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Abstract

Full Text

CHEMISTRY

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STRUCTURE OF THE SPECTRAL ABSORPTION BANDS OF THE COMPLEXES $Co(H_2O)_6^{2+}$ AND $Co(OR_1R_2)_6^{2+}$ IN SOLUTIONS IN THE REGION 25 000–13 000 cm^{-1}

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In the spectroscopy of complex compounds it is often suggested that the nearest hydrate environment of Co^{2+} ions in dilute aqueous solutions has the structure of a regular octahedron ($^{1-4}$). Such a conception of the structure of the inner sphere of the aquo complex formed in aqueous solutions of Co(II) salts is based on the fact that, in the electronic absorption spectrum of these solutions, absorption bands with maxima at ~ 8000 cm^{-1} and 19 500 cm^{-1} are observed; the latter of these is assumed to have a doublet structure ($^{1-8}$) and to be the result of the superposition of two bands.

Fig. 1. *A*—curve of the spectral absorption of $Co(H_2O)_6^{2+}$ ions in aqueous solutions. *B*—curve

$$\frac{d\chi_2}{d\lambda} = f(\lambda).$$

λ—wavelength, χ_2—molar absorption coefficient.

The presence in the electronic spectrum of the hydrated Co^{2+} ion of three frequencies of maximum absorption is in good agreement with the assumption that the ^4F term of this ion is split by a ligand field of cubic symmetry into three components, and can be explained by transitions of the $Co(H_2O)_6^{2+}$ ion from the ground state $^4T_{1g}(F)$ to the states $^4T_{2g}(F)$, $^4A_{2g}(F)$, $^4T_{1g}(P)$.

At the same time, the assumption of cubic symmetry of the $Co(H_2O)_6^{2+}$ complex contradicts the fact of asymmetry of the field of the Co^{2+} ion, as a result of

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

which $Co(H_2O)_6^{2+}$ should have the structure of a distorted octahedron ([9]), and in the electronic spectrum of this complex not three, but a larger number of absorption-maximum frequencies should be observed.

In connection with the above, there arises a need for a detailed study of the contour of the spectral absorption curves of dilute aqueous solutions of Co(II) salts in the region 40 000-7000 cm^{-1}. Especially necessary is a careful investigation of the absorption band located in the range 25 000-15 000 cm^{-1}, since judgments concerning the symmetry of the nearest hydrate environment of the Co^{2+} ion in solutions are based to a considerable extent on the doublet structure of this band.

This investigation was carried out by us on aqueous solutions of $Co(ClO_4)_2$,

$CoSO_4$, $CoCl_2$ at an ion concentration of Co^{2+} 0.1-0.01 g-ion/l. In such systems the absorbing centers are the ions $Co(H_2O)_6{}^{2+}$ ([4], [10], [11]).

Measurement of spectral-absorption curves point by point is inevitably associated with some scatter in the optical-density readings and with the possibility of missing details in the contour of the curves. We used this method only when working in the spectral region 13,000-7000 cm^{-1}. Measurement of the absorption curves of solutions of Co(II) salts in the region 25,000-13,000 cm^{-1} was carried out on an SF-10 recording spectrophotometer. The absorption spectra,

Fig. 2. Spectral-absorption curve of solutions of $Co(ClO_4)_2 \cdot 6H_2O$ in ethyl, *n*-butyl, *n*-amyl, and *n*-octyl alcohols

Fig. 3. Spectral-absorption curve of solutions of $Co(ClO_4)_2 \cdot 6H_2O$ in acetone and in diisopropyl ketone

measured on this instrument, are reproduced very well; the spectral slit width is sufficiently small (0.5-1.5 mμ), and omissions of details in the structure of the absorption bands are excluded.

Figure 1 shows the spectral-absorption curve of $Co(H_2O)_6{}^{2+}$ ions obtained in our experiments. The curve has not a doublet, but a considerably more complex structure. The inflection points on this curve are observed especially well when the spectrum is recorded on a sheet of unruled paper and at an optical density of the solution of 0.3-0.6. The same figure gives the curve $d\chi_2/d\lambda = f(\lambda)$, obtained by graphical differentiation of the absorption curve. From the data presented it is seen that, in the region 25,000-15,000 cm^{-1}, the absorption band of $Co(H_2O)_6{}^{2+}$ ions in solution is the result of superposition not of two, but of at least four absorption bands.

The intensity distribution in the spectrum of the solutions studied did not change upon introduction into them of large amounts of $HClO_4$ (up to 5 g-mol/l). This fact rules out the assumption of overlap between the absorption bands of $Co(H_2O)_6{}^{2+}$ ions and the absorption bands of hydroxo complexes of Co(II).

