

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

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We investigated the optical properties of Co^{2+} cations in the aqueous and alcoholic solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ 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 $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ are calculated. The parameters D_t and D_s are also calculated on the basis of our experimental data. The parameters $\delta\sigma$ and $\delta\pi$ which are connected with the symmetry of this complex are also determined.

DOI: 10.12693/APhysPolA.123.207

PACS: 78.15.+e, 78.40.Dw

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, ostensible radii 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 SPM-2 monochromator, a system of quartz lenses, a polarizer, sample holder, and a Hamamatsu S2281-01 detector. The concentration of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ 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 $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Co}(\text{H}_2\text{O})_4]^{2+}$ 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.

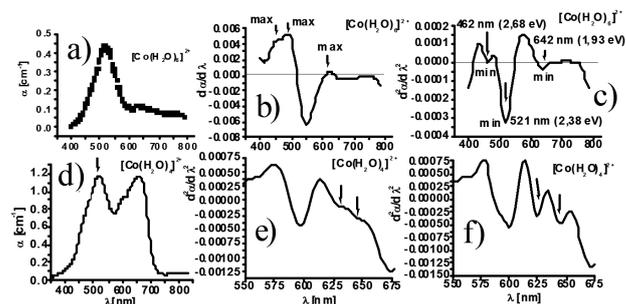


Fig. 1. Spectrum of absorption of the complexes $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Co}(\text{H}_2\text{O})_4]^{2+}$ in the spectral region 395–800 nm (a, d); calculated first derivative of the absorption coefficient in the same spectral region (b, e); calculated second derivative of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

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 $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ 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].

The ion Cl^- is situated before H_2O in the spectrochemical sequence of the ligands and our solution has $\omega = 1\%$. The result of this fact is that the tetrahedral complexes $[\text{CoCl}_4]^{2-}$ do not form in the aqueous and alcoholic medium. In the future, our investigations are connected with the augmentation of the concentration of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in the solution. Our expectation is that the tetrahedral complex anions $[\text{CoCl}_4]^{2-}$ will be created.

The matrix of the energetic states ${}^4T_{1g}(F)$ and ${}^4T_{1g}(P)$ is
$$\begin{vmatrix} -6Dq - E & 4Dq \\ 4Dq & x - E \end{vmatrix} = 0, \text{ with } E({}^4T_{2g}) = 2Dq \text{ and } E({}^4A_{2g}) = 12Dq. \text{ If } Dq = 836\text{ cm}^{-1} \text{ and } x = E({}^4P - {}^4F) = 11215\text{ cm}^{-1}, \text{ we can determine two absorption$$

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 with very small intensity. The theoretical investigation leads to the same conclusion. The double maximum which is observed in this absorption band is determined by the spin-orbit splitting of the state ${}^4T_{1g}(P)$ [4]. In our case $E({}^4T_{2g}) = 1672 \text{ cm}^{-1}$, and $E({}^4A_{2g}) = 10032 \text{ cm}^{-1}$. The exchange integrals $K(z^2, xz) = K(z^2, yz) = 17391 \text{ cm}^{-1}$ have important role when the complex $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ changes its symmetry from O_h to D_{4h} . This means that the deformation of the octahedral complex of cobalt realizes the interaction between z^2 orbital and, respectively, the orbitals xz and yz . The tetragonal distortion of the octahedral complex has full potential $V(D_{4h}) = V_{O_h} + V_{D_{4h}}$ (1). If we know the matrix elements we will have the value of the parameter Dq and the radial parameters Ds and Dt . The parameter Dt determines the difference between the equatorial and the axial center: $Dt = (4/7)[Dq(xy) - Dq(z)]$. If we use the approximation of the theory of the ligand field, then $Dq \sim (1/r)^5$, where r is the length of the bond M–O. Hence $r(xy)/r(z) = [Dq(z)/Dq(xy)]^{1/6} = 0.895$. For our complex $Dq(z) = 508 \text{ cm}^{-1}$ and $Dq(xy) = 1000 \text{ cm}^{-1}$.

The value of Dt is 280 cm^{-1} . The parameter $Ds = -350 \text{ cm}^{-1}$ is definite from the equation $\Delta_2 = 10Dq + 4Ds + 5Dt$ (Fig. 2). The symmetry of the complex is such that e_g and t_{2g} orbitals of the metal correspond only on σ anticonnecting and only on π anticonnecting orbitals [5]. The parameters $\delta\sigma$ and $\delta\pi$ 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 parameters σ and π are indirect indicator for the σ anticonnecting and π anticonnecting properties of the ligands. Finally, $\delta\sigma = -1$ and $\delta\pi = 1225$. The Racah parameters of the complex $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ are $B = 84 \text{ cm}^{-1}$ and $C = 389 \text{ cm}^{-1}$. 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).

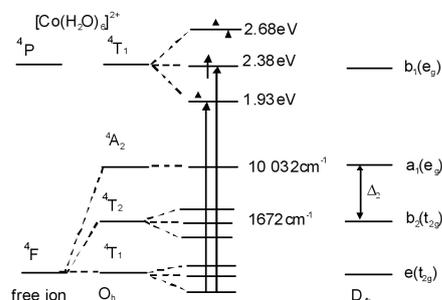


Fig. 2. Energetic diagram of the transitions of 3d electrons in the cation Co^{3+} .

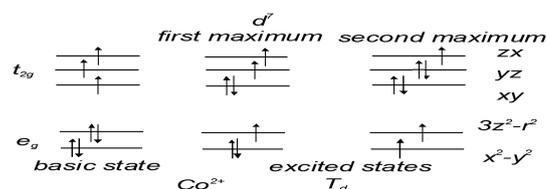


Fig. 3. The energetic diagram of Co^{2+} in T_d symmetry.

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 $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and the spin–orbit interaction has predominant role in the complex $[\text{Co}(\text{H}_2\text{O})_4]^{2+}$.

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