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Abstract

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SPECTROPHOTOMETRIC STUDY OF THE COMPOSITION AND STRUCTURE OF BROMIDE AND IODIDE COMPLEXES OF COBALT

The use of the character of the absorption band as a property in physicochemical measurements has allowed us to obtain a number of data concerning the composition and structure of cobalt chloride complexes in the crystalline state and in nitrate melt (1).

The present work is devoted to a spectrophotometric study of crystalline melts of cobalt bromides and iodides and the corresponding bromides and iodides of alkali metals, and also to a refinement of the composition and structure of cobalt bromide and iodide complexes in nitrate melt.

The method for measuring absorption spectra of crystalline substances has already been described by us (1). In the work only chemically pure substances were used. Anhydrous $CoBr_2$ was obtained by heating $CoBr_2 \cdot 6H_2O$ in a stream of dry HBr to 500° (2). Cobalt iodide was prepared by sublimation in vacuum at 800° of the product of the reaction $Co + J_2 = CoJ_2$. Lithium bromide was dehydrated with dry HBr passed through the molten salt. Anhydrous lithium iodide (3) was kindly provided to us by K. T. Dudnikova. Operations for preparing mixtures of substances were carried out in a dry chamber. Melting of cobalt iodide and its mixtures with alkali-metal iodides was performed in an atmosphere of hydrogen.

Figure 1 presents the absorption spectra of melts in the systems $CsBr—CoBr_2$ and $CsJ—CoJ_2$. Curve 1*a* represents the visible region of the absorption band of $CoBr_2$, which has an octahedral structure (4). The band has its main maximum at 625 m and an intense shoulder in the short-wavelength part of the spectrum. The absorption spectrum of CoJ_2 is not shown in the drawing. Anhydrous cobalt iodide is colored an intense black even in thin layers; its absorption band occupies the entire visible region of the spectrum and lacks clearly expressed structural details.

Curve 2*a* refers to the absorption of a melt of CsBr with $CoBr_2$ in a ratio of 0.9. As can be seen, the curve preserves the character of the octahedral band of $CoBr_2$, but its maximum is shifted into the long-wavelength region (635 m). In the spectrum of the 1 : 1 melt (curve 3*a*) a right-hand shoulder

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

appears in the region of 730 m . All these data indicate the existence of an octahedral complex compound of composition $CsCoCl_3$. The appearance of the right-hand shoulder in the spectrum of the 1 : 1 melt is probably connected with insufficient accuracy in the stoichiometry of the composition of the compound. $CsCoCl_3$ crystallizes from the melt in the form of needle-like emerald-green crystals, which, in contrast to $CoBr_2$, are comparatively stable with respect to atmospheric moisture. Powdered $CsCoCl_3$ in the course of a day changes in air into a blue hydrate form.

Curves 4*a* and 1*b* refer, respectively, to the absorption spectra of melts of CsBr with $CoBr_2$ and CsJ with CoJ_2 in a ratio of 2 : 1. Since the qualitative structure of the spectrum does not change with increasing molar fraction of cesium halide in the melt (curves 5*a* and 3*b*), the 2 : 1 melt should be regarded as an individual congruent complex compound Cs_2CoI_4. According to available data (5), Cs_2CoBr_4 has a tetrahedral structure. A similar structure

is usually also assumed for cobalt tetraiodides^(6). It may therefore be said that the absorption bands with maxima at 670, 700, and 725 mμ in the case of bromides and at 710, 740, and 790 mμ for iodides are associated with a tetrahedral crystal field.

The systems RbBr–$CoBr_2$, RbJ–CoJ_2 (Fig. 2) and the systems KBr–$CoBr_2$, KJ–CoJ_2 (Fig. 3) are close to one another. In all cases tetrahedral complexes of composition $Me_2Co\Gamma_4$ are formed. The absorption spectra of melts in these systems with a component ratio of 1 : 1 have features of octahedral and tetrahedral complexes. Melts with large molar fractions of alkali halides retain the spectral features characteristic of tetrahedral complexes. The latter fact indicates the absence of compounds with coordination in the inner sphere other than tetrahedral.

Fig. 1. Absorption spectrum of melts in the systems CsBr–$CoBr_2$ (a), CsJ–CoJ_2 (b). The numbers correspond to the following molar ratios $Cs\Gamma/Co\Gamma_2$: 1a –0; 2a –0.9; 3a –1; 4a, 1b –2; 5a –129; 2b, 3b –27

Fig. 2. Absorption spectrum of melts in the systems RbBr–$CoBr_2$ (a), RbJ–CoJ_2 (b). The numbers correspond to the following molar ratios $Rb\Gamma/Co\Gamma_2$: 1a –1; 2a, 1b –2; 3a –90; 2b –3; 3b –25

In the systems NaBr–$CoBr_2$, NaJ–CoJ_2, LiBr–$CoBr_2$, LiJ–CoJ_2, complex compounds were not detected spectrophotometrically. At the same time, judging from the change in color of the crystalline phases, in the sodium systems at

Fig. 3 and Fig. 4: absorption spectra and differential absorption curves

Figure 3: Fig. 3 and Fig. 4: absorption spectra and differential absorption curves

high temperatures very limited solid solutions are formed, in which the cobalt ions are surrounded by ligands not in an octahedron, whereas upon lowering the temperature the character of the environment becomes octahedral. In the lithium systems the solid solutions are probably also limited, although they occupy a broader range of component ratios. Moreover, in the region of high concentrations of cobalt halides, solid solutions with an octahedral environment of cobalt ions are formed immediately. In the region of high concentrations of alkali halides, nonoctahedral solid solutions are initially formed, which upon cooling undergo transformation in the solid phase.

