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<tr>
<td>Author(s)</td>
<td>Miyazaki, Morimasa</td>
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<tr>
<td>Citation</td>
<td>Bulletin of the Institute for Chemical Research, Kyoto University (1981), 58(5-6): 555-558</td>
</tr>
<tr>
<td>Issue Date</td>
<td>1981-01-31</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/2433/76913">http://hdl.handle.net/2433/76913</a></td>
</tr>
<tr>
<td>Type</td>
<td>Departmental Bulletin Paper</td>
</tr>
<tr>
<td>Textversion</td>
<td>publisher</td>
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Kyoto University
**EPR Study of Vanadium Oxide Bis(8-quinolinolate) Doped in Zinc Bis(8-quinolinolate) Dihydrate**

Morimasa Miyazaki*

Received October 8, 1980

EPR signal of vanadium oxide bis(8-quinolinolate), [VO(quin)$_2$], has been observed in the matrix of zinc bis(8-quinolinolate) dihydrate, [Zn(quin)$_2$(H$_2$O)$_2$]. EPR parameters of VO(quin)$_2$ in Zn(quin)$_2$(H$_2$O)$_2$ have been found to be similar to those of VO(quin)$_2$ in toluene. The results indicate that VO(quin)$_2$ doped in Zn(quin)$_2$(H$_2$O)$_2$ has no ligand H$_2$O to interact at the axial position.

KEY WORDS: Magnetic properties / EPR parameters / Axial interaction /

**INTRODUCTION**

Vanadium oxide bis(8-quinolinolate), [VO(quin)$_2$], [1], is generally unstable in air, and is rapidly oxidized to diamagnetic hydroxo (oxo)(8-quinolinolate) vanadium, [VO(OH)(quin)$_2$], [2]. In the matrix of zinc bis(8-quinolinolate) dihydrate, [Zn(quin)$_2$(H$_2$O)$_2$], [3], VO(quin)$_2$ is expected to be embedded because of the similar molecular shape. When VO(quin)$_2$ is embedded in the matrix, the following three possibilities can be considered.

1) VO(quin)$_2$ is oxidized to VO(OH)(quin)$_2$ by the reaction with H$_2$O.
2) VO(quin)$_2$ hydrates and becomes VO(quin)$_2$(H$_2$O)$_2$, [4].
3) VO(quin)$_2$ exists stable without distinct interactions with the matrix.
In the first case no EPR spectrum can be observed because vanadyl ion becomes diamagnetic by the conjugation with OH-. In the second case EPR parameters should be observed with some modifications as a result of the axial interaction between VO^2+ and a ligand H_2O. In the last case EPR parameters should be similar to VO(quin)_2 in the solvent such as toluene which has no axial interaction.

The structure of VO(quin)_2 doped in Zn(quin)_2(H_2O)_2 was determined from the above mentioned viewpoints.

**EXPERIMENTAL**

Preparation. VO(quin)_2 in Zn(quin)_2(H_2O)_2 was prepared by adding the aqueous solution of the mixture of VOCl_2 (5%) and ZnSO_4·7H_2O (95%) to an ethanolic solution of 8-quinolinol, and obtained as powdered precipitate. A toluene solution of Cu(quin)_2 (5%) was prepared by dissolving a powder of Cu(quin)_2 into pure toluene, where the powder had been obtained by mixing an aqueous solution of CuSO_4·5H_2O and ethanolic solution of 8-quinolinol.

Measurements. The X-band EPR spectra were measured with JES-ME-3X spectrometer using 100 KHz magnetic field modulation. The calibration of the field strength was made with Mn^{2+} doped in MgO.

**RESULTS AND DISCUSSION**

The EPR spectrum of VO(quin)_2 embedded in Zn(quin)_2(H_2O)_2 was obtained at room temperature as shown in Fig. 1. This indicates that VO(quin)_2 does not change into diamagnetic VO(OH)(quin)_2 even in this hydrated host crystal. The EPR parameters of VO(quin)_2 in Zn(quin)_2(H_2O)_2 were calculated using the following spin Hamiltonian with an axial symmetry.

\[ H_s = \beta [ g_0 H_z S_z + g_\perp (H_x S_x + H_y S_y) ] + A_\parallel I_z S_z + A_\perp (I_z S_x + I_y S_y), \]  

(1)

where \( A_\parallel \) and \( A_\perp \) are the vanadium nuclear hyperfine constants.

