Electron Paramagnetic Resonance Study of the Dimer Formation of Bis(acetylacetonato)oxovanadium(IV)

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Dimer formation of the title complex in toluene and benzene mixed solvents has been demonstrated by the EPR spectroscopy. The dimer structure and the spin-exchange energy have been examined by spectral simulation for $\Delta M_s=2$ transitions and the temperature dependence of their spectral intensities, respectively. It has been found that the structure and the magnetism are similar to those of the inversion pair of bis(benzoylacetonato)oxovanadium(IV) in a crystal which is known to show dimeric interactions in its EPR spectra. The formation constant of the dimer, K, for 2 [monomer] $\rightleftharpoons$ dimer has been determined by analyzing the concentration dependence of the dimer and the monomer EPR signals, indicating that K is remarkably solvent-dependent.

Metal complexes containing two unpaired electron centers such as metal-metal dimers, binuclear complexes, and some metalloenzymes are important and interesting subjects for investigations in chemistry.[1)] Many EPR studies of their triplet states have been reported with special emphasis on the mechanisms of the magnetic interactions between the two unpaired electrons which center on different metals.[2)] However, there have been only a few EPR investigations of the triplet state obtained by dimerization of stable mononuclear vanadyl complexes.[3)] We have observed that some vanadyl β-diketonates dimerize in solution. In this paper, we report on the observation of the dimerization of bis(acetylacetonato)oxovanadium(IV), VO(acac)$_2$, in solution and discuss the intra-dimer spin exchange interaction and the structure of the dimer. We then compare this with those of the inversion pair of bis(benzoylacetonato) oxovanadium(IV), VO(bza)$_2$, in crystal, whose EPR spectra show the presence of dimeric interactions. We also compare it with the molecular arrangement in the VO(acac)$_2$ crystal. Further, we discuss the nature of dimerization in solution.

Experimental

Materials. VO(acac)$_2$ used was obtained commercially and recrystallized from acetone. VO(bza)$_2$ was prepared and purified according to a method given in the literature.[4)] Nakarai's spectrograde solvents, toluene and benene, were used without further purification.

EPR Measurements. EPR spectra were recorded on a JEOL FE2XG spectrometer for measurements at temperatures from 77 K to room temperature and on a Varian-E112 spectrometer at temperatures from 8 to 15 K. The intra-dimer spin exchange energy (isotropic exchange coupling constant), J, was obtained from the temperature variation of the spectral intensity, I, of the $\Delta M_s=2$ transitions.[5)] Since the line widths did not change over the entire temperature range used for the measurements, the relative peak height of some specific line in the first derivative spectra was used as a substituent for I. A computer simulation of the EPR spectra was carried out by the method using a point-dipole approximation.[1a,6)]

Results and Discussion

Figures 1-a and b are the spectra observed for a

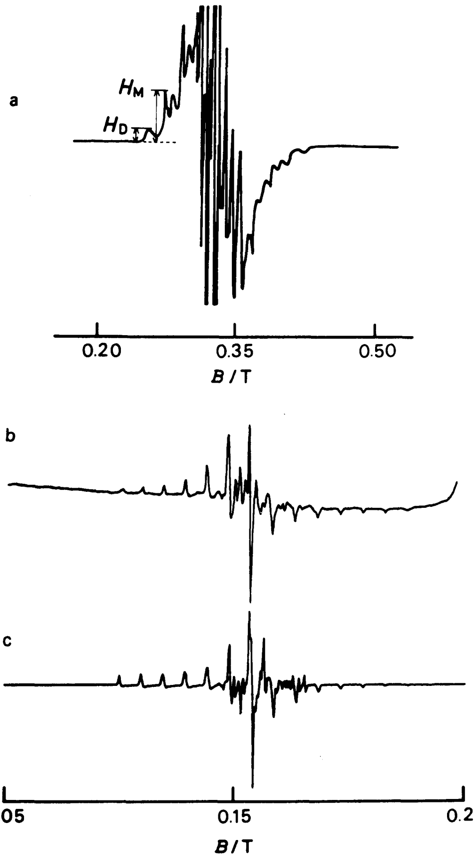

Fig. 1. The observed X-band EPR spectra of VO(acac)$_2$ in toluene-benzene (2 : 8) at 77 K (a, b) and the calculated spectrum (c). [VO(acac)$_2$]=2.00×10^{-2} mol dm^{-3}, ν=9.1597 GHz. See text for meaning of the parameters, H_D and H_M, and see also the text for the parameters used for the simulation calculation in c.

