Abstract. Formation of tetrahedral Co-complexes in CoBr₂/PEG systems is performed and analyzed. Different PEG types and new preparation methods are used. The UV-VIS absorption spectra of the samples are measured and examined. Almost pure tetrahedral and pseudo-tetrahedral bromo-Co-complexes have been achieved. A mechanism of the tetrahedral-like complex formation in CoBr₂/PEG systems is proposed.

Key words: tetrahedral Co-complexes, poly(ethylene glycol), UV-VIS spectra.

1. INTRODUCTION

The study of Co-salt/polymer systems has presented, recently, a special interest because of their various applications in numerous electrochemical fields [1]. Beside other investigation techniques (X-ray absorption, Differential Scanning Calorimetry, etc.) the Ultraviolet-Visible (UV-VIS) spectroscopy brings very important information about the local environment of the transition metal ions. Optical spectrophotometric studies show that Co-complexes formation in Co-salt/polymer systems is similar to the formation of the Co-complexes in cobalt-halides/ acetone solutions [2–4].

Early spectrophotometric studies [5, 6] of the cobalt-salt/acetone showed a stepwise formation of Co-Br complexes on the addition of increasing amounts of LiBr. There are three types of tetrahedral (or pseudo-tetrahedral) Co-complexes: [CoBr₂Ac₂], [CoBr₃Ac]⁻ and [CoBr₄]²⁻ where Ac is a ligand from the acetone molecule (probable the Oxygen ion). Lately, Mendolia [2] made a similar study on CoBr₂ in Poly(TetraMethylene Glycol) (PTMG) and Poly(Ethylene Glycol) (PEG). He also obtained the Co-complexes by adding LiBr.

In this paper we are analyzing the optical spectra of the tetrahedral Co-complexes in CoBr₂/PEG systems using various PEG chain lengths and various preparation methods. All types of tetrahedral and pseudo-tetrahedral Co-complexes
were obtained without LiBr addition. The corresponding spectral absorption bands were analyzed by the second derivative method.

2. EXPERIMENTAL

Cobalt bromide salt and PEG with average molecular weights of 400 and 1000 supplied by Aldrich, and PEG-4000 by Sci. Polymer Products were used. CoBr₂ was dried for 3 hours in a vacuum oven at 120°C to eliminate moisture.

Three types of sample were prepared. For the first, CoBr₂ salt was dissolved in PEG-1000 by heating the CoBr₂/PEG mixture at 110°C. (At room temperature PEG-1000 is solid and its melting point is around 40°C). For the second, CoBr₂ was directly dissolved in PEG-400 (which is liquid at room temperature), and for the third sample preparation, CoBr₂ salt was first dissolved in methanol. The PEG-4000 (which is solid at room temperature) was subsequently added. This solution was laid on a glass plate and stored in a desiccator for 24 hours, to allow methanol evaporation. A thin, greasy, solid layer was obtained.

The order of presentation of the three Co-complexes was chosen to correspond to the increasing number of the Br-ions in their composition.

A Varian, dual beam, Cary Model 118 spectrophotometer was used to record the visible (500–800 nm) spectra of all these samples, with a 2 nm/s scan speed and 1 nm recording steps. The spectra were obtained using a computer with a CMA 12-bits UIB AD-converter interface, subsequently processed and analyzed. The first two samples were introduced into 2 mm path length glass cells and the absorption spectrum recorded. The third (thin layer) sample was also measured.

3. RESULT AND DISCUSSION

Fig. 1 shows the recorded spectrum for the CoBr₂/PEG-1000 system at a temperature of 110°C.

It is a typical tetrahedral-like Co-complex spectrum (very intense as a consequence of the absence of the inversion centre for tetrahedral complexes).

Comparing with Fine’s [5] spectra of the bromide-complexes of cobalt in acetone solutions it is obvious that the spectrum in Fig. 1 belongs to the [CoBr₂L₂]⁻ complex (if not pure, at least clearly predominant), where L is a ligand from acetone in Fine’s case and from the oligomer in our case.

The optical absorption spectrum of the CoBr₂/PEG-400 sample, Fig. 2, was recorded at room temperature. It is closely similar to the spectrum of Fine’s [CoBr₃L]⁻ one.
The spectrum of the third sample CoBr$_2$/PEG-4000 is presented in Fig. 3. Certainly, this is the spectrum of the [CoBr$_4$]$^{2-}$ complex as indicated by the literature [5, 7].
Symmetry species of the \([\text{CoBr}_2L_2], \,[\text{CoBr}_3L]^-\) and \([\text{CoBr}_4]^{2-}\) complexes belong to the \(C_{2v}, C_3v\) and \(T_d\) point groups respectively, and the global absorption in the visible spectrum is associated with the \(^4A_2(F) \rightarrow ^4T_1(P)\) transition. This band is split as an effect of symmetry lowering from a real tetrahedron.

The positions of the elemental spectral components of the measured absorption bands have been determined by the second derivative method \([8]\). The peaks with local maxima in the input data will produce second derivative local minima with values that fall below zero. Hidden peaks (shoulders) which show no local maxima in the input data will, eventually, be found by second derivatives local minima with values that tend to be above or near zero detecting, in this way, the hidden spectral band-components.

