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Binuclear Metal Complexes. XI.[1] Substituent Effect upon Magnetisms of Binuclear Oxovanadium(IV) and Copper(II) Complexes of the Schiff Bases, 2,6-Bis[*N*-(2-hydroxy-5-substituted-phenyl)iminomethyl]-4-methylphenol

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Binuclear oxovanadium(IV) and copper(II) complexes, M_2(fsalap-R)(OMe) (R=H, CH_3, Cl, and NO_2) were synthesized and characterized, where H_3fsalap-R denotes 2,6-bis[*N*-(2-hydroxy-5-substituted-phenyl)iminomethyl]-4-methylphenol and the metal ions are connected by the phenolic oxygen and a methanolate ion. The cryomagnetic properties of the complexes except Cu_2(fsalap-NO_2)(OMe) could be interpreted on the basis of the Bleaney-Bowers equation. It was found that the $-2J$ values for the oxovanadium(IV) complexes increase in the order $(VO)_2$(fsalap-CH_3)(OMe) < $(VO)_2$(fsalap-H)(OMe) < (VO_2)(fsalap-Cl)(OMe), while those for the copper(II) complexes decrease in the order Cu_2(fsalap-CH_3)(OMe) > Cu_2(fsalap-H)(OMe) > Cu_2(fsalap-Cl)(OMe). These facts could be reasonably explained in terms of the difference in structures and spin-exchange mechanisms between the oxovanadium(IV) and the copper(II) complexes. $(VO)_2$(fsalap-NO_2)(OMe) showed a very strong antiferromagnetic spin-exchange interaction ($-2J=545\ cm^{-1}$) compared with the other complexes (180—280 cm^{-1}). On the other hand, the magnetism of Cu_2(fsalap-NO_2)(OMe) could be interpreted in terms of the Ising model.

Since both oxovanadium(IV) and copper(II) ions have one unpaired electron in each of their 3d-shells, magnetic exchange interactions of binuclear oxovanadium(IV) complexes are to be discussed in relation to those of binuclear copper(II) complexes. Many binuclear copper(II) complexes have been studied extensively.[2] On the other hand, relatively less number of binuclear oxovanadium(IV) complexes have been synthesized.[3–10] It seems interesting to synthesize binuclear oxovanadium(IV) and copper(II) complexes with the same ligand system and to compare their magnetic properties, but only few have been reported concerning such kind of research.[4,11,12] Ginsberg *et al.* synthesized binuclear oxovanadium(IV) and copper(II) complexes of the Schiff bases prepared from 5-R-salicylaldehydes and 4-R′-2-aminophenols.[4] They found that the magnitude of the spin-exchange interaction for the copper(II) complexes increases with the decreasing order of electron-withdrawing abilities of R groups. However, they could not find such regularity for the oxovanadium(IV) complexes.

In the preceeding papers of this series,[13–18] it was shown that 2,6-diformyl-4-methylphenol and its Schiff bases form stable binuclear complexes with copper(II) and nickel(II) ions. In the present study, the Schiff bases, 2,6-bis[*N*-(2-hydroxy-5-substituted-phenyl)-iminomethyl]-4-methylphenol, were used for the preparation of binuclear oxovanadium(IV) and copper(II) complexes. The Schiff bases are abbreviated to H_3-fsalap-R, in which R is H, CH_3, Cl or NO_2, the substituents being attached to 4-position of 2-aminophenol. The complexes obtained were characterized as a binuclear complex bridged by the phenolic oxygen in the 2,6-diformyl-4-methylphenol moiety and methanolate ion (Fig. 1). The complexes are denoted by M_2-(fsalap-R)(OMe). Their magnetic properties were investigated over the temperature range 77.4—300 K and discussed on the basis of the Heisenberg model and/or the Ising model.

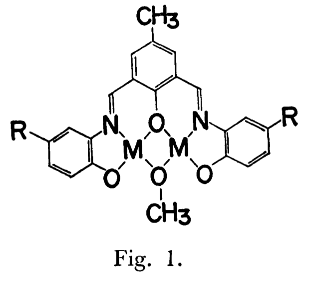


Fig. 1.

Experimental

Syntheses. The synthetic method of 2,6-diformyl-4-methylphenol is described elsewhere.[15]

$(VO)_2$(fsalap-H)(OMe). Vanadium(IV) oxodichloride (500 mg) was dissolved in absolute methanol(30 ml), and the solution was filtered to remove any insoluble materials. To this solution was added a methanolic solution(30 ml) 2,6-diformyl-4-methylphenol(164 mg) and 2-aminophenol (218 mg). Orange crystals immediately separated. After the reaction mixture was stirred at 60 °C for 3 hr, the crystals were collected, thoroughly washed with absolute methanol and dried under vacuum.

