

Note

EPR Study of Vanadium Oxide Bis(8-quinolinolate) Doped in Zinc Bis(8-quinolinolate) Dihydrate

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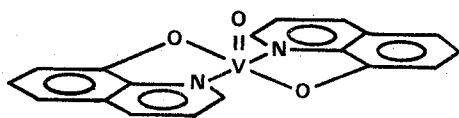
EPR signal of vanadium oxide bis(8-quinolinolate), $[\text{VO}(\text{quin})_2]$, has been observed in the matrix of zinc bis(8-quinolinolate) dihydrate, $[\text{Zn}(\text{quin})_2(\text{H}_2\text{O})_2]$. EPR parameters of $\text{VO}(\text{quin})_2$ in $\text{Zn}(\text{quin})_2(\text{H}_2\text{O})_2$ have been found to be similar to those of $\text{VO}(\text{quin})_2$ in toluene. The results indicate that $\text{VO}(\text{quin})_2$ doped in $\text{Zn}(\text{quin})_2(\text{H}_2\text{O})_2$ has no ligand H_2O to interact at the axial position.

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

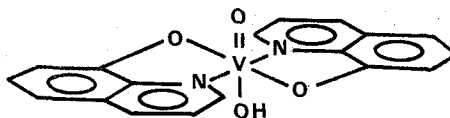
INTRODUCTION

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

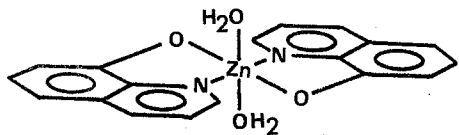
- 1) $\text{VO}(\text{quin})_2$ is oxidized to $\text{VO}(\text{OH})(\text{quin})_2$ by the reaction with H_2O .
- 2) $\text{VO}(\text{quin})_2$ hydrates and becomes $\text{VO}(\text{quin})_2(\text{H}_2\text{O})$, [4].
- 3) $\text{VO}(\text{quin})_2$ exists stable without distinct interactions with the matrix.



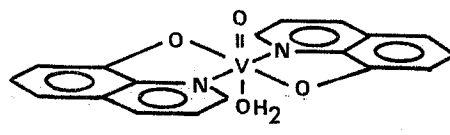
[1]



[2]



[3]



[4]

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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 $\text{VO}(\text{quin})_2$ in the solvent such as toluene which has no axial interaction.

The structure of $\text{VO}(\text{quin})_2$ doped in $\text{Zn}(\text{quin})_2(\text{H}_2\text{O})_2$ was determined from the above mentioned viewpoints.

EXPERIMENTAL

Preparation. $\text{VO}(\text{quin})_2$ in $\text{Zn}(\text{quin})_2(\text{H}_2\text{O})_2$ was prepared by adding the aqueous solution of the mixture of VOCl_2 (5%) and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (95%) to an ethanolic solution of 8-quinolinol, and obtained as powdered precipitate. A toluene solution of $\text{Cu}(\text{quin})_2$ (5%) was prepared by dissolving a powder of $\text{Cu}(\text{quin})_2$ into pure toluene, where the powder had been obtained by mixing an aqueous solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 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 $\text{VO}(\text{quin})_2$ embedded in $\text{Zn}(\text{quin})_2(\text{H}_2\text{O})_2$ was obtained at room temperature as shown in Fig. 1. This indicates that $\text{VO}(\text{quin})_2$ does not change into diamagnetic $\text{VO}(\text{OH})(\text{quin})_2$ even in this hydrated host crystal. The EPR parameters of $\text{VO}(\text{quin})_2$ in $\text{Zn}(\text{quin})_2(\text{H}_2\text{O})_2$ were calculated using the following spin Hamiltonian with an axial symmetry.

$$H_s = \beta [g_{\parallel} H_z S_z + g_{\perp} (H_x S_x + H_y S_y)] + A_{\parallel} I_z S_z + A_{\perp} (I_x S_x + I_y S_y), \quad (1)$$

where $A_{\parallel}$ and $A_{\perp}$ are the vanadium nuclear hyperfine constants.

From the Bleaney's second-order perturbation theory¹⁾, the magnetic field at which the resonance occurs is given as below.

