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Binuclear Metal Complexes
XVII.* Vanadium(V)–Copper(I) Hetero-Metal Binuclear Complexes Prepared From Oxovanadium(IV) Complexes with Quadridentate Schiff Bases and Copper(II) Halides**

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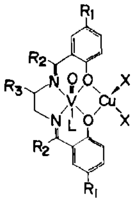
Vanadium–copper hetero-metal binuclear complexes L VOCuX$_2$·CH$_3$OH (X = Cl and Br) have been synthesized, where L denotes N,N'-bis(salicylidene)-ethylenediaminate or its homologues. The complexes were characterized on the basis of elemental analyses, infrared spectra, visible spectra, and cryomagnetic measurements, and were concluded to be of binuclear structures containing a vanadium(V) and a copper(II) ion in each molecule.



L = CH$_3$OH

Figure 1. Structure of the complexes.

Introduction

There have been many binuclear oxovanadium(IV) and copper(II) complexes, whose magnetic properties have been explained in terms of the Bleaney–Bowers equation [3]. Oxovanadium(IV) and copper(II) ions resemble each other magnetically in possessing one unpaired electron. However, spin-exchange mechanisms in binuclear complexes of oxovanadium(IV) and copper(II) are different from each other because of the difference of their electronic configurations, (3d)^1 and (3d)^9 [4, 5]. This fact explains the arising interests in the spin-exchange interaction between oxovanadium(IV) and copper(II) ions. However, oxovanadium(IV)–copper(II) hetero-metal binuclear complexes so far reported are few [6]. Selbin and Ganguly [6] obtained oxovanadium(IV)–copper(II) hetero-metal complexes by reacting N,N'-bis(salicylidene)ethylenediaminatooxovanadium(IV) and a copper(II) halide. According to them, the room temperature magnetic moments of the complexes were subnormal, suggesting an antiferromagnetic spin-exchange interaction between the metal ions. However, their result is not convincing since the large g-value determined from e.s.r. measurements is not compatible with the low magnetic moment. Therefore, in this study we have prepared vanadium–copper hetero-metal binuclear complexes using quadridentate Schiff bases in order to clarify the problem and to elucidate the spin-exchange interaction between oxovanadium(IV) and copper(II) ions. The Schiff bases were represented as H$_2$(R$_1$, R$_2$, R$_3$) (R$_1$, R$_2$, R$_3$ = H, CH$_3$), where R$_1$, R$_2$, and R$_3$ denote the substituents attached to the 5-, α-, and bridging-carbons in N,N'-bis(salicylidene)-ethylenediamine, respectively (Fig. 1). The complexes are abbreviated as (R$_1$, R$_2$, R$_3$)VOCuX$_2$·CH$_3$OH (X = Cl, Br). The complexes were characterized on the basis of elemental analyses, infrared spectra, visible spectra, and temperature dependence of magnetic susceptibility.

Experimental

Syntheses

N, N'-bis(salicylidene) ethylenediaminatooxovanadium(IV) and N,N'-Bis(salicylidene)propylenediaminatooxovanadium(IV) were obtained after the method of Bielig and Bayer [7]. N,N'-Bis(5-methylsalicylidene)ethylenediaminatooxovanadium(IV) and N,N'-bis(α-methylsalicylidene)ethylenediaminatooxovanadium(IV) were also obtained by the same method. The method for the preparation of the vanadium–copper heterometal binuclear complexes is practically the same. The synthesis of (H,Me,H)-VOCuCl$_2$·CH$_3$OH is exemplified. To a methanolic solution (20 ml) containing 2,2-dimethoxypropane (2 ml) copper(II) chloride dihydrate (340 mg) was added and the mixture was refluxed for 10 minutes. Then N,N'-bis(α-methylsalicylidene)ethylenediaminatooxovanadium(IV) (722 mg) was added to the solution. Immediately a deep purple solution was formed. After being heated for 10 minutes on a water bath, the reaction mixture was filtered to separate a