Found: C, 51.46; H, 3.60; N, 5.37%. Calcd for $C_{22}H_{18}N_2O_6V_2$: C, 51.99; H, 3.57; N, 5.51%.

$(VO)_2$(fsalap-CH_3)(OMe). This complex was obtained by nearly the same method mentioned above except for using 2-amino-4-methylphenol(264 mg) instead of 2-aminophenol. The mixture was stirred for 3 hr at 60 °C to give orange-brown crystals, which were collected, washed with absolute methanol and dried under vacuum.

Found: C, 53.95; H, 4.03; N, 5.31%. Calcd for $C_{24}H_{22}N_2O_6V_2$: C, 53.75; H, 4.13; N, 5.22%.

$(VO)_2$(fsalap-Cl)(OMe). 2,6-Diformyl-4-methylphenol (164 mg) and 2-amino-4-chlorophenol(288 mg) were dissolved in absolute methanol (40 ml), and the mixture was neutralized with 1M sodium methoxide solution(3 ml). Then this solution was added to a solution of vanadium(IV) oxodichloride (500 mg) in methanol (30 ml). Orange-brown crystals which separated were filtered and dried under vacuum.

Found: C, 45.63; H, 3.04; N, 4.66%. Calcd for C_{22}-

$H_{16}N_2O_6Cl_2V_2$: C, 45.78; H, 2.79; N, 4.85%.

(VO)$_2$(fsalap-NO$_2$)(OMe). 2,6-Diformyl-4-methylphenol (164 mg) and 2-amino-4-nitrophenol(308 mg) were dissolved in the mixture of absolute methanol (25 ml) and dioxane (25 ml). This solution was then added to a solution of vanadium(IV) oxodichloride(500 mg) in absolute methanol (30 ml), and the whole was stirred at 60 °C for 3 hr to give yellowish brown crystals. They were collected, washed with methanol and dried under vacuum.

Found: C, 43.93; H, 2.78; N, 9.22%. Calcd for $C_{22}H_{16}N_4O_{10}V_2$: C, 44.17; H, 2.70; N, 9.36%.

Cu$_2$(fsalap-H)(OMe)·CH$_3$OH. This complex was obtained by the similar method to that for (VO)$_2$(fsalap-H)(OMe) except for using copper(II) acetate monohydrate (440 mg) instead of vanadium oxodichloride. It forms brown crystals, containing one molecule of methanol.

Found: C, 52.42; H, 3.88; N, 5.44%. Calcd for $C_{22}H_{18}N_2O_4Cu_2 \cdot CH_3OH$: C, 52.56; H, 4.22; N, 5.33%.

Cu$_2$(fsalap-CH$_3$)(OMe). This complex was prepared by the similar method to that for (VO)$_2$(fsalap-CH$_3$)(OMe), using copper(II) acetate monohydrate(440 mg). It forms orange-brown crystals.

Found: C, 54.51; H, 4.46; N, 5.34%. Calcd for $C_{24}H_{22}N_2O_4Cu_2$: C, 54.44; H, 4.19; N, 5.29%.

Cu$_2$(fsalap-Cl)(OMe). The synthetic procedure of this complex resembles that for (VO)$_2$(fsalap-Cl)(OMe) except for using copper(II) acetate monohydrate (440 mg) instead of vanadium(IV) oxodichloride. It forms orange-brown crystals.

Found: C, 47.04; H, 2.95; N, 4.88%. Calcd for $C_{22}H_{16}N_2O_4Cl_2Cu_2$: C, 46.33; H, 2.83; N, 4.91%.

Cu$_2$(fsalap-NO$_2$)(OMe)·2H$_2$O. This complex was obtained by treating a methanolic solution of copper(II) acetate monohydrate(440 mg) with a solution of 2,6-diformyl-4-methylphenol(164 mg) and 2-amino-4-nitrophenol(308 mg) in methanol–dioxane(1 : 1, 50 ml). Brown crystals which separated were filtered and washed with methanol. It contains two molecules of water.

Found: C, 42.71; H, 2.97; N, 9.11%. Calcd for $C_{22}H_{16}N_4O_8Cu_2 \cdot 2H_2O$; C, 42.11; H, 2.89; N, 8.93%.