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

where

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

and

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

The final EPR parameters were calculated by the least-square method. The spectra of $\text{Cu}(\text{quin})_2$ in toluene were measured as shown in Fig. 2 for comparison. These

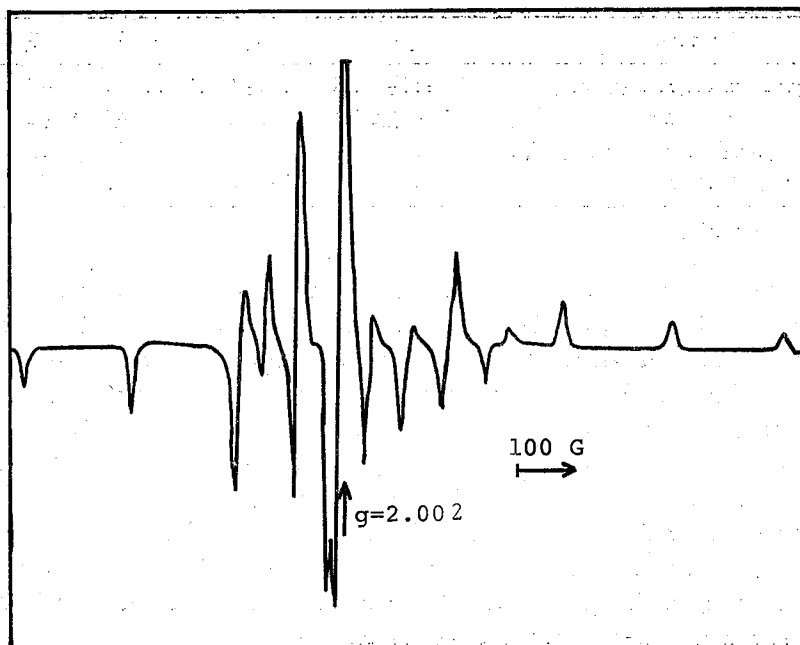


Fig. 1. The EPR spectrum of $\text{VO}(\text{quin})_2$ in $\text{Zn}(\text{quin})_2(\text{H}_2\text{O})_2$ at room temperature.

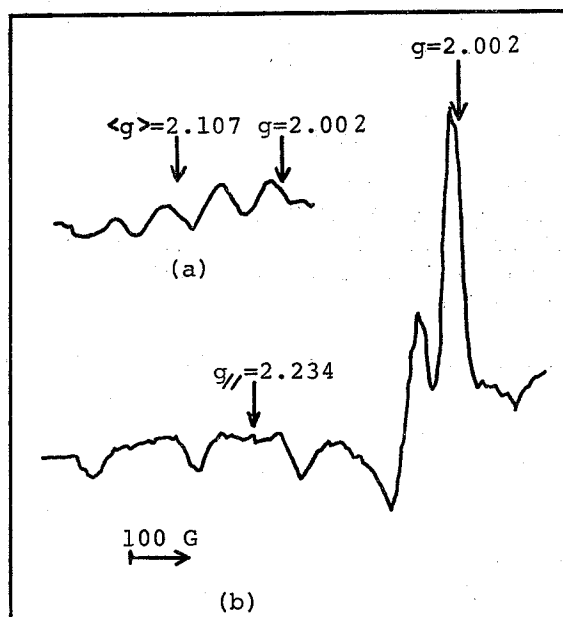


Fig. 2. The EPR spectra of $\text{Cu}(\text{quin})_2$ in toluene at room temperature (a) and 77° K (b).

Table I. EPR parameters of VO(quin)₂ and Cu(quin)₂

Compound	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}(G)$	$A_{\perp}(G)$	Ref.
VO(quin) ₂ in Zn(quin) ₂ (H ₂ O) ₂	1.950 ± 0.002	1.980 ± 0.001	166 ± 2	57 ± 1	*
VO(quin) ₂ in toluene	1.946 ± 0.003	1.980 ± 0.003	174 ± 2	60 ± 2	2)
Cu(quin) ₂ (H ₂ O) ₂ in Zn(quin) ₂ (H ₂ O) ₂	2.287	2.066	-160	-31	3)
Cu(quin) ₂ in toluene	2.234	2.044	-170	-53	*

*: This work

EPR parameters obtained are listed in Table I, together with the values of VO(quin)₂ in toluene and Cu(quin)₂(H₂O)₂ in Zn(quin)₂(H₂O)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(H₂O)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(H₂O)₂. Therefore it is concluded that VO(quin)₂ has no ligand H₂O molecule at the axial position.

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