TABLE I. Elemental Analyses of Complexes.[a]

	Found (%)				Calcd (%)			
	C	H	N	Cu	C	H	N	Cu
(H,H,H)VOCuCl$_2$·CH$_3$OH	40.94	3.54	5.78	10.81	40.86	3.63	5.61	11.72
(H,H,H)VOCuBr$_2$·CH$_3$OH	34.63	2.81	4.71	10.45	34.72	3.09	4.77	10.81
(H,H,Me)VOCuBr$_2$·CH$_3$OH	35.49	3.07	4.74	10.25	35.84	3.34	4.65	10.54
(H,Me,H)VOCuCl$_2$·CH$_3$OH	43.70	4.39	5.67	11.40	43.24	4.20	5.31	12.04
(H,Me,H)VOCuBr$_2$·CH$_3$OH	36.86	3.56	4.59	10.19	37.01	3.60	4.54	10.30
(Me,H,H)VOCuBr$_2$·CH$_3$OH	36.65	3.89	4.30	10.48	37.01	3.60	4.54	10.30

[a](H,H,H) = $C_{16}H_{14}N_2O_2$, (H,H,Me) = $C_{17}H_{16}N_2O_2$, and (H,Me,H) = (Me,H,H) = $C_{18}H_{18}N_2O_2$.

small amount of insoluble materials. The filtrate was allowed to stand in a H_2SO_4-dessicator until purple prisms separated. They were collected, washed with a small amount of absolute methanol and dried *in vacuo*.

Colors and elemental analyses of the complexes are given in Table I.

Measurements

Carbon, hydrogen and nitrogen analyses were carried out at the Service Center of Elemental Analysis, Kyushu University. Copper analyses were carried out using a Shimazu Atomic Absorption-Flame Spectrophotometer Model 610S, where an aqueous solution for the measurement was prepared by thermally decomposing the sample in the presence of sulfuric acid and dissolving the resulting metal sulfate in dilute hydrochloric acid containing a small amount of methanol. Infrared spectra were measured using a Hitachi Infrared Spectrophotometer Model 215 on a KBr disk. Visible spectra in methanol were measured using a Shimazu Multipurpose Spectrophotometer Model MSP-5000. Magnetic susceptibility was measured by the Faraday method from liquid nitrogen temperature to room temperature. Diamagnetic correction was carried out using Pascal's constants [8].

Results and Discussion

Although our synthetic method of the hetero-metal complexes was similar to Selbin–Ganguly's method, we could obtain purer crystals. However, we should be aware that the hetero-metal binuclear complexes were occasionally contaminated with monomeric or homo-metal binuclear species. In the reaction between N,N'-bis(5-methylsalicylidene)-ethylenediaminatooxovanadium(IV) and copper(II) chloride, for example, the main product was N,N'-bis(5-methylsalicylidene)ethylenediaminatocopper(II). The purity of hetero-metal binuclear complexes, therefore, seems highly dependent on the relative stabilities and the relative solubilities of the hetero-metal complex and other species in the solution and hence, syntheses of pure hetero-metal complexes with N,N'-bis(5-methylsalicylidene)propylenediamine, N,-N'-bis(α-methylsalicylidene)propylenediamine, and N,N'-bis(α-ethylsalicylidene)ethylenediamine were unsuccessful. The copper content is slightly smaller than the calculated value in the case of (H,H,H)-VOCuCl$_2$·CH$_3$OH, (H,H,H)VOCuBr$_2$·CH$_3$OH, and (H,Me,H)-VOCuCl$_2$·CH$_3$OH. These facts imply the presence of a small amount of impurity such as a monomeric oxovanadium(IV) or a monomeric copper(II) complexes. The formation of the hetero-metal complexes also depends on the substituent R_1 attached to the 5-position of the salicylaldehyde moiety. For example, in the case of R_1 = Br and NO_2 it was unsuccessful to synthesize hetero-metal complexes. It is likely that the electron donating nature of the R_1 substituent exerts some effect on the hetero-metal complex formation.

