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SPIN—SPIN COUPLING IN OXOVANADIUM(IV) COMPLEXES

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CONTENTS

ABBREVIATIONS

sal	salicylaldehyde
5-Cl-sal	5-chlorosalicylaldehyde
5-Br-sal	5-bromosalicylaldehyde
5-CH_3-sal	5-methylsalicylaldehyde
5-NO_2-sal	5-nitrosalicylaldehyde
3-NO_2-sal	3-nitrosalicylaldehyde
5-methoxy-sal	5-methoxysalicylaldehyde
3-methoxy-sal	3-methoxysalicylaldehyde
hydrox	2-hydroxy-1-naphthaldehyde
ophen	o-phenanthroline
dipy	2,2′-dipyridyl
DMF	dimethylformamide
d-tartH_2	*d*-tartaric acid
dl-tartH_2	*dl*-tartaric acid
salenH_2	*N,N*′-ethylenebis(salicylideneimine)
oxine	8-hydroxyquinoline
TIP	temperature independent paramagnetism

A. INTRODUCTION*

Transition metal ions usually form two different types of complexes viz. (i) magnetically dilute and (ii) magnetically condensed complexes. The magnetically dilute complexes are the complexes in which the metal ion is not involved in magnetic exchange with the neighbouring metal ions. In the magnetically condensed complexes the metal ion is involved in magnetic exchange with the neighbouring metal ions through exchange forces. The most extensively studied complexes in the second category are the copper(II) complexes and a comprehensive review has been published by Kato et al. [1]. The present review surveys the coordination chemistry of oxovanadium(IV) complexes involved in magnetic exchange. Two comprehensive reviews dealing mainly with magnetically dilute oxovanadium(IV) complexes have appeared [2, 3]. The $3d^9$ Cu^{2+} and $3d^1$ VO^{2+} ions both belong to the $s = \frac{1}{2}$ system; in this article we attempt to compare their magnetic exchange behaviour. The sign of the spin—orbit coupling constant (λ) is negative for copper(II) complexes and positive for oxovanadium(IV) complexes [4]. As a result the copper(II) complexes of the first category should exhibit magnetic moments higher than the spin-only value of 1.73 B.M. and the oxovanadium(IV) complexes of the first category should record magnetic moments very close to the spin-only value when the orbital contribution is completely quenched. However, if the orbital contribution is not completely quenched the magnetically dilute oxovanadium(IV) complexes may exhibit magnetic moments even less than the spin-only value and magnetic moments may decrease with lowering of temperature. In such complexes it is difficult to separate out the antiferromagnetic effect and the crystal field effect. Fortunately for most oxovanadium(IV) complexes the orbital contribution is almost completely quenched and this is assumed in the following discussion. Complexes with antiferromagnetic spin—spin coupling have room temperature magnetic moments well below the 1.73—2.2 B.M. for copper(II) complexes and the 1.68—1.78 B.M. for oxovanadium(IV) complexes. Complexes with a ferromagnetic interaction usually have room temperature magnetic moment higher than the spin-only value of 1.73 B.M. Most workers report magnetic moments only at room temperature and magnetic exchange, specially the ferromagnetic type, remains undetected in many cases. In fact not a single authentic example of an oxovanadium(IV) complex involved in a ferromagnetic type of spin—spin exchange has been reported to date, although several authentic copper(II) complexes involved in ferromagnetic exchange have appeared in the literature [5, 6]. The lack of precise structural information has often deterred chemists from studying the magnetic susceptibilities of the complexes with normal magnetic moments at different temperatures.

The coupling of two $s = \frac{1}{2}$ spins of an interacting pair of ions leads to a

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* In this review complexes with subnormal magnetic moments are referred to as subnormal complexes.

singlet state ($S = 0$) and a triplet state ($S = 1$) separated by the exchange integral, J. The population of the molecules in the two spin states follows the Maxwell—Boltzmann distribution law. In antiferromagnetic coupling the diamagnetic singlet state is the ground state and magnetic moments of the complexes would decrease as the temperature is lowered, due to the population of the singlet state at the expense of the paramagnetic triplet state. On the other hand with ferromagnetic spin—spin exchange the triplet state is the ground state and the magnetic moments of the complexes would increase as the temperature is lowered. The susceptibility expression in these systems is given by the Bleaney—Bowers equation [7]:

$$\chi_{A'}\,(\mathrm{corr}) = \frac{g^2N\beta^2}{3kT}\,[1 - \tfrac{1}{3}\exp(J/kT)]^{-1} + N_\alpha \tag{1}$$

where N_α is the temperature independent paramagnetism term and the other symbols have their usual significance.

