

옥소바나듐(IV)-카르복실레이트 착물의 자기적 및 적외선 분광학적 성질

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Magnetic and Infrared Spectral Studies of Oxovanadium(IV)-Carboxylate Complexes

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요 약. 카르복실기를 갖는 리간드들과 옥소바나듐(IV) 사이에 형성되는 착화합물 VO(picn)₂, VO(htmq)₂, VO(quin)₂ 및 VO(pyra)₂·2H₂O 들을 합성하여 그들의 IR 및 자기적 특성을 조사하였다. 이들의 자화율 값과 V=O 결합의 신축진동수 값으로부터 VO(picn)₂ 및 VO(htmq)₂ 착화합물에 있어 강한 분자간 상호작용이 존재하는 것으로 추정하였다. IR 데이터를 근거로할 때 4개의 옥소바나듐(IV) 착물들에 있어 카르복실기는 모두 한자리 배위자로서 작용함을 알 수 있었다.

자유리간드와 옥소바나듐 착물의 IR 스펙트럼을 비교 검토함으로써 중심원자와 리간드주개원자들로 구성되는 배위권에서의 기본진동 형태를 분류하고 착물 형성후 나타난 새로운 IR 흡수띠들을 분류한 진동 형태와 대응시켰다.

ABSTRACT. Four oxovanadium(IV) complexes with carboxylate ligands, VO(picn)₂, VO(htmq)₂, VO(quin)₂ and VO(pyra)₂·2H₂O have been prepared and studied. Infrared spectral data coupled with the results of magnetic susceptibility study strongly suggest that there are relatively strong intermolecular interactions in VO(picn)₂ and VO(htmq)₂. In all oxovanadium(IV) complexes studied in this work, the carboxylate ligand coordinates to the metal ion in the unidentate fashion. Some fundamental vibration modes of oxovanadium(IV) complexes were empirically assigned from the difference in the spectrum of metal complex with free ligand.

INTRODUCTION

There has been considerable interest and controversy concerning oxovanadium complexes.^{1,2} Through the hole formalism, the oxovanadium(IV) with a d^1 configuration is known to be somewhat similar to copper(II) ion with a d^9 configuration. Copper(II) complexes with antiferromagnetic exchange are well known.^{3,4} On the contrary, only a few examples are known with oxovanadium(IV) complexes. The magnetic

properties of oxovanadium(IV) complexes have been intensively studied,^{5,6} and most oxovanadium(IV) complexes have magnetic moment close to the spin-only value of 1.73 B.M.. However, some oxovanadium(IV) complexes have unusual magnetic properties due to dimerization or polymerization in the solid state.⁶

Vibrational spectroscopy has been also known to be an effective tool for the study of the nature of metal-ligand interactions. The present study was undertaken to discover the mode of

complexation of oxovanadium(IV) ion with some carboxylate ligands and elucidate the type of intramolecular interaction in these complexes if it exists. The oxovanadium complexes of the type $(VO)_2$ were prepared where LH is picolinic acid N-oxide, 4-hydroxy-7-trifluoromethyl-3-quinolinic carboxylic acid, quinaldic acid and 2-pyrazine carboxylic acid. Their stereochemistry is ascertained by analytical, magnetic and IR spectral studies.

EXPERIMENTAL

Preparation of the complexes. Picolinic acid N-oxide(picn), 4-hydroxy-7-trifluoromethyl-3-quinolinic carboxylic acid(htmq), quinaldic acid(quin), and 2-pyrazine carboxylic acid(pyra) were purchased from Aldrich chemical Co. and were used without further purification.

Oxovanadium(IV) complexes with these ligands were prepared by the use of same synthetic procedure; stoichiometric amount of sodium salt of the corresponding ligand was added dropwise to a solution of oxovanadium sulfate in distilled and deionized water. The precipitate was collected by filtration and washed successively with hot water, ethanol and ether, air-dried and analyzed. Vanadium metal in some complexes was determined by the method of the zero current potentiometric titration using EDTA.⁸ The potentiometer used was type RAT-11S versatile recording autotitrator. Indicate electrode used was a mercury electrode manufactured in our laboratory, and a calomel electrode was used as a reference electrode. The

analytical results are summarized in Table 1.