frozen toluene–benzene (2:8 in volume) solution of $VO(acac)_2$ at 77 K. They show the presence of two species: one is the usual $S=1/2$ mono-nuclear species, which shows sharp absorption lines; the other is a species showing a spectral pattern similar to that of powder of $VO(bza)_2$, which is known to have dimeric interactions between the molecules in the inversion pair in crystal.[3b] The latter EPR spectral pattern of $VO(acac)_2$ accompanies a weak signal at a half magnetic field of about 0.16 T. These spectral features indicate the formation of a dimer having a triplet state. Since the intensity ratio of the dimer to the monomer increases with the concentration of the complex, they are in equilibrium in solution.

Intra-Dimer Spin Exchange Interaction. The EPR signal intensity of the triplet state is proportional to the paramagnetic susceptibility under the absence of microwave power saturation, and is expressed as

$$I = C/T \times (3+\exp(-2J/kT))^{-1}, \qquad (1)$$

where C is a proportionality constant.[7] Therefore, the isotropic spin exchange energy, J, can be determined from measurements of the temperature dependence of the EPR signal intensity. The half-field signal corresponding to the $\Delta M_s=2$ transitions was used for the purpose, since it did not overlap with any signals of the monomer species. The observed temperature dependence of the signal intensity is shown in Fig. 2, where the solid line indicates the relative intensity changes calculated by Eq. 1 with J of $0\,cm^{-1}$, indicating that the intra-dimer spin exchange interaction is as small as in the inversion pair of $VO(bza)_2$ in crystal whose J value is $0.018\,cm^{-1}$;[3b] thus, there may be no strong isotropic spin exchange interaction in the vanadium pair.

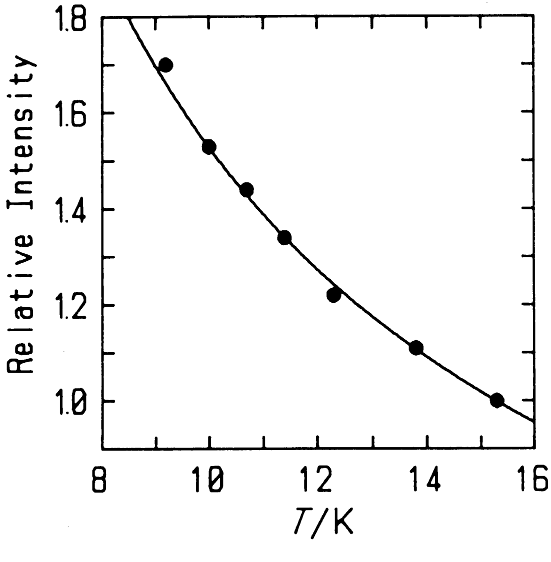

Fig. 2. Temperature variations of the relative intensities in $\Delta M_s=2$ spectra. ●: experimental data, ——: calculated with $J=0\,cm^{-1}$.

In addition to the isotropic singlet–triplet splitting, the interaction between the vanadium(IV) ions in the dimer leads to a zero-field splitting within the triplet state. The zero-field splitting parameter, D, comprises two terms: $D=D_{dd}=D_{so}$.[8] D_{dd} is the through space magnetic dipole interaction and D_{so} is the contribution arising from the spin-orbit coupling interaction. In the following, D is treated as mostly arising from the through space dipole interaction, D_{dd}.

Dimer Structure and Exchange Mechanism. The observed triplet state EPR spectra were analyzed by computer simulation using a point-dipole approximation: the point dipoles are placed on the vanadium ions, which are expressed by the coordinate system shown in Fig. 3. Neglecting the effects of D_{so} has been shown to be valid for many cases of parallel-planar dimer complexes.[2] Computer simulations were attempted for the both $\Delta M_s=1$ and $\Delta M_s=2$ transitions, though a better fit was obtained for the $\Delta M_s=2$ transitions.