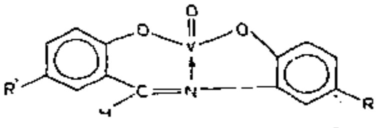
B. SYNTHESES, MAGNETIC AND SPECTRAL PROPERTIES OF OXOVANADIUM(IV) COMPLEXES

(i) Complexes with tridentate Schiff bases

Most of the oxovanadium(IV) complexes with subnormal magnetic moments have been prepared from the tridentate dibasic Schiff bases containing ONO or ONS donor atoms. The tridentate dibasic character of these ligands forces the VO^{2+} ion to dimerise leading to oxovanadium(IV) complexes with anomalous magnetic properties.

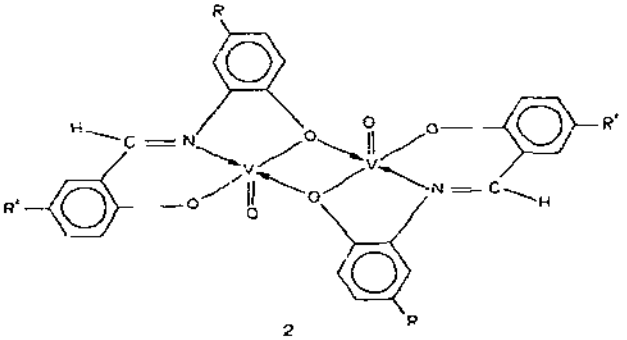
Synthesis of subnormal oxovanadium(IV) complexes was first described by Zelentsov [8] in 1961. The complexes were prepared from Schiff bases derived from salicylaldehyde or substituted salicylaldehyde and orthoaminophenol. These Schiff bases coordinate through ONO donor sets as dibasic tridentate ligands.

The room temperature magnetic moments of the complexes (1, R = H, R′ = H, Cl, Br and R = NO_2, R′ = Br) are in the range 0.77—1.55 B.M. [9] (see Table 1).



1 R = H, R′ = H, CH_3, Cl, Br, NO_2,
R = Cl, R′ = H, Cl;
R = NO_2, R′ = H, Br, NO_2

In 1966 Ginsberg et al. [10] prepared Zelentsov's complexes as well as some new complexes (1) of this series and studied the magnetic properties of the complexes in detail from 1.4 to 300°K. Zelentsov prepared the complexes by reacting an aqueous solution of vanadyl chloride with a methanolic solution of the ligand and concluded from analytical results that the R = H, R′ = H, Cl, Br complexes crystallize as monohydrates [9]. The analytical and infrared spectral data of these compounds (1) as prepared by Ginsberg et al. indicate an anhydrous nature for these complexes. The preparation of the complexes by Ginsberg et al. differs from that of Zelentsov only in the use of ethanol instead of methanol as solvent and in refluxing the mixture. They used 10% less than the stoichiometric amount of the ligand presumably to avoid the formation of the undesirable solvated monomeric complex. The magnetic moments of these complexes (with the exception of R = NO_2, R′ = NO_2) decrease considerably as the temperature is lowered. The temperature dependence of the susceptibility (Fig. 1) is characteristic of intramolecular antiferromagnetic exchange and the susceptibility vs. temperature curve obeys eqn. (1). They suggested a dimeric structure (2) for these complexes analogous to that proposed for the corresponding copper(II) complexes [11]. By measuring the susceptibilities of the complexes at 1.4 or 4.2°K they estimated the percentage of paramagnetic oxovanadium(IV) impurity to range from 0.4—2%.



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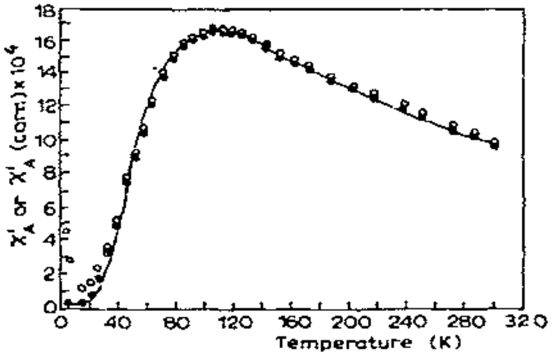
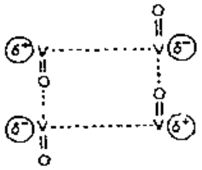


Fig. 1. Temperature dependence of the magnetic susceptibility of complex 1 (R = H, R′ = Br): O, $X_{A'}$; ●, $X_{A'}$ (corr). The solid line is a least-squares fit to eqn. (1), $g = 1.89$, $J = 115$ cm^{-1}, $N_\alpha = 30 \times 10^{-6}$. Reprinted with permission from Inorg. Chem., 5 (1966) 1656. Copyright by the American Chemical Society.

