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The structural distortion and Zeeman splitting of the complexes $CrCl_2(H_2O)_4^{2+}$ and $Cr(H_2O)_6^{2+}$

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In this work, we discuss the physicochemical properties of the complex $CrCl_2(H_2O)_4^{2+}$ in 1% solution of C_2H_5OH and the complex $Cr(H_2O)_6^{2+}$ in 1% aqueous solution of $CrCl_2.6H_2O$. The spin magnetic moment and the magnetic susceptibility are calculated after Zeeman splitting in the complexes.

Key words: structural distortion, Zeeman splitting, $CrCl_2(H_2O)_4^{2+}$, $Cr(H_2O)_6^{2+}$.

INTRODUCTION

The alcoholic 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 $CrCl_2(H_2O)_4^{2+}$ 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. Many authors have studied the absorption of the compound $CrCl_2.6H_2O$, but they not give information about the exact number of d electron transitions and about Zeeman splitting there. This is the main aim in our work.

EXPERIMENTAL

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.

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RESULTS AND DISCUSSION

The familiar colors of the transition metal ions in solutions are due to absorption bands which have their origins in electronic transitions within the 3d shell. The electric field of the nearest neighbour anions splits the energy levels of the unpaired d-electrons and electronic transitions between these split energy levels give rise to the observed "crystal field" spectra [1]. The measurement of absorption spectrum of 3d metal ions solutions helps us to understand how many unpaired d electrons are in the different complex structures. The absorption coefficient of $CrCl_2(H_2O)_4^{2+}$ and $Cr(H_2O)_6^{2+}$ complexes has been measured to be between 450 and 850 nm (Figs.1a and 2a). The calculated first derivative of the absorption coefficient at photon energy $[d\alpha/d(h\nu)]$ 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 (Figs.1b and 2b). This is the reason for the calculation of the second derivative of the absorption coefficient $[d^2\alpha/d(h\nu)^2]$ (Figs.1c and 2c). The absorption coefficient is calculated using the formula: (1) $\alpha = (1/d)\ln(I_0/I)$, where I_0 is the intensity of the incident light, I is the intensity of the passing light and d is the sample thickness. The interesting peculiarity in the absorption spectrum of $CrCl_2(H_2O)_4^{2+}$ is the presence of the "double exciton" at 450 nm (Fig. 1a). This exciton corresponds to the double excitation of two neighboring Cr^{2+} ions and the transition $^5T_2 \rightarrow {}^5E$ realizes at this wavelength [2]. The three

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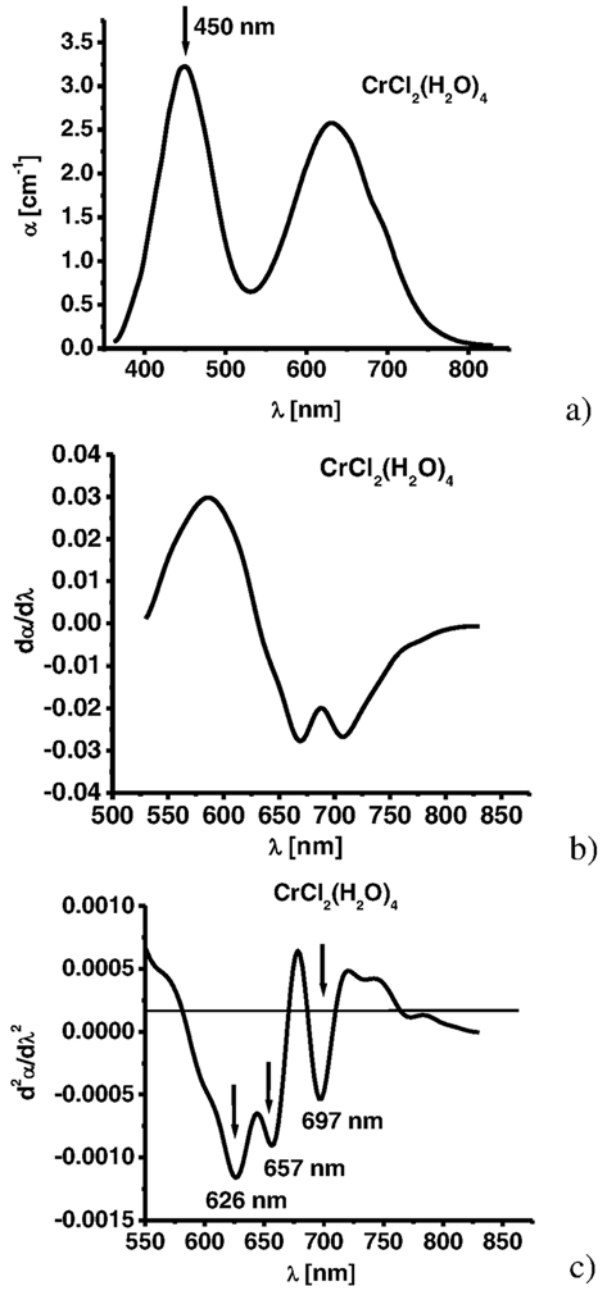