The data obtained, as well as the data of the preceding work^(1), convincingly show that cobalt ions in crystalline halide complex compounds can create around themselves both octahedral and tetrahedral coordinations.

The tendency toward entry into octahedra rapidly decreases along the series F^(7)—J in accordance with the decrease in the strength of the crystal field. At the same time, along this same series the strength of the Co—Γ bond also decreases. Indeed, in the chloride system not a single tetrahedral complex (in air) undergoes hydration, i.e., transition to an aquacomplex. In the bromide system K_2CoBr_4 becomes hydrated. In the iodide system only Cs_2CoJ_4 is stable toward atmospheric moisture. These facts also indicate a rapid decrease in the stability of complex compounds along the series Cs—Na. Since the latter is not connected with a change in

forces of the crystal field, the notion of a counterpolarizing or screening action of the outer sphere cannot serve as an explanation for the change in the stability of the complexes. The decrease in the stability of the complex cobalt halides in the series Cs—Na is probably explained by the increase, in the same series, of the lattice energies of the alkali-metal halides.

Data on the absorption spectra of crystalline complex compounds make it possible to approach in a new way the interpretation of the results of spectrophotometric measurements in nitrate melts (8). From Figs. 1 and 3 (8)

Fig. 3. Absorption spectra of melts in the systems KBr—$CoBr_2$ (*a*), KJ—CoJ_2 (*b*). The numbers correspond to the following molar ratios K /Co$_2$: 1*a*—1; 2*a*, 1*b*—2; 3*a*—100; 2*b*—41

Fig. 4. Differential absorption curves of 0.00248 *M* solutions of $Co(NO_3)_2$ in a nitrate melt containing various amounts of KBr (*a*) and KJ (*b*). The numbers correspond to the differences between the following pairs of molar concentrations K : 1*a*—1.000 and 0.319; 2*a*—0.319 and 0.160; 3*a*—0.160 and 0.000; 1*b*—0.319 and 0.200; 2*b*—0.200 and 0.080; 3*b*—0.160 and 0.080; 4*b*—0.080 and 0.000

it is evident that, with increasing concentration of alkali halide in a nitrate melt containing $Co(NO_3)_2$, the absorption curves tend to assume the form characteristic of tetrahedral complexes. The stepwise complex formation and the formation of the highest tetrahedral complex ion $[Co\ _4]^{2-}$ are especially clearly manifested in the differential light-absorption curves presented in Fig. 4 (constructed from the data of (8)). As can be seen, in both the bromide and iodide systems at least three types of complex ions are formed. Taking into account that the center of gravity of the absorption band of the octahedral ion $[Co(NO_3)_6]^{4-}$ belongs at 550 mμ, of octahedral $[CoBr_6]^{4-}$ at 625 mμ, of tetrahedral $[CoBr_4]^{2-}$ at 725 mμ, and of tetrahedral $[CoJ_4]^{2-}$ at 790 mμ, the complex ions formed in the nitrate melt must be assigned a tetrahedral structure and the composition $[Co(NO_3)_2Br_2]^{2-}$ (640 mμ), $[Co(NO_3)Br_3]^{2-}$ (700 mμ), $[CoBr_4]^{2-}$ (720 mμ), $[Co(NO_3)_2J_2]^{2-}$ (possibly 640 mμ), $[Co(NO_3)J_3]^{2-}$ 700 or 760 mμ), $[CoJ_4]^{2-}$ (780 mμ).

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REFERENCES

1. I. V. Tananaev, B. F. Dzhurinskii, DAN, **139**, No. 1 (1961).
2. G. Crut, Bull. Soc. chim. France, (4), **35**, 550 (1924).
3. I. V. Tananaev, S. M. Petushkova, G. V. Shpineva, ZhNKh, **3**, issue 5, 1071 (1958).
4. R. Newman; R. M. Chrenko, Phys. Rev., **115**, No. 5, 1147 (1959).
5. G. N. Tishchenko, Z. G. Pinsker, Abstract of dissertation of G. N. Tishchenko, Moscow, 1953.
6. R. N. Holm, F. A. Cotton, J. Chem. Phys., **31**, No. 3, 788 (1959).
7. M. A. Poraĭ-Koshits, Abstract of dissertation, Moscow, 1959; DAN, **134**, No. 5, 1104 (1960).
8. I. V. Tananaev, B. F. Dzhurinskii, DAN, **135**, No. 1, 94 (1960).

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