TABLE II. Infrared and Visible Spectral Bands of Complexes.

	Infrared (cm^{-1})		Visible (ε) ($\times 10^{-3}$ cm^{-1})
	Skel	V=O	
(H,H,H)VOCuCl$_2$·CH$_3$OH	1560	975	17.5 (710)
(H,H,H)VOCuBr$_2$·CH$_3$OH	1555	980	17.7 (730)
(H,H,Me)VOCuBr$_2$·CH$_3$OH	1560	980	17.7 (770)
(H,Me,H)VOCuCl$_2$·CH$_3$OH	1550	980	18.0 (970)
(H,Me,H)VOCuBr$_2$·CH$_3$OH	1550	980	18.0 (850)
(Me,H,H)VOCuBr$_2$·CH$_3$OH	1550	975	16.9 (760)

In Table II one of the skeletal vibrations and the V=O stretching vibration of the complexes are shown. The skeletal vibration for the monomeric oxovanadium(IV) complexes is found around 1540–1535 cm^{-1}, while this band shifts by 15–20 cm^{-1} to a higher frequency region in the hetero-metal complexes. A similar trend in the skeletal vibration was found when N,N'-bis(salicylidene)ethylenediaminatocopper(II) and its homologues form binuclear complexes with copper(II) chloride or copper(II)

TABLE III. Temperature Variation of Magnetic Susceptibility.

(H,H,H)VOCuCl$_2$·CH$_3$OH												
T(K)	83.5	103.7	121.9	143.3	164.6	186.4	206.2	225.9	247.0	266.8	274.5	296.6
$\chi_M \times 10^6$	474	375	330	273	243	229	201	199	166	165	168	147
$\chi_M^a \times 10^6$ (8.4%)	51	35	41	27	29	39	30	43	23	33	39	28
(H,H,H)VOCuBr$_2$·CH$_3$OH												
T(K)	81.2	102.1	124.0	147.4	167.7	189.3	209.9	231.5	253.2	275.5	296.9	
$\chi_M \times 10^6$	336	289	223	184	187	164	161	138	131	126	124	
$\chi_M^a \times 10^6$ (5.7%)	41	55	30	22	44	38	47	35	36	39	43	
(H,H,Me)VOCuBr$_2$·CH$_3$OH												
T(K)	81.7	103.0	124.8	146.2	168.5	189.3	210.6	232.7	254.4	275.9	297.8	
$\chi_M \times 10^6$	233	185	152	142	112	115	114	97	93	83	76	
$\chi_M^a \times 10^6$ (3.5%)	53	42	34	41	25	37	44	34	35	30	27	
(H,Me,H)VOCuCl$_2$·CH$_3$OH												
T(K)	85.7	106.5	128.1	148.2	167.9	187.8	208.5	228.6	249.8	271.7	296.3	
$\chi_M \times 10^6$	401	337	260	260	216	205	188	164	150	153	133	
$\chi_M^a \times 10^6$ (7.3%)	43	49	21	53	33	42	41	30	27	40	30	
(H,Me,H)VOCuBr$_2$·CH$_3$OH												
T(K)	87.4	106.0	126.9	147.5	166.3	186.9	206.1	226.9	249.4	269.1	297.8	
$\chi_M \times 10^6$	43	49	45	53	40	36	35	35	36	42	38	
(Me,H,H)VOCuBr$_2$·CH$_3$OH												
T(K)	87.4	108.5	129.1	149.4	169.9	190.3	210.7	231.3	253.4	274.2	295.5	
$\chi_M \times 10^6$	53	39	39	43	41	29	40	31	33	42	34	

$^a\chi_M^a$ is the susceptibility corrected by assuming the paramagnetic impurity shown in parenthesis, where the magnetic susceptibility of impurity is estimated at 1400×10^{-6} e.m.u./mol at 300 K.

bromide [9]. Hence, the higher-energy shift of the band has been used for a diagnosis of the formation of phenolic oxygen bridge. Therefore, it may be concluded that in (R$_1$, R$_2$, R$_3$)VOCuX$_2$·CH$_3$OH the vanadium and the copper atoms are bridged by the phenolic oxygens. No marked change in frequency of the V=O stretching vibration was found between a monomeric oxovanadium(IV) and a corresponding hetero-metal complexes.