The J (R, R′) values of the complexes calculated according to eqn. (1) are in the order:

$J(\mathrm{H,NO_2}) > J(\mathrm{Cl,Cl}) \sim J(\mathrm{H,H}) \sim J(\mathrm{Cl,H}) \sim J(\mathrm{H,CH_3}) \sim J(\mathrm{H,Br}) > J(\mathrm{H,Cl})$

Substituents at R and R′ positions influence J in a different manner in oxovanadium(IV) and copper(II) complexes of the same ligands. In copper(II) complexes the electron withdrawing groups at the R′ position enhance the exchange interaction but cause a decrease in the interaction when substituted at the R position [12]. With the exception of the complexes (R = H, R′ = NO_2; R = H, R′ = Cl) the J values are not sensitive to substitution in oxovanadium(IV) dimers. This difference is attributed to a difference in exchange mechanism operating in oxovanadium(IV) and copper(II) complexes. The symmetries of the orbitals containing the unpaired electron in copper(II) and oxovanadium(IV) complexes are different. In copper(II) complexes the unpaired electron is in the $d_{x^2-y^2}$ orbital (e_g set) and electronic spin—spin coupling takes place by superexchange through the bridging atoms in tridentate ligands. The magnitude of J depends on the overlap of metal ion orbital ($d_{x^2-y^2}$) and the orbitals of the bridging atoms of the ligands. In square pyramidal oxovanadium(IV) complexes the unpaired electron is in the d_{xy} orbital (t_{2g} set) and this orbital has the proper symmetry for a σ overlap with the d_{xy} orbital of the adjacent vanadium atom. The authors believe that the magnetic exchange in these oxovanadium(IV) complexes is mainly due to this σ metal—metal interaction mechanism [10]. Apparently the magnetic exchange pathway via $d_{x^2-y^2}$ overlap is considered to be insignificant as d_{xy}—$d_{x^2-y^2}$ mixing would occur only in the excited state. The superexchange through the vanadyl oxygen atom (z component of spin) is also considered negligible for a similar reason. The relative independence of J on R and R′ suggests that the overlap between the $3d_{xy}$ orbitals is independent of small changes in the effective charge on the vanadium atoms and that J is primarily dependent on the degree of overlap between the d_{xy} orbitals [10]. There are two electronic effects operating in these complexes. By substituting an electron withdrawing group at R or R′ the effective charge on the vanadium atoms is increased and as a result the d_{xy} orbitals contract which causes a decrease in d_{xy}—d_{xy} overlap. At the same time the polarising effect of each atom on its partner is enhanced causing an increase in d_{xy}—d_{xy} overlap. The authors believe that these two opposing effects cancel each other for most of the ring substitutents studied [10]. A tetrametallic structure (3) with V=O···V interaction has been proposed for the complex (1, R = H, R′ =



NO_2) in order to explain the higher J value [10]. In this tetrametallic structure the effective charge of one vanadium atom in each pair increases and that of its partner decreases resulting in an increase in the magnetic interaction between the two adjacent vanadium atoms. This tetrametallic structure is also supported by the infrared spectral data of the complex. The complex with $R = NO_2$, $R' = H$ has only a small TIP term and does not follow the singlet—triplet susceptibility curve. This compound is novel in the sense that the spins are completely coupled with sole population being in the diamagnetic singlet state. Although several examples of copper(II) complexes having a sole population of the singlet state are known [13], this is the first and only example in oxovanadium(IV) chemistry. The IR spectrum provides no evidence for bridging through the vanadyl oxygen atom and the complex probably has a different structure [10].

The complex with $R = NO_2$, $R' = NO_2$ does not obey the dimer susceptibility equation and is a Curie—Weiss* paramagnet with $\theta = 1.4°K$ and $\mu_{eff} = 1.62$ B.M. The authors suggest that the complex is a five coordinated monomer in which a molecule of solvent occupies a coordination position [10].

On treatment of the complex (2, $R = H$, $R' = Cl$) with pyridine the dimer breaks and the monopyridine adduct of the compound is formed. The monopyridine complex obeys the Curie—Weiss law with $\theta = 2°K$ and $\mu_{eff} = 1.75$ B.M. [10]. The dimeric structure is also lost on treatment of the complex (2, $R = R' = H$) with an ethanolic solution of ophen with the formation of oxovanadium(IV) heterochelate, VO(sal-*o*-aminophenol)(ophen) [14].

