SPECTROPHOTOMETRIC STUDY OF ETHANOL SOLUTIONS OF CoCl$_{2}$ AND CoBr$_{2}$ AT HIGH CONCENTRATIONS OF Cl^{-} AND Br^{-} ANIONS

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Fig. 1. Spectral absorption curves of crystals Cs_2CoCl_4 and Cs_3CoCl_5 (1), and of a $CoCl_2$–C_2H_5OH–LiCl solution (2); $C_{CoCl_2} = 0.01\,M$; $C_{LiBr} = 4.5\,M$.

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Abstract

Full Text

CHEMISTRY

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SPECTROPHOTOMETRIC STUDY OF ETHANOL SOLUTIONS OF $CoCl_2$ AND $CoBr_2$ AT HIGH CONCENTRATIONS OF Cl^- AND Br^- ANIONS

(Presented by Academician I. I. Chernyaev, April 4, 1963)

Information on the composition of complex compounds formed in ethanol solutions of Co(II) halides is contradictory [1–7]. There are no data on the structure of these complexes.

The spectral absorption curves of the system $CoBr_2$–C_2H_5OH–LiCl, measured at varying LiBr concentration by S. A. Shukarev and O. A. Lobanova, give grounds to suppose the existence in this system of several Co(II) compounds.

In the present work an attempt is made to determine the composition and structure of those Co(II) halide complexes which are formed in anhydrous ethyl alcohol at extremely high concentrations of Cl^- and Br^- anions. On an SF-10 recording spectrophotometer, with a spectral slit width of 1–1.5 mμ, we measured the absorption curves of solutions of the following composition: $CoCl_2$ –C_2H_5OH–LiCl and $CoBr_2$–C_2H_5OH–LiBr. The concentration of Co^{2+} ions was varied from $5 \cdot 10^{-4}$ g/l to 10^{-1} g-mol/l; the concentration of LiCl and LiBr was varied from 0 to 4.5 g-mol/l.

Fig. 1. Spectral absorption curves of crystals Cs_2CoCl_4 and Cs_3CoCl_5 *(1)*, and of a $CoCl_2$–C_2H_5OH–LiCl solution *(2)*;
$C_{CoCl_2} = 0.01\,M$; $C_{LiBr} = 4.5\,M$

An increase in the concentration of LiCl and LiBr in solutions of $CoCl_2$ and CoBr was accompanied by an increase in optical density in the region 500–750 mμ, a shift of the absorption curves toward lower frequencies, and the appearance of new absorption maxima. At concentrations $C_{LiCl} > 1.5$ g-mol/l and $C_{LiBr} > 2.5$ g-mol/l, the spectrum of the solutions becomes stabilized; a further increase in

Fig. 2. Spectral absorption curves of crystals Cs_2CoBr_4 and Cs_3CoBr_5 (1), and of a $CoBr_2$—C_2H_5OH—LiBr solution (2); $C_{CoBr_2} = 0.01\ M$; $C_{LiBr} = 4.5\ M$.

Figure 2: Fig. 2. Spectral absorption curves of crystals Cs_2CoBr_4 and Cs_3CoBr_5 (1), and of a $CoBr_2$—C_2H_5OH—LiBr solution (2); $C_{CoBr_2} = 0.01\ M$; $C_{LiBr} = 4.5\ M$.

the concentration of Li halides is not reflected in the positions of the absorption maxima, nor in their relative intensity. This fact can be explained only by the formation of Co(II) acid complexes in which all the coordination valences of the Co^{2+} ion are saturated by Cl^- and Br^- anions.

The question of the composition and structure of these complexes was resolved by the method of classical structural spectral analysis—comparison of the spectra of the systems studied with the spectra of crystalline complexes [8–21] of known composition and structure. The absorption curves measured by us in the region 600–750 mμ for solutions of $CoCl_2$ and $CoBr_2$ (at a Li halide concentration of 4.5 g-mol/l) are very similar to the absorption curves of crystals Cs_2CoCl_4, Cs_3CoCl_5 and Cs_2CoBr_4, Cs_3CoBr_5 reported in the literature [8,14–16,21]. Absor
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the absorbing centers in these double salts are complex ions $[CoГ_4]^{-2}$, having the form of a tetrahedron ([22,23]).

However, the literature data on the spectra of the crystals differ somewhat from one another, which can be explained by different values of the spectral slit width in the experiments of different authors and by differences in the calibration of the spectral instruments. Therefore, the absorption spectra of the complexes Cs_2CoCl_4, Cs_3CoCl_5, Cs_2CoBr_4, and Cs_3CoBr_5 were measured by us anew on an SF-10 spectrophotometer. The data of measurements carried out in the spectral region 600–750 mμ are given in Figs. 1 and 2.

