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FERROMAGNETIC SPIN-EXCHANGE INTERACTION IN COPPER(II)-OXOVANADIUM(IV) COMPLEXES WITH 3-FORMYLSALICYLIC ACID-DIAMINE SCHIFF BASES. THE IMPORTANCE OF GROUND ELECTRONIC CONFIGURATION IN SPIN-SPIN COUPLING1)

Naoyuki TORIHARA, Hisashi OKAWA,* and Sigeo KIDA
Department of Chemistry, Faculty of Science, Kyushu University,
Hakozaki, Higashi-ku, Fukuoka 812

Copper(II)-oxovanadium(IV) hetero-metal binuclear complexes with 3-formylsalicylic acid-diamine Schiff bases were prepared and their magnetic properties were explored in the temperature range 78-300°K. They obeyed the Curie-Weiss law ($\chi_M=C/(T-\theta)$) with positive Weiss constant ($\theta=18\sim20$°K), indicating ferromagnetic spin-exchange interaction between the metal ions. The magnetic properties of the present complexes were discussed in comparison with those of Cu(II)-M(II) complexes with the same ligands.

Hetero-metal binuclear complexes are of interest in connection with spin-exchange interaction and charge-transfer between metal ions. Since copper(II) and oxovanadium(IV) ions have one unpaired electron on each 3d-orbital, in spite of the difference in their electronic configuration, it seems interesting to examine the spin-exchange interaction between copper(II) and oxovanadium(IV) ions. However, there have been obtained very few copper(II)-oxovanadium(IV) hetero-metal binuclear complexes.2)

In the previous papers of this series,3-6) we have prepared copper(II)-M(II) (M(II)=Cu(II), Ni(II), Co(II) and Mn(II)) hetero-metal binuclear complexes with 3-formylsalicylic acid-diamine Schiff bases (abbreviated as H_4fsaR; R=en, pn, bn, etc.) and examined the spin-exchange interaction between the metal ions. This paper relates to the synthesis and magnetic investigation of CuVO(fsaR) in comparison with CuM(fsaR)·nH_2O.

Synthesis of CuVO(fsaR) was carried out as follows: Cu(H_2fsaen)·$\frac{1}{2}H_2O$ (200mg) was dissolved in a methanolic solution (50 ml) of $LiOH \cdot H_2O$ (95 mg). The solution was once filtered to separate a trace of insoluble impurity and to this solution was added a methanolic solution of $VOCl_2$ (80 mg) to give grey-blue crystals. They were collected by filtration and throughly washed with DMF in order to separate unreacted $Cu(H_2fsaen)\cdot\frac{1}{2}H_2O$.

CuVO(fsapn) and CuVO(fsabn) were obtained in the same way as that for CuVO(fsaen). Elemental analyses are given in Table 1.

Table 1. Elemental analyses of CuVO(fsaR)

	Found(%)			Calcd(%)		
	C	H	N	C	H	N
CuVO(fsaen)	44.85	2.45	5.84	44.78	2.51	5.80
CuVO(fsapn)	45.86	2.90	5.73	45.93	2.84	5.64
CuVO(fsabn)	47.19	3.23	5.64	47.02	3.16	5.48

Reflectance spectra of CuVO(fsaR) are similar to each other and show absorption bands at 13,000, 17,000-18,000 and 23,000 cm^{-1}. These spectra quite resemble that of bis(acetylacetonato)oxovanadium(IV),7) which has d-d bands at 13,000, 17,000 and ∼24,000 cm^{-1}. The broadening of the band at 17,000-18,000 cm^{-1} for the present complexes may be caused by the superposition of the d-d band due to the copper(II) bound at the N_2O_2-donating site. In fact $Cu(H_2fsaR)$ possesses d-d band near 18,000 cm^{-1}. Therefore, the electronic spectra are consistent with the structure possessing copper(II) at the "inside" donating site and oxovanadium(IV) at the "outside" donating site (Fig. 1). Infrared spectra of the complexes show a strong band near 990 cm^{-1} attributable to the V=O stretching vibration.

Magnetic susceptibility was measured in the temperature range from liquid nitrogen temperature to room temperature by Faraday method. The inverse magnetic susceptibilities of CuVO(fsaR) obey the Curie-Weiss law with a relatively large Weiss constant (θ=20 for CuVO(fsaen), 20 for CuVO(fsapn) and 18°K for CuVO(fsabn)), demonstrating a ferromagnetic spin-exchange interaction between copper(II) and oxovanadium(IV) ions. In Fig. 2 the Curie-Weiss plot for CuVO(fsaen) is shown. In the course of this study, Kahn et al.2) prepared a methanol-adduct of CuVO(fsaen) by nearly the same method as that previously described by us for obtaining $CuM(fsaR)\cdot nH_2O$. Their complex also shows a ferromagnetic spin-exchange interaction between the metal ions.

