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Pyrimidines as Ferromagnetic Exchange Couplers in Dinuclear Oxovanadium(IV) Complexes

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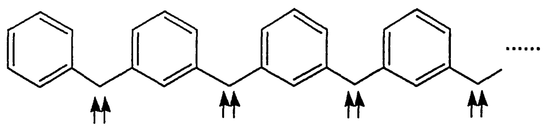
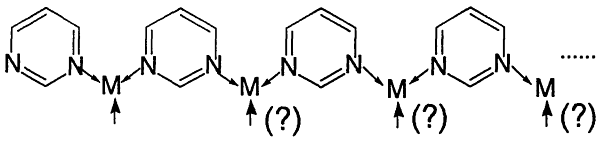
The intramolecular magnetic interactions between 1/2 spins of two oxovanadium (IV) ions were studied in the complexes L[VO(hfac)$_2$]$_2$ (hfac = hexafluoroacetylacetonate, L = 4-methyl-, 4,6-dimethyl-, 4-amino- and unsubstituted-pyrimidines, and quinazoline). The magnetic measurements revealed that the vanadium spins were ferromagnetically coupled through the pyrimidine bridges with $J/k_B = 1.1 - 2.7$ K. The intermolecular ferromagnetic interaction was found in the case of L=pyrimidine.

It is well known that oligo-carbenes and radicals linked with *m*-phenylenes have high-spin ground states (for example, **A**).1) Although the spin polarization mechanism, *i.e.*, topological symmetry of the π-electron network,2) was shown to be valid for some oxygen or nitrogen perturbed systems,3) it is not clear whether this mechanism can be applied to organic coordination compounds containing transition metals as spin sources (**B**). Hendrickson *et al.* reported that some dinuclear titanium(III) complexes bridged by the dianion of 2,4-dimercaptopyrimidine and related anions exhibited various intramolecular ferro- or antiferromagnetic coupling.4) Oshio reported that the dinuclear Fe(III) complex containing a resorcinol bridge showed intramolecular ferromagnetic coupling.5) We synthesized systematically dinuclear transition metal complexes containing a pyrimidine or pyrazine ring as a bridging ligand, and studied their magnetic properties.6) We report here that several dinuclear oxovanadium(IV) complexes bridged by pyrimidines are triplet molecules in their ground states.

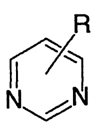


A

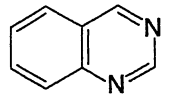


B

The yields, melting points, and elemental analyses of the dinuclear oxovanadium(IV) complexes, L[VO(hfac)$_2$]$_2$, bridged by various pyrimidines (L) are summarized in Table 1.7) The magnetic susceptibilities were measured on a Quantum Design MPMS SQUID magnetometer at 0.5 T in a temperature range down to 1.8 K. The magnetization curves were obtained on an Oxford Instruments Faraday balance equipped with a 7 T coil. The diamagnetic contribution of the organic part was estimated from Pascal's constants.



PM : R = H
MPM : R = 4-Me
DMPM : R = 4,6-Me$_2$
APM : R = 4-NH$_2$



QZ

Table 1. The yields, melting/sublimation points, and elemental analyses of L[VO(hfac)$_2$]$_2$

L	Yield / %	Color (shape)	mp / °C	Anal. C, H, N (calc.) / %		
PM	64	brown (plates)	140 (subl.)	27.36 (27.66)	0.87 (0.77)	2.79 (2.69)
MPM	54	brown (plates)	140 (subl.)	28.32 (28.43)	1.09 (0.95)	2.80 (2.65)
DMPM	21	brown (powder)	140 (subl.)	28.92 (29.18)	1.40 (1.13)	2.61 (2.62)
APM	52	brown (powder)	200 (subl.)	27.40 (27.27)	1.08 (0.86)	4.05 (3.97)
QZ	71	black (blocks)	149.5	30.68 (30.79)	1.15 (0.92)	2.84 (2.56)