The complexes 2 exhibit a vanadyl stretching frequency in the range 990 ± 20 cm^{-1}. Two of the complexes (2, $R = Cl$, $R' = H$; $R = R' = Cl$) have two ν(V=O) bands separated by 10 cm^{-1}. The splitting of the V=O band results from the unit cell group splitting or crystal packing effect which causes the vanadium atoms in the dimer to be non-equivalent [10]. The electronic spectrum of the complex (2, $R = R' = H$) exhibits two bands at 12900 and 17850 cm^{-1} due to the $d_{xy} \rightarrow d_{xz}, d_{yz}$ and $d_{xy} \rightarrow d_{x^2-y^2}$ transitions respectively [14] (see Table 3).

Ginsberg et al. did not record the ESR spectra of these interesting complexes and they have used theoretical g_{av} values of 1.83—1.92 for calculation of J. The g_{av} values used by them seem to be low for oxovanadium(IV) complexes. Syamal [15] has recently recorded the ESR spectrum of the complex (2, $R = R' = H$) in polycrystalline solids. It exhibits a single line spectrum with $g_{av} = 1.99 \pm 01$ (see Table 2) at room temperature and at liquid nitrogen temperature, with no half field band or hyperfine splitting of the high field spectrum even at liquid nitrogen temperature. Such lack of features in the ESR spectrum may be attributed to the relaxation effect arising from intermolecular electron spin exchange interactions.

Subnormal oxovanadium(IV) complexes (4) of Schiff bases have been

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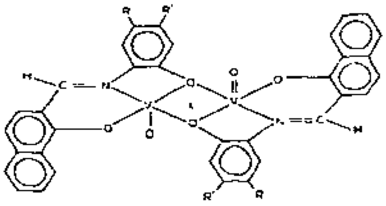
* The Curie—Weiss law is used in the form $\chi_{A'}(\text{corr}) = \dfrac{C}{T-\theta}$ throughout this review.

derived from 2-hydroxynaphthaldehyde and substituted *o*-aminophenol [14]. The magnetic properties of these complexes are also very similar to the complexes studied by Ginsberg et al. *J*(R, R′) of these complexes are in the order:



4 R = H Cl NO_2 C_6H_5
R′ = H, NO_2

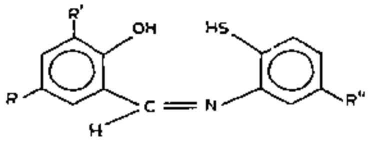
$J(NO_2,H) > J(Cl,H) > J(H,H)$. These authors also noticed that the *J* values are somewhat insensitive to the ring substituents. The ESR spectra of the complexes (4, R = R′ = H; R = Cl, R′ = H) in polycrystalline solids at room temperature exhibit two parallel lines (H_{z1} and H_{z2}), two perpendicular lines ($H_{\perp 1}$ and $H_{\perp 2}$) and a broad line around 1600 gauss due to the $\Delta M = 2$ transition. The appearance of the half field band supports conclusively the presence of the triplet state dimeric species in these complexes. The half field spectra show hyperfine splittings of 85 gauss at liquid nitrogen temperature and as a result the expected 15 lines are observed. The high field spectra of these complexes also exhibit hyperfine splittings at liquid nitrogen temperature. The authors were unable to determine the coupling constants *A* and *B* due to overlap of parallel and perpendicular lines. The complex (4, R = NO_2, R′ = H) exhibits only a single line spectrum with $g_{av} = 1.98$ both at room temperature and liquid nitrogen temperature [14].

Carlisle et al. [16, 17] have independently prepared two of the complexes (4, R = R′ = H; R = Cl, R′ = H) and two more subnormal complexes (R = H, R′ = NO_2; R = C_6H_5, R′ = H). The magnetic data reported by these two groups of workers do not agree with each other and a reinvestigation of the work seems to be in order. Previous studies have shown that *J* is usually insensitive to ring substituents [10]. Hence *J* of complex (2, R = R′ = H) and complex (4, R = R′ = H) should not differ appreciably. *J* of complex (2, R = R′ = H) is -125 cm^{-1} using a theoretical g_{av} value of 1.85. Syamal and Theriot have reported a *J* value of -151 cm^{-1} for complex (4, R = R′ = H) using an experimental g_{av} value of 1.99, while Carlisle et al. reported *J* values of their complexes in the range -49 to -58 cm^{-1} using theoretical g_{av} values of 1.80—1.82. The complex (4, R = R′ = H) does not obey eqn. (1); it is suggested the presence of the isomeric forms or a different structure [17]. The room temperature magnetic moment of complex (4, R = R′ = H) as prepared by Carlisle et al. is 1.84 B.M while Syamal and Theriot report a magnetic moment of 1.54 B.M. The latter authors did not observe any extra line in the ESR spectra of the complexes which could be attributable to monomeric oxovanadium(IV) impurity. It is the present reviewer's view that the complexes prepared by Carlisle et al. may contain paramagnetic impurity which would explain the low J values. Carlisle et al. have observed that their magnetic data fit both eq. (1) and the equation for an infinite linear chain of Ising spins but favour the dimetallic structure even though the Ising model is a better fit to the magnetic data.