In the above simulation calculations, no effect of an isotropic spin exchange interaction was taken into account. The isotropic spin exchange energy, J, has an effect to cause an energy separation between the singlet and triplet $M_s=0$ levels, while the dipolar interaction, D_{dd}, separates between the $M_s=\pm1$ and the $M_s=0$ levels in the triplet manifold. Unless J is so large that only the transitions within the triplet manifold are observed, the spectral pattern for the $\Delta M_s=1$ transitions will depend on the both J and D_{dd}. However, the $\Delta M_s=2$ transitions depend only on D_{dd}.[9] In the present case, J and D_{dd} are of the same magnitue ($J\sim0\,cm^{-1}$ and $D_{dd}\sim0.02\,cm^{-1}$) and, hence, a point-

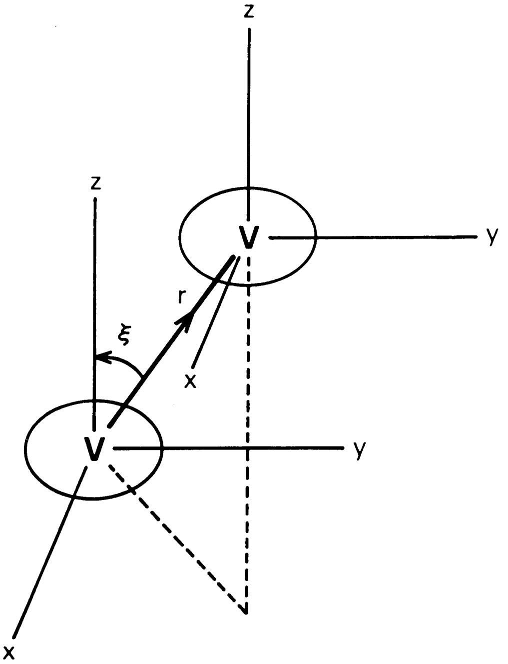

Fig. 3. Coordinate system for the dimer.

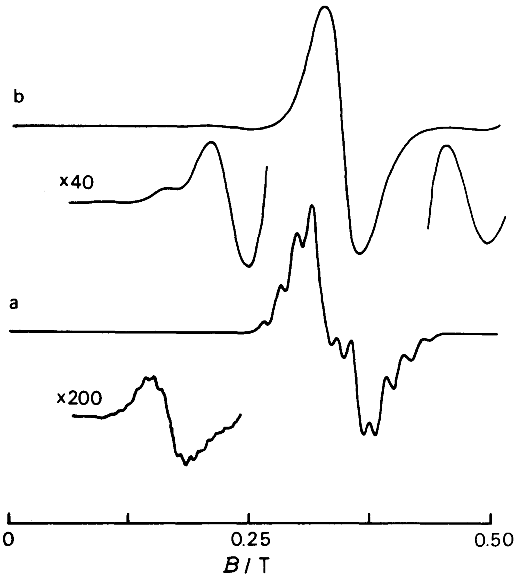

Fig. 4. Polycrystalline EPR spectra of VO(bza)$_2$ (a) and VO(acac)$_2$ (b) at room temperature (ν=9.4500 GHz).

dipole approximation which disregards singlet-triplet splitting may not be a really good approximation for a simulation calculation for the $\Delta M_s=1$ transitions. In order to precisely calculate the resonance magnetic field for the $\Delta M_s=1$ transitions, mixing of the singlet and triplet states must be taken into account.[2c]

The following parameters were obtained from the spectral simulation for the $\Delta M_s=2$ transitions: $g_{\parallel}=1.940$, $g_{\perp}=1.989$, $A_{\parallel}=0.0087\ \mathrm{cm}^{-1}$, $A_{\perp}=0.0024\ \mathrm{cm}^{-1}$, $r=5.3$ Å, $\xi=35°$, $\nu=9.1597$ GHz. The simulated spectrum is shown in Fig. 1-c. The r and ξ values indicate that the dimeric structure is similar to that of VO(bza)$_2$ in crystal, which has a pair-wise stacked structure with r of 5.7 Å and ξ of 36.3°.[3b] The polycrystalline EPR spectrum of the VO(bza)$_2$ in the $\Delta M_s=1$ transition region (Fig. 4) is very similar to the frozen solution spectrum of VO(acac)$_2$. Simpson et al. showed that the magnetic interactions observed for the VO(bza)$_2$ crystal system occur mainly between the molecules in the inversion pair, and that interaction with the neighboring pairs affect only the line widths of the spectra.[3b] As inter-dimer interactions in frozen solutions are, in general, small enough to be neglected;[10] the similarity of the observed spectra of VO(acac)$_2$ to those of VO(bza)$_2$ indicates that the magnetic interactions within the dimer and their mechanism are nearly the same as those of the pair in the VO(bza)$_2$ crystal.

