Electron transitions in Cr\(^{2+}\) in the aqueous solutions of MgSO\(_3\).6H\(_2\)O:Cr

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Abstract. In this work, the absorption of the complex [Cr(H\(_2\)O\(_6\))]\(^{2+}\) is measured in the spectral region 375 – 900 nm. The aqueous solutions of MgSO\(_3\).6H\(_2\)O:Cr are prepared with the concentrations 0.4%, 0.6% and 0.8%. The energies of the electron transitions in Cr\(^{2+}\) are calculated. The role of Jahn-Teller effect and the spin-orbit coupling is evaluated also. The magnetic susceptibility for chromium octahedral complex is calculated at room temperature.

1. Introduction
The cations of 3d metals in water 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 aqueous solutions of 3d ions salts manifest optical activity and interesting properties in magnetic field. This fact helped us when we decided to investigate these ionic liquids. In this work, the most important accent is on the existence and influence of [CrH\(_2\)O\(_6\)]\(^{2+}\) complex. Our analyses give answer of questions which are connected with the peculiarities of electron transitions in the complex and with the stability in this complex. The main aim in our work is the investigation of optical properties of complex [CrH\(_2\)O\(_6\)]\(^{2+}\) in the aqueous solutions with different concentrations.

2. Experimental details
The experimental set up for the measurement of the absorption coefficient in the visible region consisted of the following: a halogen lamp with a stabilized 3H-7 rectifier, a SPM-2 monochromator, a system of quartz lenses, a polarizer, a crystal sample holder, and a Hamamatsu S2281-01 detector. The thickness of the used cuvette is \(d = 0.995\) cm. The basic substance in the solutions is CrCl\(_2\).6H\(_2\)O. The basic components in both aqueous solutions are: Mg\(^{2+}\), SO\(_4^{2-}\), 2Na\(^+\) + 2Cl\(^-\) and Na\(^+\) + HSO\(_3^-\).
3. Results and Discussion
The absorption coefficient of the investigated samples has been measured to be between 375 nm and 900 nm (figure 1).

Figure 1. Absorption spectra of aqueous solutions of MgSO$_3$.6H$_2$O:Cr with the concentrations 0.4%, 0.6% and 0.8%.

The first derivative of the absorption coefficient at photon energy is calculated to be in the 375-700 nm spectral region. The $[d\alpha/d(h\nu)]$ determines only the number of electron transitions in a Cr$^{2+}$ ions and it does not give an exact information about the energy position of these transitions (figure 2). This is the reason for the calculation of the second derivative of the absorption coefficient $[d^2\alpha/d(h\nu)^2]$ (figure 3). The absorption coefficient is calculated using the formula:

$$\alpha = \frac{(1/d)\ln(I_0/I)}{d}$$  \hspace{1cm} (1)

where $I_0$ is the intensity of the incident light, $I$ is the intensity of the passing light and $d$ is the sample thickness.

In the case of large crystal field splitting 10Dq and partially occupied shell t$_{2g}$, the system moment is isotropic in spite of big value of the orbital moment (figure 4). Sometimes, the t$_{2g}$ electrons could be compared with p electrons [1]. The orbital system moment becomes anisotropic when the O$_h$ is tetragonally distorted. The two groups of orbitals e$_g$ and t$_{2g}$ in O$_h$ are splitted additionally in D$_{4h}$ of four groups (a$_{1g}$, b$_{1g}$, b$_{2g}$ and e$_g$). The groups of orbitals a$_{1g}$, b$_{1g}$ and b$_{2g}$ are non-degenerate and the orbital group (e$_g$) remains double degenerate. The energy of the system changes when it must realize the transition O$_h$ → D$_{4h}$. If our complex ML$_6$ (in the symmetry O$_h$) transforms to ML$_4$X$_2$ (in the symmetry D$_{4h}$) we have to choose preliminary the deformation direction. If the ligand X determines weaker ligand field we can expect that the electrostatic repulsion between d electrons and charges of ligand X is weaker in comparison with the other two coordination axes. The picture is analogous, if the M – X distances are longer than M – L distances. This is the situation of the octahedron extended along z axis. The splitting eg → a$_{1g}$, b$_{1g}$ realizes by the transition O$_h$ → D$_{4h}$ and we know that the energy of a$_{1g}$ (d$_{z^2}$) is smaller than this of b$_{1g}$ (d$_{x^2}$ – d$_{y^2}$). The parallel splitting t$_{2g}$ → b$_{2g}$ + e$_g$ satisfies inequality e$_g$ (d$_{xz}$, d$_{yz}$) < b$_{2g}$(d$_{xy}$). This result follows the fact that d orbitals a$_{1g}$ and e$_g$
have angular part which includes the coordinate $z$ [13]. The real orbital functions are used as a basis for the states $e_g$ and $t_{2g}$ [2].