The V=O frequencies of the type (4) complexes lie in the range 955—1000 cm^{-1}. The complexes exhibit only one d—d band in the region 14280—16000 cm^{-1}. On treatment of the complex (4, $R = R' = H$) with a strong chelating ligand such as ophen the dimer is broken with formation of the heterochelate complex VO(hydrox-*ortho*-aminophenol)(ophen) [14].

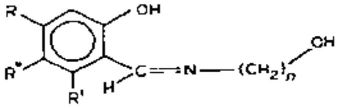
The proposed structures (2 and 4) for these subnormal oxovanadium(IV) complexes have not been verified by single crystal X-ray studies due to the non-crystalline nature of the complexes. The insolubility of the complexes in common solvents preclude molecular weight determination. The ESR and electronic spectral studies have been carried out in the solid state only.

Subnormal oxovanadium(IV) complexes with sulfur donor ligands were first reported by Lee et al. [18]. The ligands (5) have ONS donor sites and are derived from substituted salicylaldehyde or 2-hydroxynaphthaldehyde and *o*-aminothiophenol. The magnetic moments of these complexes are in the range 1.27—1.52 B.M. at room temperature. The temperature dependence of magnetic susceptibilities support the presence of antiferromagnetism in these complexes. A dimeric structure similar to that of complex (2) is proposed. From a qualitative comparison it appears that the oxovanadium(IV) complexes with ONS donor atoms are more involved in antiferromagnetic exchange than the oxovanadium(IV) complexes with ONO donor atoms. The ESR spectra of these interesting complexes have not been recorded. The V=O stretching wavenumber of the complexes lies in the range 900-1005 cm^{-1} and some of these complexes exhibit splitting of the V=O band due to unit cell group splitting or crystal packing effect. The complexes possess one broad absorption band in the range 13300—20000 cm^{-1} which has been assigned to a d—d transition [18].



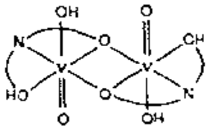
5 $R = H, Cl, Br, NO_2$,
$R' = H, Cl$;
$R'' = H, Cl$

Poddar et al. have described the synthesis of an oxovanadium(IV) complex of *N*-(hydroxyethyl)salicylideneimine (6, $n = 2$, $R = R' = R'' = H$) having a magnetic moment of 1.42 B.M. at room temperature [19]. The complex has also been prepared independently by Kuge and Yamada and they report a room temperature magnetic moment of 1.06 B.M. [20]. These authors also



6 R = H, Cl, Br, NO_2, OCH_3,
R' = H, NO_2, OCH_3,
R'' = Cl, Br, H,
n = 2, 3

reported some more subnormal complexes (6, n = 3, R = R' = R'' = H; R = H, R' = OCH_3, R'' = H). The magnetic data of the complex (6, n = 2, R = R' = R'' = H) as reported by these two groups of workers differ appreciably and Syamal et al. [21] reinvestigated the magnetic properties of the complexes in detail. The room temperature magnetic moment of the n = 2 and n = 3 complexes are in the range 0.89—1.41 and 1.34—1.58 B.M. respectively. For both series the magnetic moments decrease considerably with lowering of temperature characteristic of antiferromagnetic exchange. The g_{av} value of these complexes (1.99) was determined by ESR measurements and used for the calculation of J by fitting the magnetic data to eq. (1). The J values of the n = 2 complexes are larger than those for the n = 3 complexes which suggests that the antiferromagnetic exchange interaction is stronger in n = 2 complexes than in the n = 3 complexes. This difference in the degree of magnetic interaction has been attributed to the difference in size of the chelate ring (5 or 6 membered) arising out of variation in number of carbon atoms. The J values of the n = 2 complexes substituted in the R position are higher than those of the ligands substituted in the R' position. For n = 3 complexes the J values are relatively insensitive to ring substituents with the exception of R = R'' = H, R' = NO_2 derivative. Poddar et al. suggested the structure 7 for these complexes in which the ligands behave as tridentate monobasic ligands