The molecular configuration of VO(acac)$_2$ in a crystal is schematically shown in Fig. 5.[11] One can see that the molecules in the crystal are associated in pairs in an inversion manner with $r=5.55$ Å and $\xi=31.5°$, as in the VO(bza)$_2$ crystal. The distance between the nearest molecular pairs is 6.14 Å. It is interesting that these r and ξ values are nearly equal to those of the VO(bza)$_2$ pair in a crystal, in spite of the different ligands and crystal structures. It is also interesting that the r and ξ evaluated above for the frozen solution agree with those for the VO(acac)$_2$ crystal; the dimer structure in a frozen solution may be similar to that of the inversion pair in a crystal. The structure of the inversion pair in the VO(acac)$_2$ crysal, where the methine carbon of the partner molecule occupies the apical position of the vanadium atom, is also similar to those of the dimers formed by Cu(acac)$_2$ and the related copper(II) complexes.[8,12] This suggests that a so-called π-π interaction between the π systems constituted from the metal and β-diketonate ligands may be an important driving force for dimerization.[13] It may be notable that the r for the vanadyl complexes are longer than those of copper(II) complex dimers because of the doming effect of the vanadyl oxygen, which causes an out-of-plane displacement of the vanadium atom.

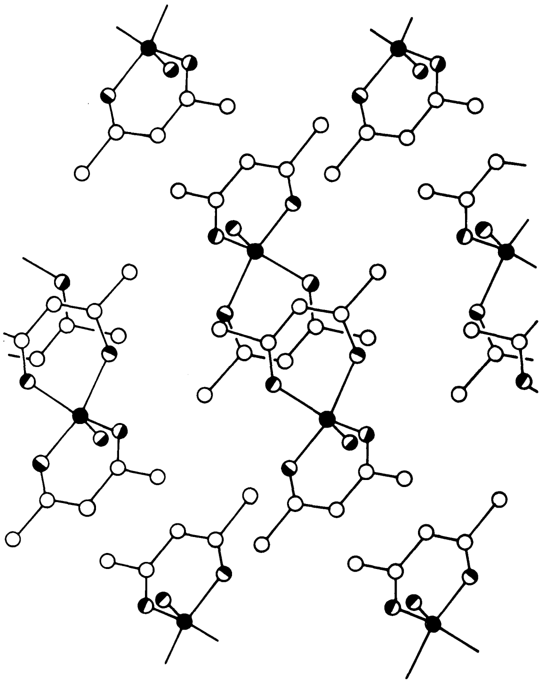

Fig. 5. The shematically represented crystal structure of VO(acac)$_2$.[11] ●: vanadium atom, ◐: oxygen atom, ○: carbon atom.

The exchange interactions between paramagnetic centers have been actively investigated over the last few years.[1d,2a,14,15] As was pointed out by Kahn, J can be expressed as the sum of two components: $J=J_{\mathrm{AF}}+J_{\mathrm{F}}$. The former is a negative antiferromagnetic contribution and the latter is a positive ferromagnetic one.[1b,16] In a symmterical d_1-d_1 system, J_{AF} and J_{F} vary proportionally to $-s^2$ and j, respectively, where s is the overlap integral between the two magnetic orbitals, and j is the two-electron exchange integral between the two metal centers. Since the magnetic orbital in VO(acac)$_2$, which is approximately d_{xy}, is non-bonding to the ligands, the overlap between the ligand orbitals in the dimer pairs would not contribute greatly to j; the exchange interaction through the π-orbitals of the ligands would not make a large contribution. On the other hand, though the d_{xy} orbitals of the two magnetic centers would overlap to some extent with the vicinity of the inversion center of the dimer, the radial distribution functions for these orbitals are very small for large values of r (=5.3 Å). Thus, s^2 and j can not have large values and, hence, J becomes very small, as was shown by the above experiment. The J value in vanadyl complexes must be much smaller than those in the dimers of similar copper(II) complexes,[2c)] since in copper(II) complexes the unpaired electron orbital (magnetic orbital), $d_{x^2-y^2}$, has a greater interaction with their ligand orbitals, which may contribute to the J values.