The strength of the three-dimensional harmonic oscillator determines from the ratio of the real intensity and the intensity of the radiation of the electron. $f = 1$ for such “ideal electron”. The transitions of the oscillator classify by the strength $f$ and this connects the theory with the experiment.

**Figure 2a.** The calculated first derivative of absorption coefficient to the wavelength in the spectral region 375-700 nm.

**Figure 2b.** The calculated first derivative of absorption coefficient to the wavelength in the spectral region 375-700 nm.

**Figure 2c.** The calculated first derivative of absorption coefficient to the wavelength in the spectral region 375-700 nm.

$f = 1$ for the allowed transition; for single symmetric band:

$$f = 4.32 \times 10^{-9} \int \varepsilon(\lambda) d\lambda,$$

where $\varepsilon(\lambda)$ not depends on the concentration of the solutions [3]. The next equation
describes the connection between the oscillator strength $f_i$ and the transition moment of the impurity band $Q_i$, where $\nu_i$ is the frequency of the band centre. The strength of the oscillator $f_1 = 0.0196 \times 10^{-5}$ for [Cr(H$_2$O)$_6$]$^{2+}$ (0.4% solution), $f_2 = 0.31 \times 10^{-5}$ for [Cr(H$_2$O)$_6$]$^{2+}$ (0.6% solution) and $f_3 = 0.0405 \times 10^{-5}$ at room temperature ($T = 300K$). This means that the transitions are spin-allowed with forbidden pairing [4]. The transition moment of the impurity bands has next three values $Q_1 = 0.0599 \times 10^{-3}$, $Q_2 = 0.238 \times 10^{-3}$ and $Q_3 = 0.0862 \times 10^{-3}$.

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Q_i = \left( \frac{f_i}{\nu_i \times 1,096 \times 10^{11}} \right)^{1/2}
\]

(3)

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**Figure 3a.** The calculated second derivative of absorption coefficient to the wavelength in the spectral region 375-700 nm.

**Figure 3b.** The calculated second derivative of absorption coefficient to the wavelength in the spectral region 375-700 nm.

**Figure 3c.** The calculated second derivative of absorption coefficient to the wavelength in the spectral region 375-700 nm.
In this work, we have considered the Condon-Shortley parameters $F_2 = B + C/7$ and $F_4 = C/35$ for $[\text{Cr(H}_2\text{O)}_6]^{2+}$ [5]. These parameters are symbols which characterize the integrals of the electrons repulsion in the impurity ion. Each of the terms expressions which determines the energy dependence between the levels by the maximum multiplicity. The second parameter C stands for the energy difference between the different multiplicity terms. The Racah parameters are determined experimentally and for $\text{Cr}^{2+}$ ion, they have the following values: $B = 810 \text{ cm}^{-1}$ and $C = 3565 \text{ cm}^{-1}$, therefore $\gamma = C/B = 4.40$ [6].

The Jahn-Teller effect manifests in the octahedral chromium complexes and their symmetry changes to $D_{4h}$. This symmetry is unstable and the manifestation of spin-orbit interaction leads to the final symmetry $C_{4v}$. The parameters $D_q$, $D_s$ and $D_t$ are calculated by the equations:

$\Delta_1 = -3D_s + 5D_t = 1395 \text{ cm}^{-1}$

$\Delta_2 = 10D_q + 4D_s + 5D_t = 5436 \text{ cm}^{-1}$

$\Delta_3 = -4D_s -5D_t = 1289 \text{ cm}^{-1}$

Their values are respectively $7213 \text{ cm}^{-1}$, $383 \text{ cm}^{-1}$ and $49 \text{ cm}^{-1}$.