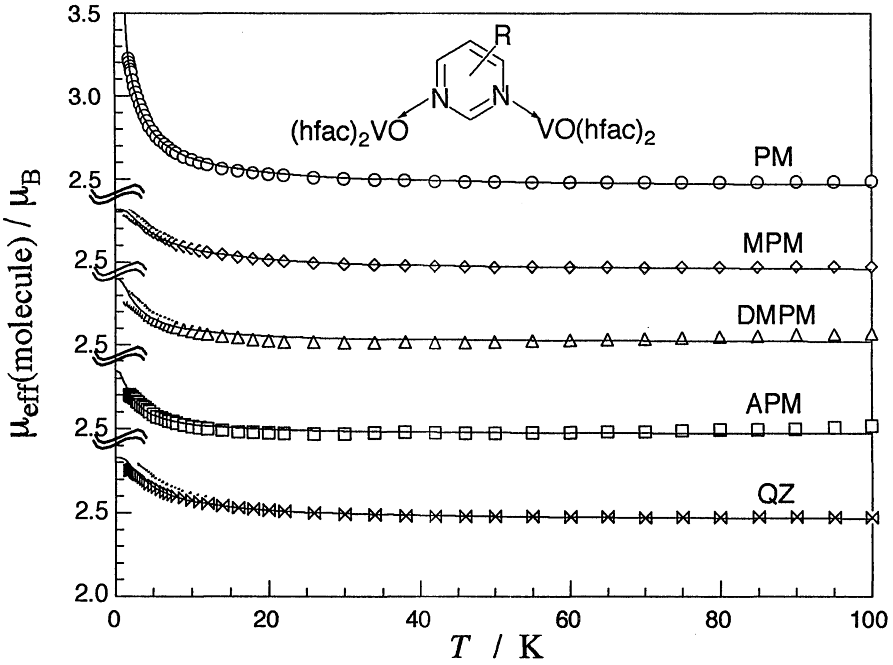


Fig. 1. Temperature dependences of the effective magnetic moments for L[VO(hfac)$_2$]$_2$ containing various pyrimidines. For abbreviation of the ligands, see the text. The solid lines represent the fits to the equation of the singlet-triplet model.

Figure 1 shows the temperature dependences of the effective moments for L[VO(hfac)$_2$]$_2$ (L = PM, MPM, DMPM, APM, and QZ). The effective moments increased with decreasing temperature for all of the pyrimidine complexes investigated here, indicating that the 1/2 spins of vanadium ions are ferromagnetically coupled. In the cases of L = MPM, DMPM, APM, and QZ, the moments reached the values (2.8-2.9 μ_B) expected for the triplet molecules with $g = 2$. The experimental values of the effective moment were analyzed on the basis of the singlet-triplet model (Eq. 1 with $\theta = 0$ K),[8] and the solid lines in Fig. 1 and the parameters in Table 2 were obtained. In the case of L = PM, the effective moment exceeded that of the triplet state with decreasing temperature. It was analyzed by the modified function (Eq. 1), in which θ was introduced as a Weiss mean field parameter, to give $\theta = +0.49$ K.

$$\chi = \frac{2Ng^2\mu_B{}^2}{k_B(T-\theta)} \frac{1}{3+\exp(-2J/k_BT)} \qquad (1)$$

In order to clarify whether the spins are coupled in an intra- and/or intermolecular fashion, the magnetizations were measured at cryogenic temperatures. Those of MPM[VO(hfac)$_2$]$_2$ fell exactly on the

Table 2. Best fit parameters for L$[VO(hfac)_2]_2$

L	PM	MPM	DMPM	APM	QZ	PZ	MPZ a)	DMPZ b)
g	1.99	1.99	2.05	2.01	2.00	~2.c) (1.92 d))	1.99 d)	1.93 d)
J / k_B e)	2.23f)	2.74	1.44	1.11	2.25	-33.3 (-27.5 d))	-9.7 d)	-5.8 d)

a) Methylpyrazine. b) 2,5-Dimethylpyrazine. c) This value could not be determined precisely because of ambiguity of the purity. d) See ref. 9. e) The exchange parameter J is defined by Heisenberg Hamiltonian $H = -2J_{12}S_1 \cdot S_2$. f) The Weiss temperature defined by Eq. 1 in the text was estimated to be 0.49 K.

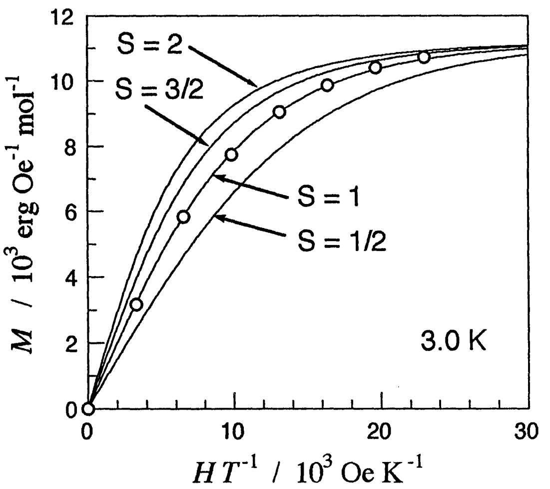


Fig. 2. Magnetization curve of MPM$[VO(hfac)_2]_2$ at 3.0±0.1 K. The solid lines represent theoretical curves with S = 1/2, 1, 3/2, and 2.