Measurements. Infrared spectra were measured with a 215 Hitachi Infrared Grating Spectrophotometer in the region 4000—650 cm^{-1}, using KBr-disk and hexachlorobutadiene-mull methods. ESR spectra(X-band) of polycrystalline samples were measured with a JEOL ESR-apparatus model JESME-3X at −100 °C and at room temperature. Magnetic susceptibilities were measured by the Faraday method in the range from liquid nitrogen temperature to room temperature. Pascal's constants[19] were used for diamagnetic correction. Mercuric tetrathiocyanatocobaltate(II) was used as a magnetic standard. The effective magnetic moments at room temperature were calculated from the expression, $\mu_{\mathrm{eff}}=2.828\sqrt{(\chi_{\mathrm{A}}-N\alpha)T}$

Results and Discussion

In the IR spectra of the complexes no absorption band due to the formyl group was found in the region 1700—1620 cm^{-1} and a strong band was found around 1600 cm^{-1}. This band may be attributed to the C=N stretching vibration. The V=O stretching vibration of (VO)$_2$(fsalap-R)(OMe) (R=H, CH$_3$, and Cl) was observed near 990 cm^{-1}. On the other hand, the V=O stretching vibration of (VO)$_2$(fsalap-NO$_2$)(OMe) shifted to a region of considerably low frequency (900 cm^{-1}). This fact implies that (VO)$_2$(fsalap-NO$_2$)(OMe) has a different molecular structure from other oxovanadium(IV) complexes. In the spectrum of Cu$_2$(fsalap-NO$_2$)(OMe)·2H$_2$O was observed a broad band around 3200 cm^{-1}, which was assigned to the O–H vibration of water. This complex showed a loss of weight corresponding to two moles of water, when it was heated at 70 °C for several hours under vacuum. It recovered the weight when it was left standing in the atmosphere at room temperature. Therefore, it should be noted that Cu$_2$(fsalap-NO$_2$)(OMe) possesses a different structure from other Cu$_2$(fsalap-R)(OMe) complexes.

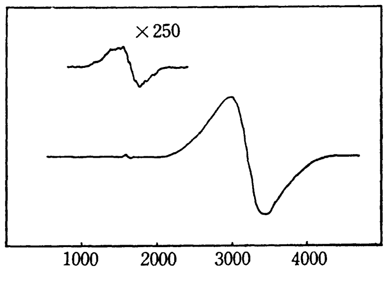


Fig. 2. ESR spectrum of (VO)$_2$(fsalap-H)(OMe) at room temperature.

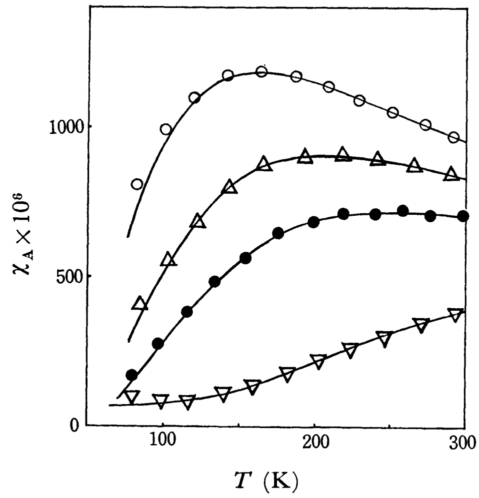


Fig. 3. Temperature dependeuce of magnetic susceptibilities of (○) (VO)$_2$(fsalap-CH$_3$)(OMe), (△) (VO)$_2$(fsalap-H)(OMe), (●) (VO)$_2$(fsalap-Cl)(OMe), and (▽) (VO)$_2$(fsalap-NO$_2$)(OMe).

The ligand field bands of the complexes could not be identified because of the intense absorption due to the ligand in visible region.

The ESR spectra of the complexes (polycrystalline sample) were measured. All spectra resemble each other. As an example the spectrum of (VO)$_2$(fsalap-H)(OMe) is shown in Fig. 2. A broad band around 3200 Guass (2000 G width) and a weak band near 1600 G were tentatively assigned to the $\Delta M_s=1$ and $\Delta M_s=2$ transitions respectively. All of these data are consistent with the structure given in Fig. 1.