Magnetic and IR measurements. A Cahn electrobalance (Cahn Ventron 2000) was used in this study using conventional Faraday method; magnetic field was controlled to 3.05 ± 0.02 KG and palladium metal (99.5%, $\chi = 567.4 \times 10^{-4}$ cgs/mole at 15.0°C) was used as a standard sample. To avoid liquidization of water vapor on the wall of the quartz sample tube, the helium gas was filled in the column. All the magnetic susceptibility data were obtained from liquid nitrogen temperature up to room temperature.

Infrared spectra ($2000\text{cm}^{-1} \sim 200\text{cm}^{-1}$) were obtained using Nujol mull on cesium iodide plates and potassium bromide pellet with a Perkin-Elmer model 621 recording spectrophotometer. Spectra were calibrated with polystyrene film. Before the IR measurement, all the complexes except for $VO(\text{pyra})_2 \cdot 2\text{H}_2\text{O}$ were vacuum dried until the IR absorption bands attributed to water modes disappeared.

RESULTS AND DISCUSSION

Analytical results show a 1 : 2 metal to ligand stoichiometry in all cases. They are insoluble in water and complexes studied has been found to be in the range of 2.00~1.2 B.M. at room temperature. The effective magnetic moment of these complexes did not vary appreciably in the range of experimental temperature and all the complexes studied in this work exhibit a straight line when the inverse value of susceptibility is plotted against temperature, satisfying Curie-Weiss equation. The effective magnetic moment of $VO(\text{htmq})_2$ is found to be 1.25 B.M., which is abnormally lower than the spin-only value (~ 1.73 B.M.) for a d^1 configuration. This subnormal value may be due to the presence of exchange coupled antiferromagnetism in this complex. Zelentsov⁹ suggested for the magnetic

Table 1. Analytical results of vanadyl content

Compound	% Calculated	% Content of VO_2^+
$VO(\text{htmq})_2$	11.51	11.34 ± 0.03
$VO(\text{picn})_2$	19.51	19.68 ± 0.05
$VO(\text{pyra})_2 \cdot 2\text{H}_2\text{O}$	19.17	19.39 ± 0.05
$VO(\text{quin})_2$	16.28	16.18 ± 0.01

abnormality of oxovanadium(IV) complexes of substituted N-(2-hydroxyphenyl)salicylideneimine a dimeric oxygen bridged structure, which provides an appropriate symmetry for the $3d_{xy}$ orbitals of vanadium(IV) to overlap with each other and form strong metal-metal bond. Syamal¹⁰ in a series of Schiff base complexes of the type $\text{VO(ONS)} \cdot n \text{H}_2\text{O}$ proposed a binuclear structure on the basis of their subnormal magnetic moment (1.27~1.52 B.M.). Similarly, Poddar *et al.*¹¹ and Kuge and Yamada¹² also observed subnormal magnetic moment in the case of oxovanadium(IV) complexes of bidentate schiff base and suggested the oxygen bridged dimeric structure (see Fig. 1). Casey and Thackery¹³ suggested that the oxovanadium(IV) acetate complexes have both $\text{V}=\text{O} \cdots \text{V}$ interaction and carboxylate bridges as shown in Fig. 1. The exchange interactions in oxovanadium(IV) acetate occur through the bridging carboxylic groups by overlap of the vanadium d_{xy} orbital with the symmetry orbitals of the COO^- groups ($2p\pi\text{O}-2p\pi\text{C}-2p\pi\text{O}$). Such interionic exchange due to $\pi \rightarrow d_{xy}$ and $d_{xy} \rightarrow \pi^*$ leads to

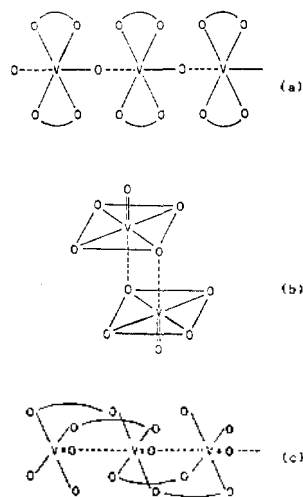


Fig. 1. Intermolecular O—V—O polymeric interaction (a), dimeric interaction(b), and carboxylate bridges (c) in the type of VO_2 complexes.

the antiferromagnetic type spin-spin exchange.¹⁴ In all cases discussed above, oxovanadium(IV) complexes possess the reduced magnetic moments.