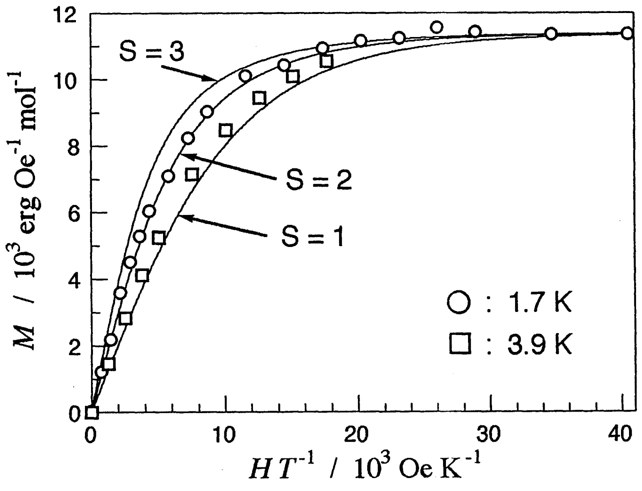


Fig. 3. Magnetization curves of PM$[VO(hfac)_2]_2$ at 1.7±0.1 K and 3.9±0.1 K. The solid lines represent theoretical curves with S = 1, 2, and 3.

Brillouin function with $S = 1$ at 3.0 K, indicating that the molecule has a ground triplet state without any appreciable intermolecular magnetic interaction (Fig. 2). On the other hand, the magnetization curves of PM$[VO(hfac)_2]_2$ exceeded that of the Brillouin function with $S = 1$ and the saturation was more evident at lower temperatures (Fig. 3). The magnetization curve coincided nearly with that of $S = 2$ at 1.7 K. This finding is consistent with the positive θ value obtained above. These facts indicate that the crystal of PM$[VO(hfac)_2]_2$ involves intermolecular as well as intramolecular ferromagnetic interactions.

In contrast to the pyrimidine complexes, the corresponding pyrazine complex PZ$[VO(hfac)_2]_2$ exhibited a decrease of the magnetic moment with decreasing temperature, indicating that the vanadium spins are antiferromagnetically correlated. Analysis of this behavior by the singlet-triplet model gave a negative J value (-33.3 K). This finding agrees well with the results of Hendrickson *et al.* for the complexes containing pyrazine and methylated pyrazines,[9] as summarized in Table 2.

The experimental results that the pyrimidine-bridged bis(oxovanadium) complexes are triplet molecules in their ground states and isomeric pyrazine-bridged complexes singlet molecules can be interpreted qualitatively in terms of the spin polarization mechanism. This mechanism is compatible with the results that the magnetic interaction was not affected much by substituents on the pyrimidine or pyrazine ring. Figure 4 shows a possible explanation of the triplet pyrimidine complexes by a direct pπ-dπ overlap.[10] Another nσ-dσ pathway is conceivable as follows:[12] $d_{xy}(V)\alpha$—$n\sigma(N)(\alpha\cdots\beta)\cdots p\pi(N)\beta$; $(\alpha\cdots\beta)$ means that excess α- and β-spins are induced near the V and N atoms respectively. The detailed mechanism of the magnetic interactions must be discussed in connection with the molecular structures, especially with the symmetry and geometry between the magnetic orbital of the metal ions and the π-orbital of the ligands.

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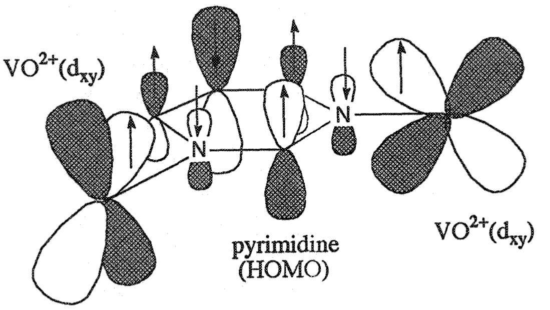

Fig. 4. Schematic spin polarization through a d_{xy} (V) - π(HOMO of pyrimidine) overlap in the pyrimidine-bridged bis(oxovanadium) complexes.

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7) All of the complexes investigated here were prepared by refluxing a dichloromethane solution of oxovanadium(IV) hexafluoroacetylacetonate, $VO(hfac)_2$, and the bridging ligand with molar ratio 2:1 for 1 h. The polycrystalline samples were obtained by concentration of the solvent followed by addition of a small amount of hexane. The samples used for magnetic measurements and elemental analyses were purified by repeated recrystallizations from a dichloromethane-hexane mixed solvent.

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10) The magnetic orbital of oxovanadium is d_{xy} and the pyrazine in $PZ[VO(hfac)_2]_2$ is suggested to be equatorial.[9] The resultant $d_{xy}(V)$-π(PZ) overlap gives rise to the antiferromagnetic interaction between vanadium spins through the π-system of PZ.[9,11] In the cases of the pyrimidine ligands, when the $d_{xy}(V)$ and π(pyrimidine) orbitals have similar overlap, the spins are expected to be ferromagnetically coupled, as illustrated in Fig. 4.

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