The effective magnetic moments of the complexes at room temperature are lower than the spin-only value, 1.73 B.M.. The magnetic susceptibilities were measured at various temperatures. As shown in Figs. 3 and 4, the magnetisms of the complexes except Cu$_2$-

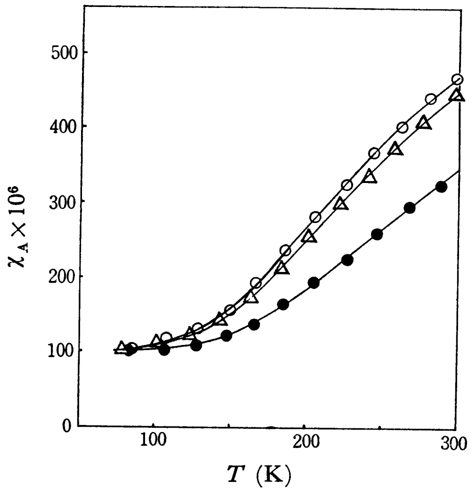


Fig. 4. Temperature dependence of magnetic susceptibilities of (●) Cu_2(fsalap-CH_3)(OMe), (△) Cu_2-(fsalap-H)(OMe), and (○) Cu_2(fsalap-Cl)(OMe).

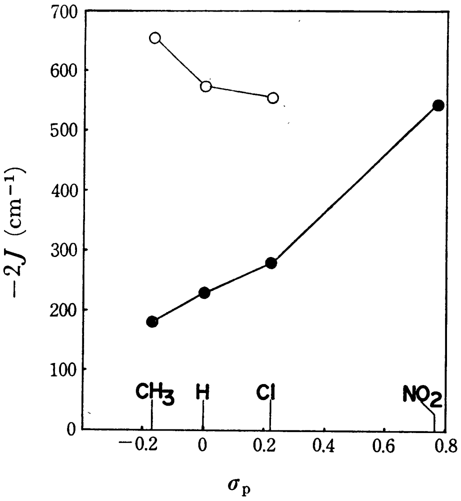


Fig. 5. The relations between the $-2J$ values and Hammett's σ_p values for (●) $(VO)_2$ (fsalap-R)(OMe) and for (○) Cu_2 (fsalap-R) (OMe).

(fsalap-NO_2)(OMe) (anhydrous form) can be interpreted on the basis of the Bleaney-Bowers equation,[20)]

$$\chi_A = \frac{Ng^2\beta^2}{3kT}\left[1+\frac{1}{3}\exp\left(-2J/kT\right)\right]^{-1} + N\alpha,$$

where J is the exchange integral between a magnetically coupled pair and $N\alpha$ is the temperature independent paramagnetism. The agreements between theoretical and experimental $\chi_A - T$ curves are satisfactory when the parameters, g, J and $N\alpha$, are assumed as listed in Table 1. Slight deviations from the theoretical curves at low temperature may be attributed to a trace of paramagnetic impurities. The effective magnetic moments of the complexes are also given in Table 1.

As seen in Table 1, with the increasing order of electron-withdrawing abilities of the substituents the $-2J$ value (singlet-triplet energy separation) increases in the case of the oxovanadium(IV) complexes, but decreases in the case of the copper(II) complexes, This is more clearly shown by Fig. 5 in which the $-2J$ values are plotted *versus* Hammett's σ_A values.

It is well known that many oxovanadium(IV) complexes have square-pyramidel structures with the oxygen atom at the apex, vanadium atom being slightly lifted from the vasal plane. The electron-donating substituent at the 4-position in 2-aminophenol moiety increase the electron density on the phenolic oxygen atom and *vice versa*. According to an electrostatic model,[12)] it is expected that the deviation of vanadium atom from the vasal plane is the largest for $(VO)_2$(fsalap-CH_3)-(OMe) and the smallest for $(VO)_2$(fsalap-Cl)(OMe) among the present complexes. Since the direct coupling between d_{xy}-orbitals is expected to be the dominating factor for the spin-exchange interaction in binuclear oxovanadium(IV) complexes,[12,22,23)] the overlapping of d_{xy}-orbitals increases in the order $(VO)_2$-(fsalap-CH_3)(OMe) < $(VO)_2$(fsalap-H)(OMe) < $(VO)_2$-(fsalap-Cl)(OMe), whereby the $-2J$ value increasing in this order.