The magnetic susceptibility data for VO(picn)_2 and VO(quin)_2 were obtained from 90K to 282K. The effective magnetic moments of VO(picn)_2 and VO(quin)_2 are larger than the spin-only value and are 1.97 and 1.81 B.M., respectively. The Weiss constant θ is +5.88 for VO(picn)_2 . Although the Weiss constant is positive, it is plausible to suggest that the anomalously high magnetic moment of VO(picn)_2 and VO(quin)_2 arise from the ferromagnetic interactions between the molecules through the formation of $\text{V}=\text{O} \cdots \text{V}$ chain. Cavell *et al.*¹⁵ have previously reported that the complexes $\text{VO}(\text{S}_2\text{PX}_2\text{O})_2$ ($\text{X}=\text{F}$ and CH_3) have abnormally high magnetic moments of 2.25 and 2.13 B.M. with positive Weiss constant ($\theta=+17$ and $+10$). Other oxovanadium(IV) complexes having high magnetic moment were also reported.^{16,17} When the orbital contribution is completely quenched the magnetic moment of the oxovanadium(IV) complexes is 1.73 B.M.. However if the orbital contribution is not completely quenched the magnetically dilute oxovanadium(IV) complexes may exhibit magnetic moments even less than spin only value.¹⁰ Normal oxovanadium(IV) complexes usually have the magnetic moments in the range of 1.65~1.80 B.M.. The magnetic moment of the $\text{VO(pyra)}_2 \cdot 2\text{H}_2\text{O}$ complex is 1.61 B.M. which is close to the normal value of oxovanadium(IV) complex. The magnetic moment and magnetic susceptibility data for oxovanadium(IV) complexes are summarized in the Table 2 and the effective magnetic moments plotted against temperature are shown in Fig. 2. In Fig. 3, the inverse susceptibility per mole of VO(picn)_2 are plotted against temperature.

The assignments in the IR spectra were made

Table 2. Magnetic susceptibility and magnetic moment data for oxovanadium(IV) complexes^a

Complex	Temp. (K)	$\chi_M (\times 10^{-3})$	$\mu_{\text{eff.}}$	θ
VO(picn) ₂	278	1.770	1.97	5.87
VO(quin) ₂	282	1.448	1.81	0.73
VO(htmq) ₂	261	0.904	1.25	46.51
VO(pyra) ₂ ·2H ₂ O	281	1.191	1.61	9.00

^a The magnetic moment was calculated with the Curie equation: $\mu_{\text{eff.}} = 2.84 \{ \chi_M (T - \theta) \}^{1/2}$.

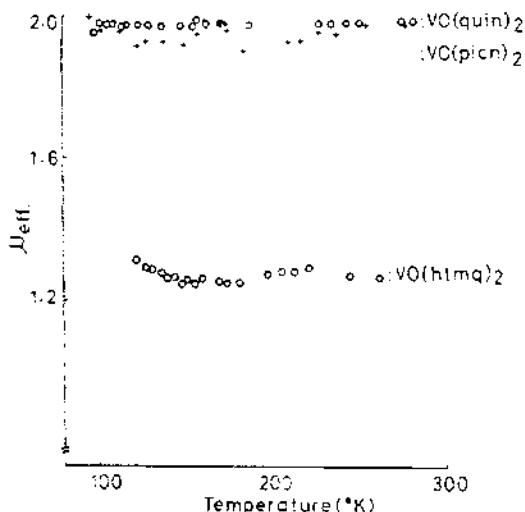


Fig. 2. The effective magnetic moment vs. temperature curves for oxovanadium(IV) complexes.