Fig. 1. a) The absorption coefficient α(E), b) first derivative dα/dE and c) second derivative $d^2\alpha/dE^2$ of the complex $CrCl_2(H_2O)_4^{2+}$

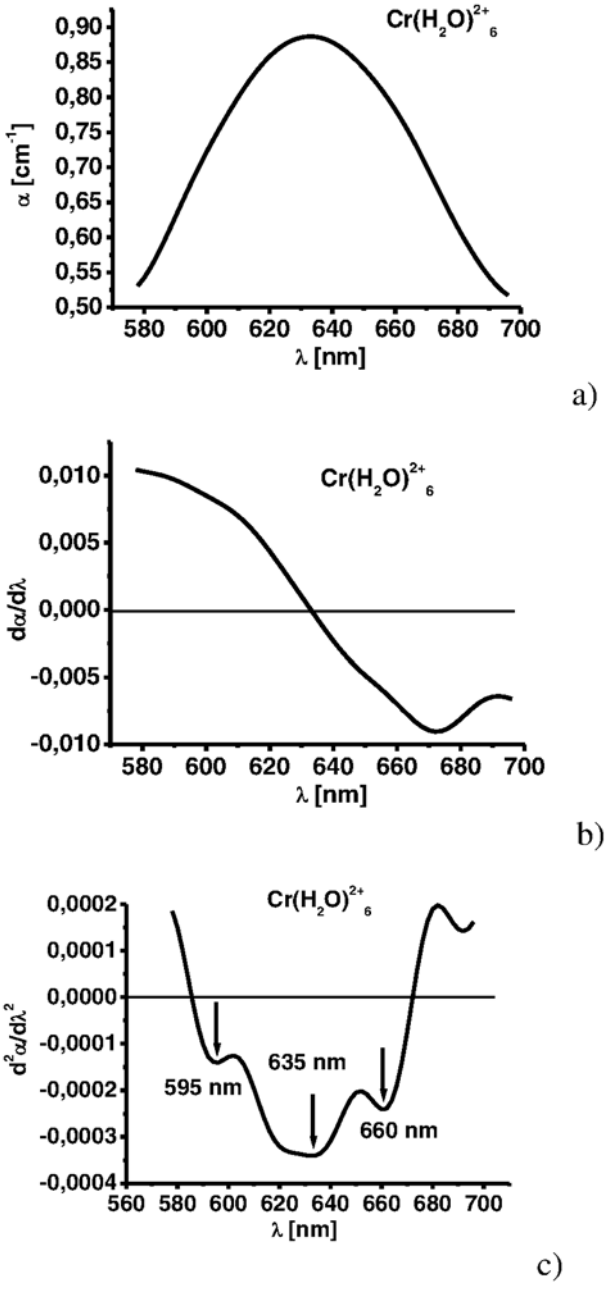

Fig. 2. a) The absorption coefficient α(E), b) first derivative dα/dE and c) second derivative $d^2\alpha/dE^2$ of the complex $Cr(H_2O)_6^{2+}$

electron transitions in the chromium ion realize from the level $^5E(^5D)$ to the level $^3T_1(^3H)$ (Fig. 3). The Cr^{2+} ions are paramagnetic. If the metal complexes $CrCl_2(H_2O)_4^{2+}$ and $Cr(H_2O)_6^{2+}$ interact with the external magnetic field then the spin magnetic moment is expressed as

