Behavior of Co$^{2+}$ Cations in the Aqueous and Alcoholic Solution of CoCl$_2$·6H$_2$O

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We investigated the optical properties of Co$^{2+}$ cations in the aqueous and alcoholic solution of CoCl$_2$·6H$_2$O at room temperature. We measured the absorption spectra of these solutions in the spectral region 395–800 nm. The Racah parameters and the exchange integrals of the aqueous complex [Co(H$_2$O)$_6$]$^{2+}$ are calculated. The parameters $D_0$ and $D_x$ are also calculated on the basis of our experimental data. The parameters $\delta$ and $\delta^2$ which are connected with the symmetry of this complex are also determined.

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1. Introduction

The cations of 3d metals in water and alcohol create aqueous complexes. The creation and stability of the aqua cations are important. The number of water molecules which are connected with the metal by the direct bonds metal–oxygen determines the properties of the complex. The classical investigations, for example: mobility of the ions, ionic radius of the hydration ions and the entropy of hydration do not give detailed information for the aqua ions. This is the reason for the investigation of their spectral properties. These properties depend on the composition and the symmetry of the surrounding medium. The aim of this work is connected with the investigation of the spectral properties of Co$^{2+}$ in the aqua complexes.

2 Experimental results and discussion

The experimental setup for measurement of the absorption coefficient in the visible region consists of the following: a halogen lamp with a stabilized 3H-7 rectifier, a 2500 monochromator, a system of quartz lenses, a detector, a SPM-2 monochromator, a system of quartz lenses, a polarizer, sample holder, and a Hamamatsu S2281-01 detector. The concentration of CoCl$_2$·6H$_2$O in the water and the ethanol is 1%. The color of the aqueous solution is pink and the color of the alcoholic one is blue. This means that they are respectively two kinds of the cobalt complexes — octahedral and tetrahedral. The thickness of the cuvette is $d = 0.995$ cm. The absorption spectra of the complexes [Co(H$_2$O)$_6$]$^{2+}$ and [Co(H$_2$O)$_4$]$^{2+}$ in the spectral region 395–800 nm are presented in Fig. 1a,d. It is seen that the cobalt structure has complicated shape and we calculated the first derivative of absorption coefficient for determination of the number of electron transitions in these ions (Fig. 1b,e). The second derivative of the absorption coefficient is calculated for the establishment of the exact energetic position of the electron transitions (Fig. 1c,f).

The electronic spectra of the cobalt complexes can give very important structural information in many cases. Most six coordinated complexes have high spin electronic configuration. Their basic state is $^4T_{1g}$ and the spin-orbit interaction is considerable. The band around 20000 cm$^{-1}$ for the octahedral complex [Co(H$_2$O)$_6$]$^{2+}$ is determined by the transition $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$. The spectral shoulder appears from the short wavelengths of the absorption spectrum in view of the fact that the spin-orbit interaction in the excited state $^4T_{1g}(P)$ removes the degeneracy [1].

Fig. 1. Spectrum of absorption of the complexes [Co(H$_2$O)$_6$]$^{2+}$ and [Co(H$_2$O)$_4$]$^{2+}$ in the spectral region 395–800 nm (a, d); calculated first derivative of the absorption spectrum in the same spectral region (b, e); calculated second derivative of the absorption coefficient (c, f).

The ion Cl$^-$ is situated before H$_2$O in the spectrochemical sequence of the ligands and our solution has $\omega = 1\%$. The result of this fact is that the tetrahedral complexes [CoCl$_4$]$^{2-}$ do not form in the aqueous and alcoholic medium. In the future, our investigations are connected with the augmentation of the concentration of CoCl$_2$·6H$_2$O in the solution. Our expectation is that the tetrahedral complex anions [CoCl$_4$]$^{2-}$ will be created.

The matrix of the energetic states $^4T_{1g}(F)$ and $^4T_{1g}(P)$ is

$$\begin{vmatrix} -6D_q - E & 4D_q \\ 4D_q & -x - E \end{vmatrix} = 0,$$

with $E(4T_{2g}) = 2D_q$ and $E(4A_{2g}) = 12D_q$. If $D_q = 843$ cm$^{-1}$ and $x = E(4P - 4F) = 11215$ cm$^{-1}$, we can determine two absorption
bands in our case (Fig. 1a). The absorption band which corresponds with the transition $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ must be situated at 15576 cm$^{-1}$ (Fig. 1). Very small absorption is observed $[2, 3]$ in this spectral region and this shows that if the theory is correct then the transition $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ must appear because two of the electrons which are coupled on the following transition: one electron with unpaired spin $\sigma$ and another electron with unpaired spin $\pi$. The manifestation of the first maximum explains the tetrahedral complex consists of two maxima (Fig. 3). The parameters $\sigma$ and $\pi$ are determined as follows: $\delta\sigma = \sigma_z - \sigma_{xy} = -(12/8)Ds - (15/8)Dt$, $\delta\pi = \pi_z - \pi_{xy} = -(3/2)Ds + (5/2)Dt$. The parameter $\sigma$ is anticonnecing and $\pi$ anticonnecing properties of the ligands. Finally, $\sigma = -1$ and $\pi = 1225$. The Racah parameters of the complex $[Co(H_2O)_6]^{2+}$ are $B = 84$ cm$^{-1}$ and $C = 389$ cm$^{-1}$. The spectral structure of Co$^{2+}$ in the tetrahedral complex consists of two maxima (Fig. 3). The manifestation of the first maximum explains with the following transition: one electron with unpaired spin traverses from $e_g$ to $t_{2g}$ orbital (Fig. 1d). The second maximum appears because two of the electrons which are coupled on $e_g$ orbital traverse to $t_{2g}$ orbital (Fig. 1f).

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3. Conclusions

The Co$^{2+}$ cations are situated in the octahedral coordination when the solution is aqueous and they are in the tetrahedral one when the solution is alcoholic. In these two cases the 3d electron transitions are three, but their spectral position is different. The different coordination gives different color of the solution and its optical properties are also different. The final conclusion is that the Jahn–Teller effect has predominant role in the complex $[Co(H_2O)_6]^{2+}$ and the spin–orbit interaction has predominant role in the complex $[Co(H_2O)_4]^{2+}$.

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References