The molar magnetic moments for (H,H,H)-VOCuCl$_2$·CH$_3$OH and (H,H,H)VOCuBr$_2$·CH$_3$OH are much lower than the values reported by Selbin and Ganguly [6]. Magnetic susceptibility of the complexes was measured from liquid nitrogen temperature to room temperature. The results are tabulated in Table III. The magnetic susceptibilities for (H,Me,H)VOCuBr$_2$·CH$_3$OH and (Me,H,H) VOCuBr$_2$·CH$_3$OH are substantially constant (~40×10^{-6} e.m.u./mol) in the temperature range 78–300 °K. On the other hand, the magnetic susceptibilities for other complexes are dependent on temperature. However, these magnetisms cannot be explained on the basis of any chemically pure monomeric or polymeric species. Judging from the trend of increasing susceptibility with lowering temperature, the paramagnetism should be attributed to a paramagnetic impurity such as monomeric copper(II) complexes or monomeric oxovanadium(IV) complexes. Accordingly, the magnetic susceptibilities were corrected by assuming a small amount of paramagnetic impurity whose susceptibility was estimated at 1400×10^{-6} e.m.u./mol at 300 °K. Corrected susceptibilities, which are also given in Table III, clearly indicate that (H,H,H)VOCuCl$_2$·CH$_3$OH, (H,H,H)VOCuBr$_2$·CH$_3$OH, (H,H,Me)-VOCuBr$_2$·CH$_3$OH, and (H,Me,H)VOCuCl$_2$·CH$_3$OH are essentially diamagnetic.

The diamagnetism of the present complexes could be interpreted in terms of the antiferromagnetic spin-exchange interaction between an oxovanadium(IV) and a copper(II) ion, granted that the spin-triplet state is above the spin-singlet state by more than 1000 cm^{-1}. However, such a strong spin-pairing between an oxovanadium(IV) and a copper(II) ion seems unlikely since their ground state configurations differ from each other (the unpaired electron is on the d_{xy} orbital in an oxovanadium(IV) complex and on $d_{x^2-y^2}$ orbital in a copper(II) complex, when x- and y-axes are taken on the equatorial coordinating atoms) [5]. Furthermore, the temperature-independent paramagnetism, Nα, is expected to be larger than

100×10^{-6} e.m.u./mol, since the Nα value is empirically estimated at *ca.* 60×10^{-6} e.m.u./mol for both copper(II) [10] and oxovanadium(IV) complexes [4, 11]. The temperature-independent paramagnetisms found for the present hetero-metal complexes are much smaller than the value expected for an oxovanadium(IV)–copper(II) cluster.

An alternative explanation for the diamagnetism of the present complexes is that they are composed of a vanadium(V) and a copper(I) ion, where the metal ions have no unpaired electron at all. In this case the temperature-independent paramagnetism should be small since the excited states capable of mixing with the ground state will be energetically very high. Thus, it is naturally concluded that the present complexes are composed of a vanadium(V) and a copper(I) ion.

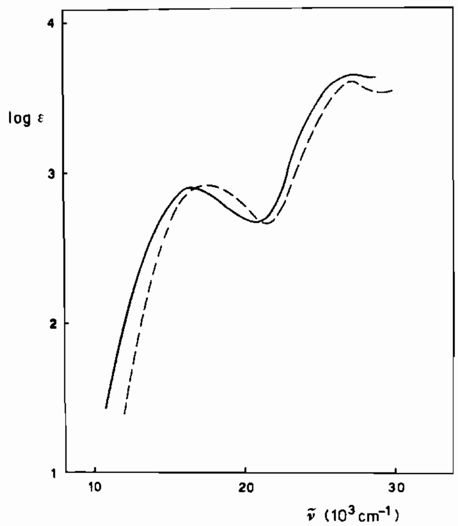


Figure 2. Absorption spectra of (Me,H,H)VOCuBr$_2$·CH$_3$OH (———) and (H,H,Me)VOCuCl$_2$·CH$_3$OH (– – –) in methanol.