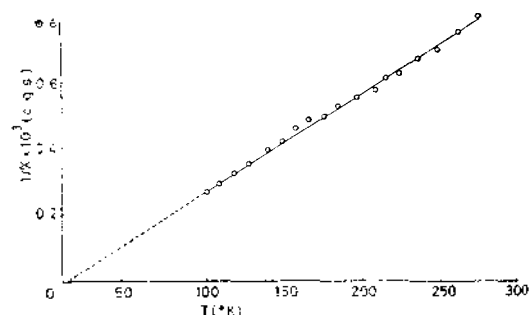


Fig. 3. The inverse susceptibility per mole of VO(picn)₂ as a function of temperature. The solid line is an experimental fit to the Curie's law.

empirically by comparing the spectra of free ligand and their complexes and by reference to

Table 3. Characteristic infrared frequencies of VO²⁺ complexes with suggested assignments

VO(picn) ₂		VO(htmq) ₂	
Frequency (cm ⁻¹)	Assignments	Frequency (cm ⁻¹)	Assignments
1680(vs, br)	$\nu_{C=O}$	1620(vs, br)	$\nu_{C=O}$
1607(s)	$\nu_{C=C}, \nu_{C=N}$	1600(s, br)	$\nu_{C=C}$ or $\nu_{C=O}$
1460(vs)		1525(s, br)	
1442(vs)		1504(sh, w)	
1380(vs, br)	ν_{C-O}	1474(m)	ν_{C-O}
1242(m)	ν_{N-O}	1406(vw)	ν_{C-O} or OH deformation
892(vs)	$\nu_{V=O(A_1)}$	1270(m)	
620(w)	$\nu_{2VO_4(A_1)}$	1237(m)	
590(m)	$\nu_{7VO_4(E)}$	1015(w)	$\nu_{V=O(A_1)}$
392(m)	OR $\nu_{3VO_4(A_1)}$ or $\nu_{8VO_4(E)}$	994(m)	$\nu_{V=O(A_1)}$
315(m)		814(s)	$\nu_{V-O \cdots V-O}$ chain
302(m)		780(m)	$\nu_{2VO_4(A_1)}$
		525(m)	$\nu_{7VO_4(E)}$
		450(sh, m)	$\nu_{3VO_4(A_1)}$ or $\nu_{8VO_4(E)}$
		440(m)	
		340(w)	

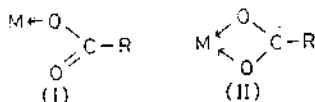
Table 4. Characteristic infrared frequencies of VO²⁺ complexes with suggested assignments^a

VO(quin) ₂		VO(pyra) ₂ ·2H ₂ O	
Frequency (cm ⁻¹)	Tentative Assignments	Frequency (cm ⁻¹)	Tentative Assignments
1639(vs)	$\nu_{C=O}$	1660(s, br)	$\nu_{C=O}$
1595(sh, s)	$\nu_{C=N}, C=C$	1594(s)	$\nu_{C=N}, \nu_{C=C}$
1567(s)		1464(s, br)	
1515(m)		1427(s)	
1463(vs, br)	ν_{C-O}	1379(s)	ν_{C-O}
1380(s)		980(s)	
981(s)			
948(m)	normal mode of		
428(m)	vibrations for		
329(m)	(O=VN ₂ O ₂) moiety		

^a: Abbreviation used; vs: very strong, s: strong, m: medium, w: weak, br: broad.

the literature⁸⁻²² on the spectra of similar compounds. The characteristic IR frequencies of four oxovanadium(IV) complexes with suggested assignments are listed in Table 3 and 4. IR spectrum of ligands containing carboxylic, N-oxide and hydroxyl functional group are greatly affected by the complexation with the VO²⁺ ion. Extensive IR studies have been done on metal complexes of carboxylic acids.²³ Aromatic compounds with a low degree of substitution

generally exhibit bands at 1600, 1580, 1500 and 1460cm^{-1} .²⁴ The free ligands show a broad band at ca. 1710cm^{-1} for carbonyl $\nu_{\text{C=O}}$ stretching vibration. In the spectrum of picolinic acid N-oxide, another broad and strong band appear at 1680cm^{-1} . This band might be due to stretching vibration associated with intramolecular hydrogen bonding. Flett²⁵ reported that some carboxylic acids are capable of forming hydrogen bond and the C=O stretching frequency is reduced from the normal value of 1705cm^{-1} to 1680cm^{-1} . When the carboxylic group is chelated to the oxovanadium(IV) ion, the carboxyl band is greatly shifted to lower frequency region. The coordination of carboxylate to metal ion may be one of the followings; in the unidentate complex (structure I), separation between



