The Electron Spin Resonance of the Trinuclear Vanadyl Pyrophosphate Complex

Akinori Hasegawa, Yoshio Yamada and Masaji Miura

Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima

(Received October 30, 1968)

An aqueous solution of the vanadyl pyrophosphate (1 : 1) complex has shown a characteristic ESR spectrum which has never been observed in any other vanadyl complexes. Yakovenko and Mustaev recently proposed $Na_2VOP_2O_7 \cdot 6H_2O$ as the molecular formula for this complex.[1] The observed spectrum (Fig. 1) can not, however, be interpreted in terms of any of the present models of a mononuclear or binuclear complex.

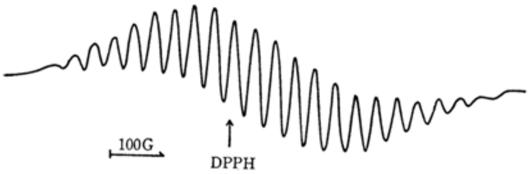

Fig. 1. ESR spectrum of aqueous solution of vanadyl pyrophosphate complex at 25°C

The molecular formula of this system, therefore, has been investigated further by various methods. The amount of water eliminated from the crystal was determined gravimetrically, and that of sodium ions, by atomic absorption spectrophotometry. The molecular weight has been measured by means of a vapor-pressure osmometer with this system. Assuming the complex to be trinuclear, its molecular weight is 1120, a value which is in good agreement with the calculated value, 1077. The results of all these measurements have definitely indicated the trinuclear formula of $[Na_2VOP_2O_7]_3 \cdot 12H_2O$.

Thus, in the trinuclear complex, exchange interaction among three vanadyl ions should be taken into account. The spin Hamiltonian is shown in the form:

$$\mathscr{H} = g\beta H \sum_{i=1}^{3} S^{(i)} + a \sum_{i=1}^{3} S^{(i)} I^{(i)} + J \sum_{i>j=1}^{3} S^{(i)} S^{(j)}, \quad (1)$$

where $J \gg a$ is assumed. With this assumption and the mixing of the two doublet states with the quartet state, Hudson and Luckhurst showed that the ESR transitions allowed for the quartet state to occur at:[2]

$$h\nu = g\beta H + \frac{a}{3}(m^{(1)} + m^{(2)} + m^{(3)}). \quad (2)$$

The vanadyl pyrophosphate complex may, therefore, be expected to give a spectrum composed of 22 lines and with a splitting of 36.4 gauss. This splitting is one-third of that of 109 gauss observed in vanadyl pyrophosphate (1 : 2), which shows no spin exchange.

Transitions for the two doublet states are also allowed at:

$$h\nu = g\beta H + \frac{a}{3}(m^{(1)} + m^{(2)} + m^{(3)}) \pm \frac{2a}{3}(m^{(1)^2} + m^{(2)^2} + m^{(3)^2} - m^{(1)}m^{(2)} - m^{(2)}m^{(3)} - m^{(3)}m^{(1)})^{1/2}. \quad (3)$$

The spectrum predicted for these transitions is constructed with 144 irregularly spaced lines. As the intensity of these lines is very weak compared with that for the quartet, the quartet state appears predominantly in the spectrum of the trinuclear complex. The spectrum simulated with these assumptions shows a satisfactory agreement with that observed.

Hudson and Luckhurst, using Redfield's theory, explained the distinctive change in the spectrum of the triradical with a rise in the temperature in terms of the spin exchange interaction.[2] In the present case, however, no such change can be observed. This may be attributed to the condition $J \gg a$. In order to estimate the value of J, measurements of the magnetic susceptibility were carried out at various temperatures above 77°K.

According to Kambe's theory,[3] the effective Bohr magneton for this complex obeys the equation:

$$\mu_{\mathrm{eff}} = \left[\frac{5\exp(-3J/2kT) + 1}{\exp(-3J/2kT) + 1} \right]^{1/2}. \quad (4)$$

By comparing this relation with the observed values, $J \simeq 30\ \mathrm{cm}^{-1}$ was obtained, where it must be noticed that the sign of J is the reverse of the conventional one. This value completely satisfies the condition of $J \gg a$, a being $99 \times 10^{-4}\ \mathrm{cm}^{-1}$. The large antiferromagnetic exchange interaction may suggest that the spin exchanges through the π bonds of O–P–O in pyrophosphate.

---

1) R. T. Yakovenko and A. K. Mustaev, *Inst. Neorg. Fiz. Khim.*, **1966**, 30.

2) A. Hudson and G. R. Luckhurst, *Mol. Phys.*, **13**, 409 (1967).

3) K. Kambe, *J. Phys. Soc. Japan*, **5**, 48 (1950).