It seems interesting to compare the magnetic properties of CuVO(fsaR) with

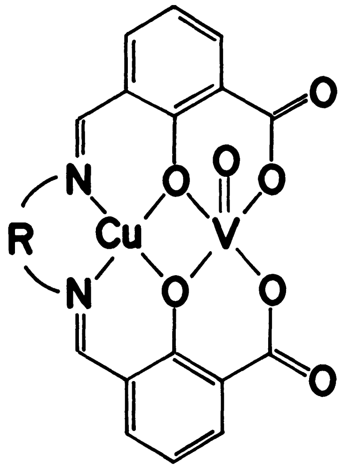

Fig. 1.

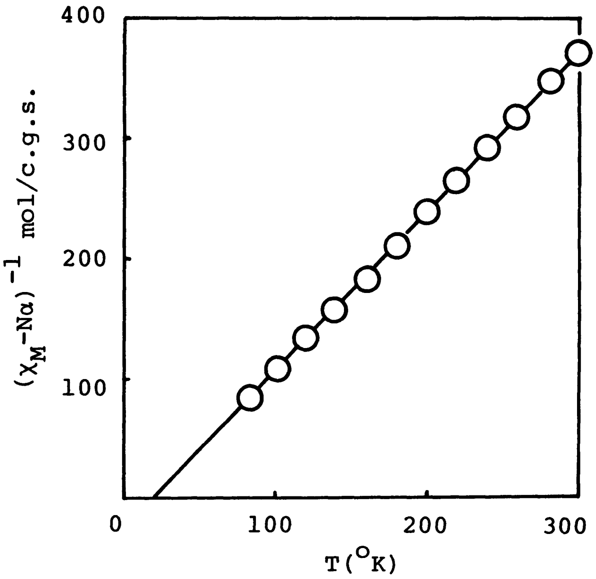

Fig. 2. Temperature variation of inverse molar susceptibility of CuVO(fsaen). Temperature-independent paramagnetism, Nα, is estimated at 120×10^{6}c.g.s./mol.

those of CuM(fsaR)·nH_2O. In Table 2 the exchange integrals (and Weiss constants) for CuM(fsaen)·nH_2O and CuM(fsapn)·nH_2O are tabulated. It is evident that in the complexes except CuVO(fsaR) an antiferromagnetic spin-exchange interaction operates between the metal ions.

Table 2. Exchange integrals (cm^{-1}) and Weiss constants (°K) for CuM(fsaen)·nH_2O and CuM(fsapn)·nH_2O

M(II)	Cu(II)	Ni(II)	Co(II)	Mn(II)	V(IV)O
CuM(fsaen)	-330	-75	-35	-22	(+20)*
CuM(fsapn)	-328	-34	-36	-26	(+20)*
Ref.	8	3,4,5	3,4	6	This work

*Weiss constant

It is well known that the unpaired electron of copper(II) occupies $d_{x^2-y^2}$ orbital (x- and y-axes are taken on the donating atoms). Single crystal X-ray analysis demonstrated that the cobalt(II) ion in CuCo(fsaen)·$3H_2O$ has a psuedooctahedral configuration with water molecules at the apical positions.$^{9)}$ The configuration around the nickel(II) in CuNi(fsaR).nH_2O is also expected to be pseudo-octahedral from electronic spectra.$^{3)}$ Accordingly, the ground state electronic configurations for nickel(II) and cobalt(II) ions in CuNi(fsaR)·nH_2O and CuCo(fsaR)·nH_2O may be approximated by $(e_g)^2$ and $(e_g)^2(t_{2g})^1$ respectively. We are not aware of the exact configuration around the manganese(II) in CuMn(fsaR)·H_2O, but it is in high-spin state with the electronic configuration of $(d_{x^2-y^2})^1(d_{z^2})^1(d_{xy})^1(d_{xz})^1(d_{yz})^1$. On the other hand, oxovanadium(IV) complexes generally have an unpaired electron on d_{xy} orbital. Judging from the electronic configurations of the second metal ion (M^{2+}), we may conclude that an antiferromagnetic spin-exchange interaction in $\mathrm{Cu(II)}\begin{smallmatrix}\diagup\mathrm{O}\diagdown\\ \diagdown\mathrm{O}\diagup\end{smallmatrix}\mathrm{M(II)}$ system is mainly due to the spin-spin coupling between the electron on $d_{x^2-y^2}$ orbital of copper(II) ion and the electron on $d_{x^2-y^2}$ orbital of M(II) ion.

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