$\nu_{\text{C=O}}$ and $\nu_{\text{C-O}}$ is much larger than that of the bidentate complex (structure II). Upon complexation, the C-O stretching frequency is also greatly reduced and the $\nu_{\text{C-O}}$ of metal complexes containing carboxylic group appeared at ca. 1380cm^{-1} . In ruthenium complexes of carboxylate, the separation between $\nu_{\text{C=O}}$ and $\nu_{\text{C-O}}$ for the unidentate and for bidentate

complexes are reported to be ca. 250cm^{-1} and 50cm^{-1} respectively.²⁶ In all the oxovanadium(IV) complexes studied, the separation is greater than 250cm^{-1} . This indicates that in VO(picn)₂, VO(quin)₂, VO(htmq)₂ and VO(pyra)₂, carboxylate ligand coordinates to the oxovanadium(IV) ion in the unidentate fashion. A broad and strong band appeared in spectra of free ligands (1030cm^{-1} for picolinic acid N-oxide, 1055cm^{-1} for 2-quinaldic acid, 1104cm^{-1} for 4-hydroxy-7-trifluoromethyl-quinolinic acid, and 1021cm^{-1} for pyrazine carboxylic acid). This band disappeared upon complex formation, and is assigned to the deformation vibration of hydroxyl group of -COOH. The complexation did not change the C=C double bond stretching frequencies as expected. The C=N double bond stretching frequency of ring skeleton could not be determined since the energy difference between the C=N double bond stretching and C=C double bond stretching is very small. The N-oxides of pyrimidines have been examined and compared with the pyridine N-oxide by Wieley and Slaymaker²⁷ and by Katrizky.²⁸ The N-oxide absorption occurs in the $1300\sim 1250\text{cm}^{-1}$ range. A strong band of N-oxide appeared at 1254cm^{-1} for picolinic acid N-oxide. This band is shifted to 1242cm^{-1} upon complex formation. Upon complexation,

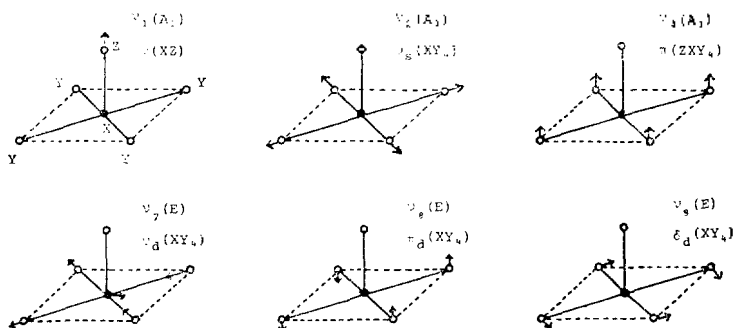
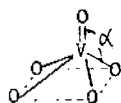


Fig. 4. Infrared active normal modes of vibration of tetragonal-pyramidal $\text{O}=\text{VO}_4$.

the new modes of vibration arises from the formation of $O=VO_4$ moiety. *Fig. 4* shows six IR active normal mode of vibration of tetragonal pyramidal chromophore of C_{4v} symmetry. According to the normal mode analysis of vibration for $O=VO_4$ moiety having C_{4v} symmetry, Γ_{vib} reduces to $3A_1 + 2B_1 + 2B_2 + 3E$, where B_1 and B_2 vibration mode is not infrared active. Among six IR active band, the ν_1 represent vanadium-oxygen double bond stretching and its magnitude was initially considered to be directly proportional to the strength of the metal-oxygen interaction. However, the shift of $\nu_1(V=O)$ mode has been shown also to be dependent upon coordination numbers and the type of donor molecules.²⁹ In terms of Ballhausen and Gray(BG) molecular orbital scheme, the bonding between the sixth position opposite to the $V=O$ bond axis by solvent or other donor molecule is achieved. The X-ray crystallographic data³⁰ show that the loss of a donor molecule from the sixth position give rise to an increase in $O=V$ -(equatorial donor atom) bond angle α which, in turn, increase the $V=O$ stretching frequencies.



