established that the pleochroism of all the studied ···

of the substances is reduced to the case of "absorption," i.e., a change in the orientation of the crystal relative to the plane of vibration of the polarized beam does not shift the absorption band, but changes the value of the absorption coefficient.

The data presented show that a change in the composition of complexes of the type $CoBr_x(H_2O)_4$ $(x + y = 6)$ leads to clearly expressed changes in the electronic spectrum of the Co^{2+} ion; to an even greater degree, a change in the coordination number is reflected in the spectrum of this ion.

Fig. 1. Values of the absorption coefficient (χ_λ) for crystalline complexes of Co(II).
1 –$Co(ClO_4)_2 \cdot 6H_2O$, 2 –$CoBr_2 \cdot 6H_2O$, 3 –$CoBr_2 \cdot 2H_2O$, and values of the optical density (D_λ) of $CoBr_2$ crystals.

The absorption spectra of the system $CoBr_2$–HBr–H_2O were investigated at $CoBr_2$ concentrations from 10^{-2} g-mol/l to 1 g-mol/l; the concentration of HBr in the solution varied from 0 to 10 g-mol/l. The temperature of the solutions was kept constant (20°). One of the absorption curves of solutions of $CoBr_2$ and HBr in H_2O is shown in Fig. 2.

At an HBr concentration in the solution below 4 mol/l, in the spectrum of a $CoBr_2$ solution only frequencies characteristic of octahedral ions $[Co(H_2O)_6]^{+2}$ are observed; at $C_{HBr} \geq 4$ mol/l, frequencies of new complexes appear in the spectrum.

Comparison of the absorption spectra of solutions of composition $CoBr_2$–HBr–H_2O with the spectra of crystalline complexes of Co^{2+} gives grounds to suppose that the principal, if not the entire, mass of Co^{+2} is distributed between octahedral complexes $[Co(H_2O)_6]^{+2}$ and tetrahedral ions $[CoCl_4]^{-2}$. The absorption curves of these solutions may be regarded as the sum of the absorption curve of

Figure 2

Figure 2: Figure 2

the crystal $Co(ClO_4)_2 \cdot 6H_2O$ and the absorption curve of the crystal Cs_3CoBr_5. The latter was recorded by us on very thin layers cut from Cs_3CoBr_5, and gives a more detailed picture of the spectrum of the ion $[CoBr_4]^{-2}$ than the absorption curves obtained in the work of S. V. Grum-Grzhimailo and I. I. Plyushnina ([11]) and in one of our preceding works ([8a]).

Fig. 2. 1 —values of the absorption coefficient (χ_λ) of Cs_3CoBr_5 crystals. 2 — optical density (D_λ) of the system $CoBr_2$—HBr—H_2O; concentration of $CoBr_2$, 0.01 g-mol/l, concentration of HBr —10 g-mol/l. Thickness of the solution layer: for measurements in the region $\lambda < 600$ mμ, 5 cm; for measurements in the region $\lambda > 600$ mμ, 0.1 cm.

If it is assumed, as a first approximation, that the absorption coefficient of the Co(II) complex ions does not change on passing from the crystalline phase into solution, then, using the values of the absorption coefficient of the ions $[Co(H_2O)_6]^{+2}$ and the ions $[CoBr_4]^{-2}$, it is possible, from the Buger—Beer equation, to calculate the concentration of these ions in the system $CoBr_2$—HBr—H_2O.

Estimated values of the concentrations of the complexes, found by us by the method indicated above, at various concentrations of $CoBr_2$ and HBr in solution, are given in Table 1.

Comparison of the data on complex formation in the system $CoBr_2$—HBr—H_2O with data on complex formation in the system $CoCl_2$—HCl—H_2O ([8]) shows that there is much in common between the two systems. In both

Table 1

Distribution of Co^{+2} ions among complex compounds in the system $CoBr_2$—HBr—H_2O at varying concentrations of $CoBr_2$ and HBr, $t = 20°$, in percent

Concentration of HBr, g-mol/L	$[Co(H_2O)_6]^{+2}$ at $CoBr_2$ = 1	$[CoBr_4]^{-2}$ at $CoBr_2$ = 1	$[Co(H_2O)_6]^{+2}$ at $CoBr_2$ = 0.1	$[CoBr_4]^{-2}$ at $CoBr_2$ = 0.1	$[Co(H_2O)_6]^{+2}$ at $CoBr_2$ = 0.01	$[CoBr_4]^{-2}$ at $CoBr_2$ = 0.01
0	100	0	100	0	100	0
1	100	0	100	0	100	0
2	100	0	100	0	100	0
3	100	0	100	0	100	0
4	99.9	0.1	100	0	100	0
5	91	9	99.5	0.5	100	0
6	85	15	98.5	1.5	99.5	0.5
7	40	60	80	20	95	5

Concentration of HBr, g-mol/L	$[Co(H_2O)_6]^{+2}$ at $CoBr_2$ = 1	$[CoBr_4]^{-2}$ at $CoBr_2$ = 1	$[Co(H_2O)_6]^{+2}$ at $CoBr_2$ = 0.1	$[CoBr_4]^{-2}$ at $CoBr_2$ = 0.1	$[Co(H_2O)_6]^{+2}$ at $CoBr_2$ = 0.01	$[CoBr_4]^{-2}$ at $CoBr_2$ = 0.01
8	–	–	10	90	65	35
9	–	–	3	97	24	76
10	–	–	0	100	10	90
11	–	–	–	–	5	95

cases in the spectra of the solutions it is possible to detect only the frequencies of octahedral ions $[Co(H_2O)_6]^{+2}$ and tetrahedral ions CoG_4^{-2}. The frequencies of any other complex compounds of Co(II) cannot be detected in the spectra of these solutions.

At the same time, comparison of the data on the concentration of $[CoBr_4]^{-2}$ ions in the system $CoBr_2$–HBr–H_2O with data on the concentration of $[CoCl_4]^{-2}$ ions in the system $CoCl_2$–HCl–H_2O ([86]) shows that, at concentrations of hydrohalic acids in solution of 4–7 g-mol/L, formation of the acidocomplex $[CoBr_4]^{-2}$ proceeds less intensively than formation of the ions $[CoCl_4]^{-2}$. This phenomenon was observed in organic solvents by M. S. Barvinok ([36,v]).

At concentrations of hydrohalic acids of 7–11 g-mol/L, the tendency of Cl^- and Br^- ions toward formation of acidocomplexes $[CoG_4]^{-2}$ is already of a different character: $[CoBr_4]^{-2}$ ions are formed in higher concentrations than $[CoCl_4]^{-2}$ ions.

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