TABLE 1. MAGNETIC PARAMETERS AND EFFECTIVE MAGNETIC MOMENTS OF COMPLEXES

M_2(fsalap-R)-(OMe)		$-2J$ (cm^{-1})	g	$N\alpha \times 10^6$	μ_{eff} (K)
M	R				
VO	CH_3	180	1.87	60	1.46(291.0)
VO	H	230	1.86	40	1.37(291.2)
VO	Cl	280	1.81	45	1.25(298.0)
VO	NO_2	545	1.95	70	0.85(295.7)
Cu	CH_3	655	2.15	100	0.70(288.5)
Cu	H	570	2.15	100	0.88(298.1)
Cu	Cl	555	2.15	100	1.04(298.1)
Cu	NO_2				1.18(288.3)

On the other hand, the majority of copper(II) complexes have tetragonal structures. It has been revealed[24,25)] that the spin-pairing interaction in the binuclear copper(II) complexes increases when the equatorial bonds are strengthened. This can be interpreted in term of a superexchange pathway through p_π(Cu)-p_π(bridging atom)-d_π(Cu) orbitals.[12,26–28)] Our finding that the $-2J$ value decreases in the order Cu_2(fsalap-CH_3)(OMe) > Cu_2(fsalap-H)(OMe) > Cu_2-(fsalap-Cl)(OMe) is consistent with the above rule, because the electron density on the 2-aminophenolic oxygen atom decreases in this order and accordingly the Cu–O bond is weakened in the same order.

It is noteworthy that $(VO)_2$(fsalap-NO_2)(OMe) shows a very strong antiferromagnetic spin-exchange interaction and its V=O stretching vibration is observed at 900 cm^{-1}. Since such a shift of the V=O band to the low-frequency region is attributable to the intermolecular ···V=O···V=O··· interaction,[4,29)] it is natural to assume the polymeric structure given in Fig. 6 for $(VO)_2$(fsalap-NO_2)(OMe). Hence the configuration around vanadium(IV) ion might not be distorted tetragonal-pyramidal but pseudo-octahedral. In fact the deviation of vanadium(IV) ion from the plane in N,N'-1,3-propylenebis(salicylaldiminato)-oxovanadium(IV),[29)] whose linear chain structure of ···V=O···V=O··· bonding was demonstrated on the basis of X-ray analysis, is only 0.31 A, which is much

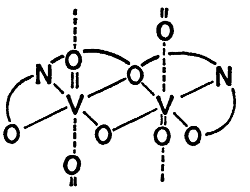
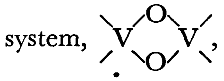


Fig. 6.

smaller than 0.54—0.58 A in the common oxovanadium(IV) complexes.[30,31] Accordingly the equatorial bonding system, , is made more coplanar, and this will bring about larger overlapping between the vanadium d_{xy}-orbitals. The intermolecular spin-exchange interaction *via* ···V=O···V=O··· bonds is very weak compared with the intramolecular spin-exchange interaction, since the magnetism of $(VO)_2$(fsalap-NO_2)(OMe) can be interpreted in terms of the Bleaney-Bowers equation. Such anomalous magnetisms have been reported for other binuclear oxovanadium(IV) complexes of the nitro-substituted Schiff bases.[4] It is likely that the strongly electron-withdrawing nitro group attached to the 4-position of 2-aminophenol moiety reduces the electron density on the phenolic oxygen atom, thereby weakening the ligand-field and allowing the axial coordination to the vanadium(IV) ion.

The magnetic property of Cu_2(fsalap-NO_2)(OMe) (anhydrous form), on the other hand, could not be interpreted on the basis of the Bleaney-Bowers equation. Its magnetism can be interpreted in terms of the Ising model. According to this model, the effective magnetic moment is expressed by the equation,[32]

$$\mu_{\text{eff}}^2 = \frac{1}{4}[\exp(4K)+(2+K^{-1})\exp(2K)-K^{-1}\times\exp(-2K)+5][\exp(2K)+\exp(-2K)+2]^{-1},$$

where K is J/kT. The good agreement of the experimental μ_{eff} values with this equation is shown in Fig. 7. Therefore, it is clear that Cu_2(fsalap-NO_2)(OMe) has a polymeric structure. However, further detailed information about the molecular structure can not be obtained at present. The high electron-withdrawing ability of the nitro group seems to play an important role in the formation of polymeric structure.

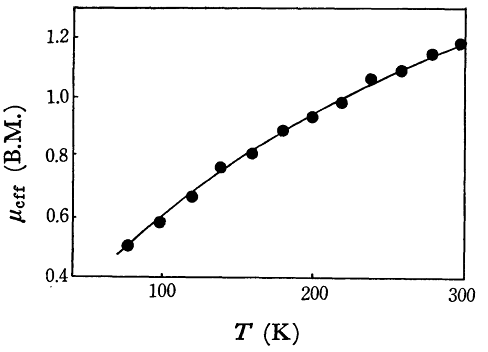


Fig. 7. Temperature dependeuce of the effective magnetic moment of Cu_2(fsalap-NO_2)(OMe). The solid line is theoretically obtained by assuming $g=2.15$ and $J=-225\ \text{cm}^{-1}$.

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