The symmetry of the complex is such that $e_g$ and $t_{2g}$ orbitals of the metal correspond only on $\sigma$ anticonnecting and only on $\pi$ anticonnecting orbitals [5]. The parameters $\delta\sigma$ and $\delta\pi$ are determined as follows:

$\delta\sigma = \sigma_z - \sigma_{xy} = -(12/8)D_s - (15/8)D_t$

$\delta\pi = \pi_z - \pi_{xy} = -(3/2)D_s + (5/2)D_t$.

The parameters $\sigma$ and $\pi$ are indirect indicator for the $\sigma$ anticonnecting and $\pi$ anticonnecting properties of the ligands. Finally, $\delta\sigma = 698$ and $\delta\pi = 483$.

It is convenient to introduce the exchange interaction $J(\text{dd})$ here, describing the intrashell exchange attraction between parallel spins [7]: $J(\text{dd}) = 1/14(F_2 + F_4)$ and the additional parameter describing the angular part of the multiplet splitting is $C(\text{dd}) = 1/14(9/7F_2 - 5/7F_4)$. The J and C are especially useful when describing the lowest state of an $l^l$ multiplet. The orbital quantum number $l = 2$ for d-electrons. According to Hund’s rule this is always the state with the highest possible spin quantum number. In our case, the values of $J(\text{dd})$ and $C(\text{dd})$ are as follows: $7830 \text{ cm}^{-1}$ and $3641 \text{ cm}^{-1}$. The next equations are fulfilled for our glass systems $F_2 = 49F_2$ and $F_4 = 441F_4$, where $F_2$ and $F_4$ are the Condon–Shortley parameters. The energy of levels $5D$ and $3H$ from the experiment is connected with $F_0$, $F_2$ and $F_4$ as follows [8]:

$E(5D) = 6F_0 - 21F_2 - 189F_4$, $E(3H) = 6F_0 - 17F_2 - 69F_4$. The energetic difference $E(3H) - E(5D) = 4F_2 + 120F_4$ is $17 516 \text{ cm}^{-1}$.

![Figure 4. Energy diagram of the Cr$^{2+}$ ion in the octahedral coordination.](image)
The Cr$^{2+}$ ions are paramagnetic. If the metal complexes Cr(H$_2$O)$_6^{2+}$ interact with the external magnetic field then the spin magnetic moment is expressed as

$$\mu_{\text{eff}} = \left[ N(N+2) \right]^{1/2},$$  \hspace{1cm} (4)

where $N$ is the number of the unpaired electrons [5]. In our case $N = 4$ and $\mu_{\text{eff}} = 4.90$ ($S = 2$). On the other hand

$$\mu_{\text{eff}} = g_e[S(S+1)]^{1/2},$$  \hspace{1cm} (5)

and $g_e = 2$. The magnetic susceptibility can be calculated by the formula

$$\chi = \frac{N}{kT} \sum_n \left( \frac{E_n^{(1)}}{E_n^{(1)}} \right)^2,$$  \hspace{1cm} (6)

where $N = 4$, $k$ is Boltzmann constant, $T = 300$ K and $E_n^{(1)}$ are the values of the energy as follow $E_1^{(1)} = 1.89$ eV, $E_2^{(1)} = 2.06$ eV, $E_3^{(1)} = 2.74$ eV and $E_4^{(1)} = 2.9$ eV. The value of $\chi$ for the complexes [Cr(H$_2$O)$_6^{2+}$] is $\chi = 3680$.

4. Conclusions
The Jahn-Teller effect is stronger than the spin-orbit interaction in [Cr(H$_2$O)$_6^{2+}$] complex. Our experimental results show that $\delta_\sigma > \delta_\pi$. Therefore, there have been observed the crystal structures order in the aqueous solutions of MgSO$_3$.6H$_2$O:Cr. The strength of the oscillator and the transition moment of the impurity band are greater for [Cr(H$_2$O)$_6^{2+}$] in 0.6% aqueous solution.

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