Typical examples of the absorption spectra of the complexes in methanol are shown in Fig. 2. Each complex has a strong band in the visible region. The band position and its molar extinction coefficient are tabulated in Table II. The intensity of the absorption is five to seven times stronger than the visible band of a monomeric oxovanadium(IV) complex. According to the results of X-ray analysis of dichloro[N,N'-bis(salicylidene)ethylenediaminatocopper(II)] copper(II) [12], the molecule has two copper(II) ions with planar (CuN_2O_2) and pseudo-tetrahedral (CuO_2Cl_2) coordination geometries, respectively, where pseudo-tetrahedral coordination is effected by the steric hindrance between the hydrogen atom of the 3-position of the aromatic ring and the chloride ion. This complex and its homologues have two d–d bands at 16–18 and at *ca.* 12 kK, which have been attributed to the planar [CuN_2O_2] and the pseudo-tetrahedral [CuO_2X_2] chromophores, respectively [13]. For the present hetero-metal binuclear complexes we may assume a structure similar to the above. However, no absorption band could be found around 12 kK for the present complexes, indicating that they have no pseudo-tetrahedral copper(II). This fact again suggests the formation of vanadium(V)–copper(I) hetero-metal complexes.

Generally vanadium(V) complexes show a strong band near 25 kK. Notably the vanadium(V) coordinated by a phenolic oxygen has a strong band in the visible region [7, 14–16]. Among them the vanadium(V) complex with N,N'-bis(salicylidene)-ethylenediamine is noticed [7, 14], whose absorption spectrum shows a band at 17.9 kK with a strong molar extinction coefficient (*ca.* 1×10^3). It is likely that this band is substantially the same in its origin as the band found for the present hetero-metal complexes. So far no assignment was made to the band in the visible region found for the vanadium(V) complexes coordinated by a phenolic oxygen. We think that this band may be assigned to the charge-transfer band from the p_π-orbital on the phenolic oxygen to the lowest vacant orbital (d_{xy}) of vanadium(V).

Since each complex possesses one molecule of methanol, it appears that methanol is coordinated to the vanadium(V) ion. Thus Fig. 1 shows the most probable structure for the present complexes. Our conclusion is in conflict with that [6] of Selbin and Ganguly. It is likely that their specimen was contaminated with a large amount of paramagnetic impurity.

The redox reaction between vanadium(IV) and copper(II) ions has been studied only in aqueous solution. In a strongly alkaline solution VO^{2+} and Cu^{2+} react to form VO_3^- and Cu^+ [17], while in an acidic solution the reaction, $Cu^+ + V^{5+} \rightarrow Cu^{2+} + V^{4+}$ proceeds quantitatively [18]. It is also known that oxovanadium(IV) chloride and copper(II) sulfate do not react in an aqueous solution [19]. The oxydation–reduction reaction between oxovanadium(IV) and copper(II) complexes with more complicated ligands might depend on the nature of the donating atoms, configuration of the complex, and so on.

Recently Patterson and Holm [20] investigated the redox reaction of copper(II) complexes with successively altering geometry and found that the copper(I) becomes more stable than the copper(II) when the configuration is distorted from planar to tetrahedral. Judging from this finding, it is likely that the distortion caused by the steric specificity at the "outside" coordination site in (R_1, R_2, R_3)VOCuX$_2$·CH$_3$OH makes it easy to reduce the copper, thereby causing the vanadium(IV) to be oxidized.

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