The EPR spectral pattern of polycrystalline VO(acac)$_2$ is different from that of a frozen solution as well as that of the VO(bza)$_2$ powder (Fig. 4). This suggests that there is an inter-pair interaction in the VO(acac)$_2$ crystal because of the shorter pair-pair distance in the VO(acac)$_2$ crystal than in the VO(bza)$_2$ crystal.

Dimer Formation Equilibria. It was mentioned above that there is a monomer(M)–dimer(D) equilibrium, $2M \rightleftharpoons D$, in solution. The equlibrium constant, K, is determined by the following relation:[2e)]

$$R - H_D/H_M = [(8KC^\circ + 1)^{1/2} - 1]/P. \quad (2)$$

In this equation, R is the ratio of the intensity heights, H_D/H_M, of some specific monomer and dimer EPR singnals, which are simultaneously observed; P is a proportionality constant; and C° is the total concentration. K and P can be determined from plots of the experimentally obtained R against C° by using a least-square method. An example of the plots is shown in Fig. 6.

Thus, the obtained K was found to be remarkably solvent dependent, as is usual in copper(II) complexes;[2e,8)] K largely increases from a toluene solution to a toluene–benzene solution with increasing benzene content. The data on K and P obtained in toluene–benzene mixed solvents with different solvent ratios are listed in Table 1.

The fact that P and the spectral pattern for the ΔM_s=2 transitions do not change with solvents indicates that only the dimer and the monomer are present in solution and that the dimer structure does not change with the solvents. The fact mentioned above, that the so-called π–π interaction between the complexes may play some role on the dimerization, raises an expectation that the presence of the π system in the solvent molecules will make some contribution to dimerization.[13)] However, the observation that K changes drastically with the ratio of toluene and benzene in spite of absence of appreciable differences between their aromaticities suggests that there may be some other factors which affect complex dimerization.

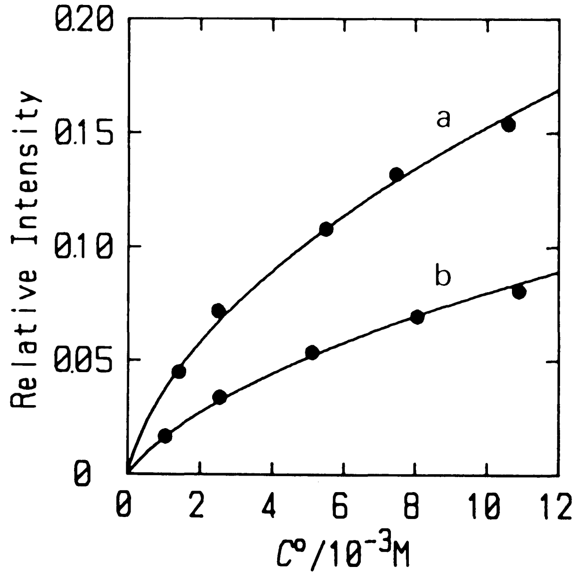

Fig. 6. Relationship between R and C° for VO(acac)$_2$ in a mixed solvent of toluene and benzene (2:8) (a) and in toluene (b). ●: experimental data, ——: calculated by the Eq. 2 using the parameters given in Table 1.

Table 1. K and P Values for Different Ratios of Toluene and Benzene

Toluene : Benzene (v:v)	K/mol dm^{-3}	P
1 : 9	1300	43
2 : 8	700	43
4 : 6	370	42
5 : 5	250	41
10 : 0	230	43

In the EPR spectra of fluid solution samples, monomer EPR signals showing eight well-resolved hyperfine lines were observed to decrease upon lowering the temperature, though no dimer signals were observed because of their extremely large anisotropy. The decrease in the monomer signal intensities upon lowering the temperature indicates that the dimer stabilizes more at lower temperatures and that the monomer-dimer equilibrium shifts to the dimer formation. The stability constants, K, obtained in the above experiments can be regarded as being those at temperatures near the freezing point.[17)] However, when the ratio of toluene to benzene increases, K appreciably decreases in spite of the freezing point decreasing. These results indicate that dimerization may be affected by a subtle balance of various kinds of interactions, such as the monomer–monomer, monomer–solvent, and dimer–solvent interactions. Further investigations on the monomer–dimer equilibria in the related complexes are in progress.

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