The oscillator strength is determined by the chemical nature of the coordinated particles and by the nature of the outer sphere of the complex.

If the absorption band of $Co(H_2O)_6{}^{2+}$ ions is indeed the result of superposition of four absorption bands, then it may be expected that, upon complete replacement of the water molecules in this complex by other oxygen-containing addends, the complex structure of the adsorption band will in some cases appear more distinctly.

Figures 2 and 3 present the spectral-absorption curves of solutions of $Co(ClO_4)_2 \cdot 6H_2O$ in anhydrous ethyl, *n*-butyl, *n*-amyl, and *n*-octyl alcohols, and also in acetone and in diisopropyl ketone.

Since the concentration of $Co(ClO_4)_2 \cdot 6H_2O$ in these solutions did not exceed 0.1 g-mol/l, it may be assumed that all the water of the inner sphere of the aquo-complex is displaced by molecules of the organic solvent and that the absorption curves shown belong to the ions $Co(OR_1R_2)_6{}^{2+}$.

Such an assumption is confirmed by the following facts.

1. The absorption spectra of solutions of $Co(ClO_4)_2 \cdot 6H_2O$ in alcohols and ketones at $C_{Co^{++}} \leq 0.1$ g-ion/l are identical with the spectra of solutions of $Co(ClO_4)_2 \cdot 4H_2O$ and

$Co(ClO_4)_2 \cdot 2H_2O$ in the same solvents, which can occur only in the absence in these solutions of complexes of the type $[Co(H_2O)_2(OR_1R_2)_4]^{2+}$.

2. Analysis of the distillate driven off at 20° from a 0.1 M solution of $Co(ClO_4)_2 \cdot 6H_2O$ in C_2H_5OH, carried out by us by Fischer' s method, showed a water content in the distillate of 0.6 g-mol/l. Since the composition of the liquid and vapor for the $C_2H_5OH{-}H_2O$ system is the same at low H_2O content, the concentration of free water in a 0.1 M solution of $Co(ClO_4)_2 \cdot 6H_2O$ in C_2H_5OH is 0.6 g-mol/l; consequently, all the water in such a solution has been displaced from the inner sphere of the complex.

The spectra of solutions of Co(II) complexes with oxygen-containing organic ligands are very similar to the spectrum of $Co(H_2O)_6^{2+}$ in aqueous solutions. Replacement of H_2O molecules in the complex by molecules of alcohols and ketones is accompanied by a small bathochromic effect (1-5 mμ) and by a change in the magnitude of the absorption coefficient (up to 20%). At the same time, the complex structure of the absorption curves of Co(II) complexes with organic addends is more clearly expressed than in $Co(H_2O)_6^{2+}$ ions in aqueous solutions. This structure appears especially sharply in the absorption curves of solutions of ketone complexes.

The presence in the absorption spectrum of the $Co(H_2O)_6^{2+}$ ion of five frequencies of maximum absorption: 8100 cm^{-1}, 16000 cm^{-1}, 19450 cm^{-1}, 20650 cm^{-1}, 21400 cm^{-1}, and not three frequencies, as is accepted in spectral investigations of the structure of $Co(H_2O)_6^{2+}$ in solutions, deprives us of the right to regard the electronic absorption spectra of dilute aqueous solutions of Co(II) salts as direct proof of the cubic symmetry of the $Co(H_2O)_6^{2+}$ ion.

The spectrum of $Co(H_2O)_6^{2+}$, as well as the spectra of $Co(OR_1R_2)_6^{2+}$ ions presented in this work, can be explained by assuming that these complexes have the structure of a distorted octahedron. At the same time, the same spectra may be assigned to Co(II) complex ions having cubic symmetry, if it is assumed that, along with electronic transitions from the ground state $^4T_{1g}(F)$ to the states $^4T_{2g}(F)$, $^4A_{2g}(F)$, $^4T_{1g}(P)$, transitions are also possible from $^4T_{1g}(F)$ to states that arise from the ^2G, ^2H, ^2D terms of the Co^{2+} ion under the action of the cubic ligand field. Literature data[12] on the energetics of the free Co^{2+} ion confirm the possibility of such an assumption: the energy of the ^2G, ^2H, ^2D states of Co^{2+} is $\sim$ 17000–23500 cm^{-1}.

An unambiguous solution of the question of the structure of $Co(H_2O)_6^{2+}$ and $Co(OR_1R_2)_6^{2+}$ ions in solutions requires additional spectral data.

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