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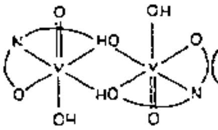

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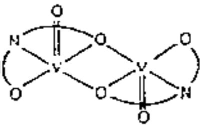

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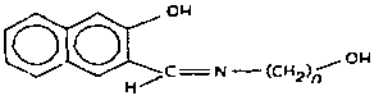
[19]. Syamal et al. did not observe any OH stretching vibration in the IR spectra of the complexes and discarded the structure 7. They proposed structure 8 in which the ligands behave as tridentate dibasic ligands [21]. The magnetic studies of Syamal et al. indicate that the magnetic moments of the complexes reported by Kuge and Yamada are in error. Russian workers [22] have also reported magnetic studies on some of these compounds and their magnetic data agree well with those of Syamal et al.

Subnormal oxovanadium(IV) complexes of Schiff bases (9) derived from

2-hydroxynaphthaldehyde and ethanolamine or propanolamine have been reported [23]. The room temperature magnetic moments are in the range 1.34—1.51 B.M. and decrease appreciably as the temperature is lowered. A comparison of J values calculated according to eq. (1) indicates that the magnetic interaction is greater in the $n = 2$ complex ($J = -281$ cm^{-1}) than $n = 3$ complex ($J = -147$ cm^{-1}). Due to this difference in magnetic behaviour the author has inferred that the alcoholic oxygen atoms of the Schiff bases are the bridging atoms rather than the phenolic oxygen atoms attached to the naphthalene ring. If phenolic oxygen atoms are the bridging atoms then J should not vary in these two complexes since the electronic environment in the chelate rings is the same. The magnetic data of these complexes are of value for the prediction of structure in the absence of structural information from single crystal X-ray. Klesova et al. [22a] have studied these two compounds independently and also noticed a similar trend in the J values.

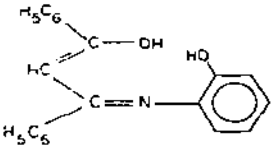


9 $n = 2,3$

The V=O stretching frequencies of complexes with ligands 6 and 9 lie in the range 880-990 cm^{-1}. The electronic spectra of the complexes exhibit three ligand field bands around 14000, 16000 and 19000 cm^{-1} which, using the scheme of Vanquickenborne and McGlynn [24]: $d_{xy} < d_{xz}, d_{yz} < d_{x^2-y^2} < d_{z^2}$ are assigned to $d_{xy} \rightarrow d_{xz}, d_{yz}$, $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{z^2}$ transitions respectively. Some of these bands are not very well developed, which often gives rise to ambiguity in their assignment. It is interesting to note that the position of ligand field bands of these subnormal complexes and normal monomeric oxovanadium(IV) complexes viz. VO(salicylaldimine)$_2$ [25] do not differ appreciably. This is also true in the case of the electronic spectra of subnormal and normal copper(II) complexes. The ESR spectra of oxovanadium(IV) complexes with the ligands 6 and 9 in polycrystalline solids exhibit half field spectra at ~1600 gauss due to the forbidden $\Delta M = 2$ transition out of the presence of a triplet state in these complexes. The half field spectrum of the complex with the ligand 9 ($n = 2$) exhibits hyperfine splittings of 78 gauss at 77°K and a 15 line spectrum was observed.

The synthesis of subnormal oxovanadium(IV) complexes of Schiff bases derived from salicylaldehyde and isopropanolamine or 2-amino-2-methyl-propanol have recently been described [26]. The complexes display room temperature magnetic moments in the range 1.0—1.1 B.M. and a dimeric structure has been proposed. Syamal and Kale have synthesized oxovanadium-(IV) complexes derived from 2-hydroxynaphthaldehyde and isopropanolamine or 2-amino-2-methyl-propanol, with room temperature magnetic moments in the range 1.3—1.5 B.M. The ν(V=O) wavenumber of the complexes occurs at 980—990 cm^{-1} [27].

Zelentsov [9a] has reported a subnormal complex with the Schiff base (10a) prepared from dibenzoylmethane and *o*-aminophenol, having a room temperature magnetic moment of 0.87 B.M. Detailed magnetic and ESR studies on the complex have not been carried out. The oxovanadium(IV) complex of the Schiff base (10b) prepared from 3-hydroxythiophene-2-aldehyde and *o*-aminophenol is involved in antiferromagnetic exchange with $J = -139$ cm^{-1} [22a].