The absorption curves of the solutions and crystals of the double salts are analogous, but the crystal curves are shifted by ~ 5 mμ toward the long-wavelength region

Fig. 2. Spectral absorption curves of crystals Cs_2CoBr_4 and Cs_3CoBr_5 (1), and of a $CoBr_2$—C_2H_5OH—LiBr solution (2); $C_{CoBr_2} = 0.01\ M$; $C_{LiBr} = 4.5\ M$

in comparison with the absorption curves of solutions of Co(II) halides. The reason for this should be sought not in phenomena of a chemical nature, but in the design features of the instrument, because of which an increase in the optical density of the samples studied is accompanied by a small displacement of their absorption maxima toward longer wavelengths. The crystals studied by us, even in very thin layers, have a large optical density (1–1.5).

For a final decision on the question of the existence in the solutions studied of the tetrahedral ions $[CoCl_4]^{-2}$ and $[CoBr_4]^{-2}$, a careful comparison was made

of the absorption spectra of solutions and crystals of double salts in the region 400–600 mμ. This portion of the spectrum is usually ignored in the spectrophotometric investigation of complex formation in solutions of Co(II) halides, since the values of the absorption coefficient of the Co^{+2} ion for light of these wavelengths are 2-3 orders of magnitude smaller than for radiation with $\lambda \sim 700$ mμ ([21]). At the same time, the crystals Cs_2CoCl_4, Cs_3CoCl_5, Cs_2CoBr_4, and Cs_3CoBr_5 have, in this spectral region, a large number of absorption bands with a sharply expressed structure ([14–16,21]).

In Figs. 1 and 2 are shown the spectral absorption curves of crystals and solutions, measured by us on an SF-10 spectrophotometer in the region 400–600 mμ with a spectral slit width of 0.5–1 mμ. The frequencies of maximum absorption on the light-absorption curves of the solutions completely reproduce the frequencies in the absorption spectra of the crystals.

Thus, at high concentrations of lithium halides, the system $CoCl_2$—C_2H_5OH—LiCl is a spectral analog of the crystals Cs_2CoCl_4 and Cs_3CoCl_5; the system $CoBr_2$—C_2H_5OH—LiBr is a spectral analog of the crystals Cs_2CoBr_4 and Cs_3CoBr_5. This fact gives grounds to assert that in the first of these systems the Co^{+2} ions form ions of composition

$[CoCl_4]^{-2}$, having tetrahedral structures; in the second system, $[CoBr_4]^{-2}$ ions are formed, having the same structure.

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named after S. M. Kirov

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REFERENCES CITED

[1] J. Groh, R. Schmidt, *Zs. anorg. Chem.*, **162**, 321 (1927).
[2] W. R. Brode, *J. Am. Chem. Soc.*, **53**, 2457 (1931).
[3] H. Dirking, *Zs. Anorg. u. allgem. Chem.*, **233**, 321 (1937).
[4] M. S. Barvinok, *Izv. AN SSSR, ser. fiz.*, **5**, 636 (1948); *ZhOKh*, **19**, 1028 (1949); **21**, 1207 (1951).
[5] L. I. Katzin, E. Gebert, *J. Am. Chem. Soc.*, **72**, 5464 (1950).
[6] K. P. Mishchenko, P. S. Pominov, *ZhFKh*, **31**, 2026 (1957).
[7] S. A. Shchukarev, O. A. Lobaneva, *ZhNKh*, **6**, 804 (1961).
[8] S. V. Grum-Grzhimailo, I. I. Plyusnina, *Kristallografiya*, **3**, 175 (1958).
[9] L. I. Katzin, E. Gebert, *J. Am. Chem. Soc.*, **75**, 2830 (1953).
[10] L. S. Katzin, *J. Am. Chem. Soc.*, **76**, 3089 (1954).
[11] O. G. Holmes, D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).
[12] J. Fergusson, *J. Chem. Phys.*, **32**, 528, 533 (1960).
[13] K. Hill, O. Howell, *Phil. Mag.*, **48**, 833 (1924).
[14] S. Yamada, R. Tsuchida, *Bull. Chem. Soc. Japan*, **27**, 436 (1954). *J. Chem. Phys.*, **22**, 1273 (1954).

[15] M. L. Schultz, *J. Am. Chem. Soc.*, **64**, 2748 (1942).
[16] M. L. Schultz, *J. Am. Chem. Soc.*, **71**, 1288 (1949).
[17] D. S. McClure, *J. Phys. Chem. Solids*, **3** (1957).
[18] K. Papadardo, *Phil. Mag.*, **4**, 219 (1959).
[19] Ch. Jørgensen, *Acta Chem. Scand.*, **8**, 1495 (1954).
[20] S. N. Andreev, V. G. Khaldin, E. V. Stroganov, *Zhurn. strukturn. khim.*, **2**, 7 (1961).
[21] S. N. Andreev, V. G. Khaldin, *DAN*, **134**, 345 (1960); **143**, 335 (1962); *ZhOKh*, **32**, 3845 (1962).
[22] H. M. Powell, A. F. Welles, *J. Chem. Soc.*, **1953**, 359.
[23] G. N. Tishchenko, Z. G. Pinsker, *DAN*, **100**, 913 (1955).

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