$$\mu_{eff} = \sqrt{N(N+2)},$$

where N is the number of the unpaired electrons. In our case N = 3 and μ_{eff} = 3.87 (S = 3/2). On the other hand

$$\mu_{eff} = g_e\sqrt{S(S+1)}$$

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

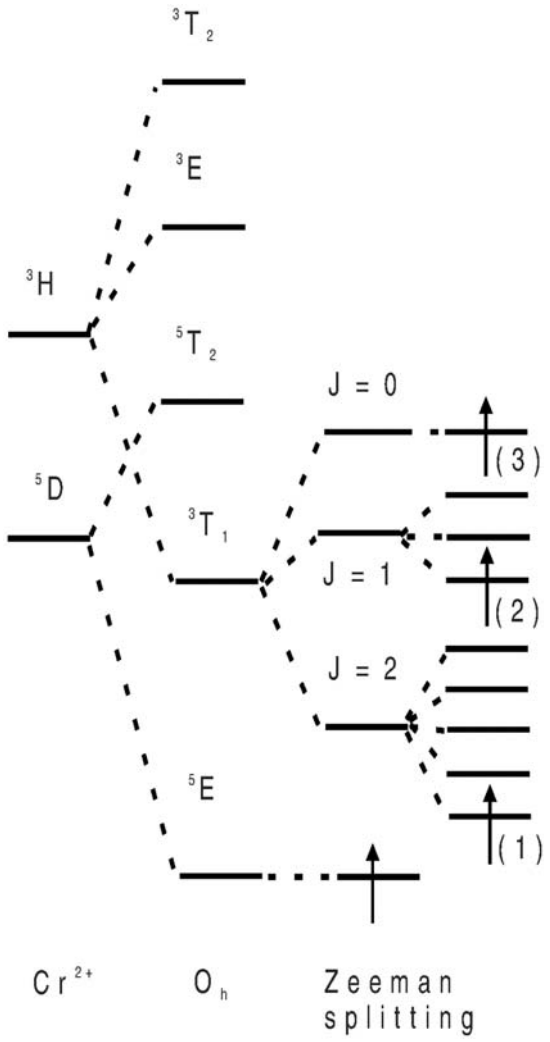

Fig. 3. The energetic diagram of Cr^{2+} ion in the octahedral symmetry

$$\chi = \frac{N}{kT}\sum_n (E_n^{(1)})^2 \ ,$$

where $N = 3$, k is Boltzmann constant, $T = 300$ K and $E_n^{(1)}$ are the values of the energy on Fig. 1c and 2c. The values of χ for the complexes $CrCl_2(H_2O)_4^{2+}$ and $Cr(H_2O)_6^{2+}$ are respectively: $\chi_1 = 728$ and $\chi_2 = 800$.

CONCLUSIONS

The interesting peculiarity in the absorption spectrum of $CrCl_2(H_2O)_4^{2+}$ is the presence of the "double exciton" at 450 nm.

Zeeman splitting appears at the level $^3T_1(^3H)$ in the chromium structure.

The magnetic susceptibility of the complex $Cr(H_2O)_6^{2+}$ has bigger value than this of the complex $CrCl_2(H_2O)_4^{2+}$.

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СТРУКТУРНА ДЕФОРМАЦИЯ И ЗЕЕМАНОВО РАЗЦЕПВАНЕ НА КОМПЛЕКСИТЕ $CrCl_2(H_2O)_4^{2+}$ И $Cr(H_2O)_6^{2+}$

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(Резюме)

В тази работа ние разглеждаме физикохимичните свойства на комплекса $CrCl_2(H_2O)_4^{2+}$ в 1% разтвор на C_2H_5OH и на комплекса $Cr(H_2O)_6^{2+}$ в 1% воден разтвор на $CrCl_2.6H_2O$. Изчислени са магнитният спинов момент и магнитната възприемчивост след Зееманово разцепване в комплексите. Интересна особеност в спектъра на поглъщане на $CrCl_2(H_2O)_4^{2+}$ е наличието на „двоен екситон“ при 450 nm. Зеемановото разцепване се проявява при нивото $^3T_1(^3H)$ в структурата на хрома. Магнитната възприемчивост на комплекса $Cr(H_2O)_6^{2+}$ има по-голяма стойност отколкото стойността ѝ за комплекса $CrCl_2(H_2O)_4^{2+}$.