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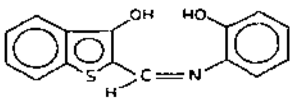
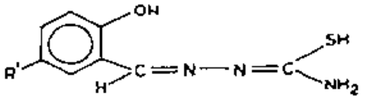
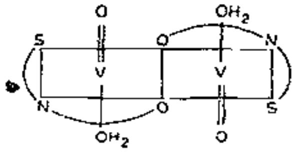


10b

Russian workers [28] have prepared several subnormal complexes of the dibasic ONS donor ligands (11) derived from salicylaldehyde and thiosemicarbazide. The room temperature magnetic moments of the complexes are in the range 1.27—1.33 B.M. The authors have proposed a dimeric structure (12) for these complexes [28].



11 R'=H, Cl, Br



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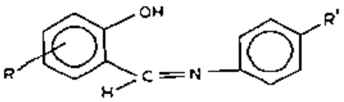
Theriot et al. [29] have described several oxovanadium complexes with tridentate Schiff bases derived from salicylaldehyde and α-aminoacids. The dimeric nature of the complexes coupled with small μ_{eff} values (0.5—0.8 B.M.) led them to believe that the complexes were oxovanadium(IV) complexes involved in antiferromagnetic exchange. However, subsequent studies indicate that the complexes are in reality oxovanadium(V) complexes [30].

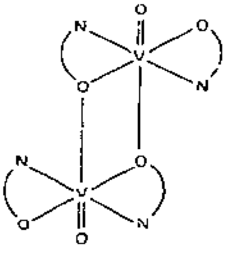
(ii) Complexes with bidentate Schiff bases

Dutta and Sengupta [31] first reported the synthesis of subnormal oxovanadium(IV) complexes of bidentate ON donor Schiff bases derived from 2-hydroxynaphthaldehyde and aniline or *p*-chloroaniline, and salicylaldehyde and sulfanilamide. The complexes have magnetic moments of 1.54 B.M. at 297°K.



13 R=H, Cl, Br, C_4H_4.
R'=H, Cl, SO_2NH_2

Kuge and Yamada [32] have prepared two more subnormal complexes with the ligand (13) (R = Cl, Br; R' = H). The complexes exhibit room temperature magnetic moments of 1.4—1.5 B.M. and structure (14) has been proposed. The complex with ligand (13) (R = C_4H_4, R' = H) has also been prepared and is believed to be magnetically dilute. The electronic spectra of the complex with the ligand (13) (R = Br, R' = H) in chloroform and in solid state are different and a monomeric structure for the complex in non-coordinating solvent is proposed [32]. Dutta and Sengupta have also prepared the complex with the ligand (13) (R = Cl, R' = H) and reported a magnetic moment of 1.75 B.M. at 295°K. The spectral bands of this complex in nujol mull and in chloroform solution occur at comparable energies suggesting a similarity of structure both in solid state and in chloroform solution [31]. Due to the disagreement between these two groups, work was initiated on these complexes in the present reviewer's laboratory [33]. The three subnormal complexes reported by Dutta and Sengupta were prepared and magnetic susceptibilities were determined from 78 to ~297°K. These complexes display magnetic moments in the range 1.69—1.72 B.M. and obey the Curie—Weiss law in the temperature range studied with θ = 2—5°K. Osmometric molecular weight measurements indicate that the complexes are monomeric in chloroform. The ESR spectra of the complexes in dilute chloroform solutions exhibit 8 line spectra (g_{av} = 1.98, average hyperfine splittings (A) around 100 gauss) characteristic of normal oxovanadium(IV) complexes. This information clearly indicates the absence of magnetic exchange [33]. Complexes with the ligand (13) (R = Cl, Br, R' = H) are under investigation in our laboratory.



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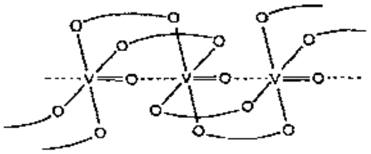
(iii) Complexes with various carboxylic acids

A large number of oxovanadium(IV) subnormal complexes have been synthesized from various carboxylic acids. Oxovanadium(IV) acetate was first prepared by Seifert in 1962 [34] and the synthesis of the complex has appeared in Inorganic Syntheses [35]. Zelentsov et al. [36] first proposed the room temperature magnetic moment (1.2 B.M.) of the complex, whose detailed magnetic studies at several temperatures have appeared [37—39]; J is $-166\ \mathrm{cm}^{-1}$ [38]. On the basis of infrared and magnetic data Casey and Thackeray [38] have proposed that oxovanadium(IV) acetate has a different structure in comparison to copper(II) acetate monohydrate. The structure (15) suggested for this complex has both V=O···V interaction and carboxylate bridges.