Intermolecular dimeric interaction where $V=O$ unit does not involve directly, will cause the increase in ν_1 frequency (see *Fig. 1a*). However, if the complexes have an intermolecular $O=V \cdots O=V$ interaction utilizing the $V=O$ unit (see *Fig. 1b*), the $V=O$ stretching band will appear at low frequency. In $VO(picn)_2$ and $VO(htmq)_2$ complexes, the $V=O$ stretching band appears at $892cm^{-1}$ and $814cm^{-1}$ respectively. This unusually low frequency compared to the usual value of ca. $960cm^{-1}$ seems to be attributed to the formation of polymeric $V-O-V-O$ chains

as shown in *Fig. 1*. In $VO(htmq)_2$, a band appears at $994cm^{-1}$ upon complexation but this band must not be arised from $V=O$ stretching vibration since this band is weak and broad. A new band appeared at $814cm^{-1}$ is sharp and strong, and are well within the range expected for $V=O$ stretching frequency, provided that the intermolecular interaction exists. The $V=O$ stretching frequencies of $VO(quin)_2$ and $VO(pyra)_2 \cdot H_2O$ complexes are $981cm^{-1}$ and $980cm^{-1}$ respectively. In most oxometal ion complexes, the axial stretching frequency $\nu_1(V=O$ stretching) is much larger than the equatorial stretching frequencies or deformation frequencies($\nu_2, \nu_3, \nu_7, \nu_8$ and ν_9 in *Fig. 4*). In general, the order of the stretching frequencies are $\nu_1 > \nu_2 \gg \nu_3$, while the order of deformation frequencies are $\nu_7 \gg \nu_8 \gg \nu_9$.^{18,19} The general frequency ranges observed for stretching and deformation vibration of oxometal complexes having C_{4v} symmetry are; for ν_2 and ν_7 ; $450 \sim 700cm^{-1}$, for ν_3 and ν_8 , $200 \sim 400cm^{-1}$ and for ν_9 , $120 \sim 250cm^{-1}$.²⁰⁻²² The ν_2, ν_7, ν_3 and ν_8 vibration frequencies of $VO(picn)_2$ and $VO(htmq)_2$ are tentatively assigned and are listed in *Table 2* and *3*. The complex $VO(quin)_2$ which has $O=VO_2N_2$ moiety with C_{2v} symmetry is expected to exhibit ten IR active absorption bands in the range of $1000cm^{-1} \sim 150cm^{-1}$. However, except for $\nu_1(V=O)$ band, other bands could not be assigned or suggested because of the lack of related informations.

CONCLUSIONS

Being cream colored and insoluble in most solvents, the $VO(picn)_2$ complex has the magnetic moment of 1.98 B.M. and its $V=O$ stretching frequency is observed to be $892cm^{-1}$. The reduction in $V=O$ stretching frequency coupled with large value of magnetic moment strongly suggest the presence of polymeric $V-$

O...V—O interaction in this complex. The solid state magnetic moment of 1.25 B.M. for VO(htmq)₂ being lower than the spin-only value of 1.73 B.M., signifies a spin-coupling interaction. Besides the possibility of polymeric V—O...V—O interaction, the reduction of magnetic moment might be caused by the presence of hydrogen bonding or the formation of carboxylate bridge. The presence of hydrogen bonding or the formation of carboxylate bridge between the VO(htmq)₂ molecules could not be confirmed due to the complexity of IR spectra in the region of 1400cm⁻¹~1000cm⁻¹. In any case, the reduction of magnetic moment via antiferromagnetic coupling is expected. The exchange integral, J was attempted to be evaluated by the use of Bleaney-Bowers equation for dimeric model. But it was found that the dimeric model is not appropriate for the VO(htmq)₂ complex. In all the metal-carboxylate complexes studied in this work, carboxylate ligand coordinated to the metal ion in monodentated fashion without an exception. Finally it is quite interesting that both VO(quin)₂ and VO(pyra)₂·2H₂O having five membered chelate rings with one nitrogen and one oxygen as donor atoms, have almost same $\nu_1(\text{V=O})$ of ca. 980cm⁻¹ and magnetic moment value close to typical spin-only value, while VO(picn)₂ and VO(htmq)₂ having six membered chelate rings and two oxygen as donor atoms, have reduced $\nu_1(\text{V=O})$ values with abnormal magnetic moments (see Fig.5).

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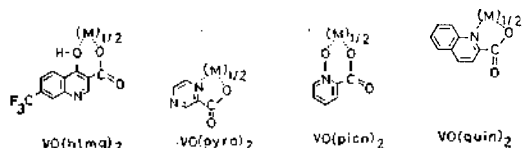


Fig. 5. The structure of oxovanadium(IV) complexes.

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