Temperature Dependent ESR Studies on Platinum Pyrimidine “Blues”: Evidence for a Structural Instability?

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Frozen samples of aqueous solutions of oxidized Pt 6-methyl-uracil “blue” were studied by ESR spectroscopy at temperatures T ranging between —196 °C and —10 °C. When T was raised a distinct change in the line pattern was observed at about —35 °C. The resulting type of spectrum is very similar to the ESR spectrum of MAGNUS’ Green Salt. The observed effect is suggested to be due to a change of the nature of the system’s electronic states possibly indicating a structural rearrangement.

Introduction

The Pt pyrimidine “blues” have recently received considerable interest as a promising potent anti-tumor drug [1]. The “blues” are derived from cis-dichlorodiammineplatinum(II) (PDD) or from the hydrolysis product cis-diaquodiammineplatinum(II) (PDDa). Broad evidence of the tumor fighting activity of the compounds has been presented [1]. Their mode of action, however, is still open to question. The same holds true for their fighting activity of the compounds possibly indicating a structural rearrangement.

The ESR spectrum of the PDDa-6-methyluracil solution after addition of the oxidizing agent (15% H₂O₂) is shown at the top of Figs. 1, 2. This type of spectrum, termed “type 0” [10], has been obtained previously, in a similar form, for a number of Pt “blues” compounds [3, 7, 11].

Frozen solution spectra of the type 0 species recorded at temperatures ranging from —196 °C to approximately —13 °C are shown in Fig. 1. Except for the expected decrease in intensity the type 0 spectrum remains unchanged for temperatures up to approximately —39 °C. However, when T is raised to —34 °C a significant and quite abrupt change in the line pattern occurs giving rise to a new type of spectrum “type X” at —34 °C. The type X line pattern is essentially retained as T is lowered to values well below the region of the type 0—type X transition. This is illustrated by spectra 6 and 7 of Fig. 1. The type 0 pattern is readily regained, however, when the sample is melted and refrozen subsequently (Fig. 1, spectrum 8).

Fig. 2 clearly illustrates the characteristic differences in the distribution of relative line intensities in the g₁- and g₉-regions of the type 0 and the type X spectra. In particular, the resolution in the g₉-region of the type X spectrum is considerably reduced as compared to the type 0 pattern. Thus, the g₉-line shape of the type X spectrum exhibits a striking similarity to the g₉-signal of the 77 K ESR spectrum obtained from a powder sample of Magnus’ Green Salt (MGS) (Fig. 2). In addition, the line intensity distribution in the g₁-part also suggests the similarity of the two spectra.

The ESR spectrum of MGS has been analyzed in terms of localized 5d₂ hole states. Thus, states extending over several, i.e. 7–9 coupled Pt centers have been assumed to account for the observed pattern [14]. The fact that the type X and MGS...
Fig. 1. ESR spectra of 0.1 M PDDa-6-methyluracil solution (g = (6-methyluracil)/(PDDa) = 1; 4 h at 70 °C) after addition of oxidizing agent (15% H₂O₂) taken at varying temperatures. The T values are given at the right hand side of each spectrum. Except for the bottom spectrum all spectra were obtained from one frozen sample. Spectrum 8 was recorded after melting the sample at RT and subsequent refreezing to the temperature indicated.

Table I. g-Values of the ESR spectra.

<table>
<thead>
<tr>
<th>Pt complex</th>
<th>g₁ (± 0.005)</th>
<th>g₂ (± 0.005)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDDa-6-methyluracil:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>type O</td>
<td>2.394</td>
<td>1.991</td>
</tr>
<tr>
<td>type X</td>
<td>2.405</td>
<td>1.998</td>
</tr>
<tr>
<td>Magnus' Green Salt</td>
<td>2.497</td>
<td>1.948</td>
</tr>
</tbody>
</table>

line patterns are practically identical concerning the hyperfine structure strongly suggests that states of this type may also be responsible for the type X.

Fig. 2. The type O and type X spectra were obtained from a 0.1 M PDDa-6-methyluracil solution (g = 1; 4 h at 70 °C) after treatment with H₂O₂, measured at 77 K (type O) and at −34 °C (type X).

The MGS spectrum was obtained from a powder sample at 77 K.

The “blues” are generally assumed to form one-dimensional (1D) oligomers. In terms of an idealized model it appears plausible to envisage those oligomers as a disordered 1D system. The disorder, as described by a random potential V₉, may arise from variations of the local ligand-to-Pt stoichiometries and from distortions of the ideal 1D geometry found for instance in the case of PDDa-a-pyrimidine from X-ray analysis [6, 7]. These effects can be expected to be especially pronounced after short reaction times. They presumably result in ligand fields of varying strength and symmetry acting on different Pt centers in the stack. Furthermore, “surface” effects due to the chain ends have to be taken into account especially for short oligomers. Assuming V₉ (root mean square) to be of the same order of magnitude as the “bandwidth” of the unperturbed system, the electronic states of the disordered system will be localized to approximately a single lattice site [15–18].

It is suggested that, as the temperature is raised, the disorder may eventually become ineffective due to the dynamics of the 1D “lattice”. Consequently, extended rather than strongly localized electronic states may be expected. The fact that the observed
type $0 \rightarrow$ type $X$ transition is irreversible as long as the sample remains frozen suggests a permanent structural rearrangement involving the surrounding solvent molecules. Further investigations have to elucidate the possible relation between the observed transition and structural instabilities such as the PEIERLS-FROELICH instability or the KOHN anomaly which are characteristic for 1D systems [19] and are known to exist for a number of quasi-metallic mixed valence complexes of Pt [20–21].