Table 1 shows the results in our case, compared to Fine’s band positions, of bromo-complexes of cobalt in acetone solutions.

The proposed spectra/complexes attribution based on the general (predominant) spectra aspect is confirmed by the band positions listed in Table 1. The differences to Fine’s results are insignificant and they can be caused by the different peak detection methods used, or by the different nature of the second coordination sphere of the Co-ion in each case.

Beside the above, we shall remark the existence of what could be perceived as three additional bands in our spectra: the second band (613 nm) of the \(\text{CoBr}_2/\text{PEG}-1000\) sample, the third band (667 nm) of the \(\text{CoBr}_2/\text{PEG}-400\) sample and the first band (611 nm) of the \(\text{CoBr}_2/\text{PEG}-4000\) sample. These bands belong to
Table 1

The band positions of our samples compared to literature data

<table>
<thead>
<tr>
<th>Sample</th>
<th>Our results</th>
<th>Fine [5]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ν [cm(^{-1})]</td>
<td>λ [nm]</td>
</tr>
<tr>
<td>CoBr(_2)/PEG-1000 (110°C)</td>
<td>17250</td>
<td>580</td>
</tr>
<tr>
<td></td>
<td>16300</td>
<td>613</td>
</tr>
<tr>
<td></td>
<td>15725</td>
<td>636</td>
</tr>
<tr>
<td></td>
<td>14850</td>
<td>673</td>
</tr>
<tr>
<td>CoBr(_2)/PEG-400</td>
<td>16325</td>
<td>613</td>
</tr>
<tr>
<td></td>
<td>15775</td>
<td>634</td>
</tr>
<tr>
<td></td>
<td>15000</td>
<td>667</td>
</tr>
<tr>
<td></td>
<td>14300</td>
<td>699</td>
</tr>
<tr>
<td>CoBr(_2)/PEG-4000</td>
<td>16375</td>
<td>611</td>
</tr>
<tr>
<td></td>
<td>15700</td>
<td>637</td>
</tr>
<tr>
<td></td>
<td>15100</td>
<td>662</td>
</tr>
<tr>
<td></td>
<td>14425</td>
<td>693</td>
</tr>
<tr>
<td></td>
<td>13800</td>
<td>725</td>
</tr>
</tbody>
</table>

moderately mixed samples in all cases. The band at 613 nm (611 nm) probably belongs to a [CoBr\(_3\)_L\(^-\)] type complex, so, the first and the third samples contain some of the [CoBr\(_3\)_L\(^-\)] complex and the band at 667 nm belongs to the [CoBr\(_4\)]\(^2\-\) complex meaning that the second sample contains a little amount of this last complex.

In spite of that, the spectra presented in Fig. 1, Fig. 2 and Fig. 3 are, each, predominant spectra of the [CoBr\(_2\)_L\(^2\)], [CoBr\(_3\)_L\(^-\)] and [CoBr\(_4\)]\(^2\-\) complexes, respectively, proven by both the general aspect of the spectra and their band positions. So, we obtained all the usual, known, tetrahedral Co-complexes without LiBr addition.

The mechanism of these complexes formation in CoBr\(_2\)/PEG systems is still not entirely well understood and it is a challenging case. The Co-coordination is dependent on the PEG type (chain length and phase) and the sample preparation methods. For the third sample (CoBr\(_2\)/PEG-4000) we attempted to explain the formation of the [CoBr\(_4\)]\(^2\-\) complex by the following mechanism. This sample was prepared using methanol as a first solvent for the CoBr\(_2\) salt, then solid PEG-4000 was added. This solution was laid on glass plates and dried, to eliminate methanol. In this procedure, octahedral Co-complexes (with 6OH\(^-\) groups from methanol) are formed when CoBr\(_2\) is dissolved in methanol and free bromine ions are produced. Then, the subsequent PEG addition favors the tetrabromo-Co-complexes formation with the abundant free bromine ions.

Br\(^-\) ions could be produced, in excess, by the formation of the O\(_h\)-symmetry Co-complexes, using the OH-ends of the PEG-chains. Having an inversion center,
these complexes can not be easily detected by optical spectroscopy, unless their concentration is rather high.

4. CONCLUSIONS

CoBr₉/PEG systems were prepared to obtain (almost) pure different tetrahedral types of Co-complexes. Three different PEG average molecular weights (chain length) and an added co-solvent (methanol) were used. The absorption spectra of the CoBr₉/PEG systems were analyzed by the second derivative method.

The comparison to the literature data [5] shows the similarities of these spectra to early spectroscopic studies of bromide complexes of cobalt in acetone solutions. The spectra of our samples seem to be of individual (almost pure) tetrahedral-like, dibromo-, C₂ᵥ, [CoBr₂L₂], tribromo-, C₃ᵥ, [CoBr₃L]⁻ and real tetrahedral, tetrabromo-, T₄ᵥ, [CoBr₄]²⁻, Co-complexes. A mechanism of the last Co-complex formation in PEG, including the role of methanol, is proposed.

REFERENCES