From the Bleaney's second-order perturbation theory\(^1\), the magnetic field at which the resonance occurs is given as below.

\[ H_{\pm M_I} = \frac{g_0}{g} \left\{ h\nu - AM_I - \frac{A_\perp}{4H_0} \left( \frac{A_{\parallel}^2 + A_{\perp}^2}{A^2} \right) [I(I+1) - M_I^2] \right\}, \]  

(2)

where

\[ g = (g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta)^{1/2} \]

and

\[ A = (A_{\parallel}^2 g_{\parallel}^2 \cos^2 \theta + A_{\perp}^2 g_{\perp}^2 \sin^2 \theta)^{1/2} \]

The final EPR parameters were calculated by the least-square method. The spectra of Cu(quin)_2 in toluene were measured as shown in Fig. 2 for comparison. These
Fig. 1. The EPR spectrum of VO(quin)$_2$ in Zn(quin)$_4$(H$_2$O)$_2$ at room temperature.

Fig. 2. The EPR spectra of Cu(quin)$_2$ in toluene at room temperature (a) and 77° K (b).
Table I. EPR parameters of VO(quin)$_2$ and Cu(quin)$_2$

<table>
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<tr>
<th>Compound</th>
<th>$g_\parallel$</th>
<th>$g_\perp$</th>
<th>$A_x(G)$</th>
<th>$A_y(G)$</th>
<th>Ref.</th>
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<tr>
<td>VO(quin)$_2$ in Zn(quin)$_2$(H$_2$O)$_2$</td>
<td>1.950±0.002</td>
<td>1.980±0.001</td>
<td>166±2</td>
<td>57±1</td>
<td>*</td>
</tr>
<tr>
<td>VO(quin)$_2$ in toluene</td>
<td>1.946±0.003</td>
<td>1.980±0.003</td>
<td>174±2</td>
<td>60±2</td>
<td>2)</td>
</tr>
<tr>
<td>Cu(quin)$_2$(H$_2$O)$_2$ in Zn(quin)$_2$(H$_2$O)$_2$</td>
<td>2.287</td>
<td>2.066</td>
<td>-160</td>
<td>-31</td>
<td>3)</td>
</tr>
<tr>
<td>Cu(quin)$_2$ in toluene</td>
<td>2.234</td>
<td>2.044</td>
<td>-170</td>
<td>-53</td>
<td>*</td>
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*: This work

EPR parameters obtained are listed in Table I, together with the values of VO(quin)$_2$ in toluene and Cu(quin)$_2$(H$_2$O)$_2$ in Zn(quin)$_2$(H$_2$O)$_2$ reported in Ref. 2 and Ref. 3 respectively. It is well known that for copper complexes EPR parameters are very sensitive to a matrix. When interaction between copper atom and the axial ligand is strong, the $g$ value increases while $|A|$ value decreases.$^{3-7)}$ The differences between $g$ values of VO(quin)$_2$ in Zn(quin)$_2$(H$_2$O)$_2$ and those of VO(quin)$_2$ in toluene are not significant. The differences in EPR parameters of VO(quin)$_2$ in those matrices are smaller than those of Cu(quin)$_2$. This means that the spin state of VO(quin)$_2$ is not affected so strong as in the case of Cu(quin)$_2$ by a matrix at the axial position in Zn(quin)$_2$(H$_2$O)$_2$. Therefore it is concluded that VO(quin)$_2$ has no ligand H$_2$O molecule at the axial position.

ACKNOWLEDGMENT

The author wishes to thank to Prof. N. Uyeda, Drs. H. Saijo and T. Kobayashi for their help throughout this work.

REFERENCES