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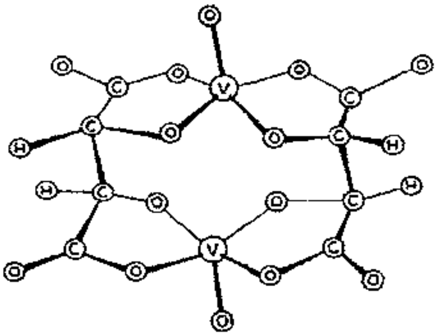
The magnetic data of the complex agree with the Ising model but do not fit the Heisenberg model. This led to the suggestion that the spin—spin exchange pathway involves the z-component of the spin but not the x- and y-components. Goodgame and Waggett [40] have made a cryomagnetic study of N,N'-propylenebis(salicylideneiminate)oxovanadium(IV) whose crystal structure consists of infinite linear chains of molecules linked by vanadyl oxygen bridges [41]. They have found that the complex obeys the Curie—Weiss law with $\theta = -7$°K indicating lack of significant spin—spin coupling between the neighbouring vanadium atoms. The results indicate that the vanadyl oxygen bridges do not contribute to the antiferromagnetic interaction due to intraionic exchange via $\sigma(\mathrm{O}_{p_z}—\mathrm{V}_{d_{z^2}})$ or $\pi(\mathrm{O}_{p_x,p_y}—\mathrm{V}_{d_{xz},d_{yz}})$ pathway in oxovanadium(IV) complexes [40]. As the unpaired electron in square pyramidal oxovanadium(IV) complexes is in the xy plane (d_{xy} orbital, b_2 symmetry molecular orbital) perpendicular to the V=O bond (z axis), spin polarization through the z-component of the spin viz. V=O···V=O··· will occur in the excited state and this exchange pathway should be insignificant. It appears that the exchange interactions in oxovanadium(IV) acetate occur through the bridging carboxylic groups by π overlap of the vanadium d_{xy} orbital with the π symmetry orbitals of the COO$^-$ groups ($2p\pi\mathrm{O}—2p\pi\mathrm{C}—2p\pi\mathrm{O}$). Such intraionic exchange due to $\pi \rightarrow d_{xy}$, $\pi_{\mathrm{n.b.}} \rightarrow d_{xy}$ and $d_{xy} \rightarrow \pi^*$ leads to the antiferromagnetic type of spin—spin exchange [40]. Bridging carboxylate groups may force the vanadium ions to come close together and direct spin—spin coupling is also possible in the V···V···V chain in the xy plane [39]. Either or both of the mechanisms may be operating in this system. Reliable estimates of the relative magnitudes of direct metal—metal bonding and indirect superexchange contributions to the singlet—triplet separation await further studies in this and related complexes. The same type of magnetic interaction exists in a large number of oxovanadium(IV) complexes of some other aliphatic and aromatic carboxylic acids [36, 39, 42—52] viz. propionic acid, pivalic acid, *n*- and isobutyric acid, *n*- and isovaleric acid, monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, dibromoacetic acid, tribromoacetic acid, dimethylacetic acid, trimethylacetic acid, phenylacetic acid, diphenylacetic acid, thioacetic acid, glutaric acid, trihydroxyglutaric acid, adipic acid, hexanoic acid, heptanoic acid, octanoic acid, benzoic acid, *m*-chlorobenzoic acid and *o*-iodobenzoic acid. These complexes possess room temperature magnetic moments ranging from 0.9 to 1.4 B.M. with exchange constants -150 to -290 cm^{-1}. The structures of these carboxylic acid complexes are believed to be analogous to that of the oxovanadium(IV) acetate. The shifts of both ν(V=O) and ν(O—C—O) stretching vibrations by 10 cm^{-1} occur on lowering the temperature from 300 to 100°K [38, 50]. These shifts are due to an increase in interaction expected for lattice antiferromagnets. The oxovanadium(IV) carboxylate complexes exhibit two *d*–*d* bands at around 10000 and 17000 cm^{-1}. The spectral bands have been assigned [38, 50] according to the Ballhausen and Gray energy level scheme [53]. Although the room temperature magnetic moments of oxovanadium(IV) formate hydrates are in the range 1.45—1.70 B.M. these complexes obey the Curie—Weiss law at 79—294°K with θ = 9—15°K. Oxovanadium(IV) malonate is also a Curie—Weiss paramagnet with μ_{eff} = 1.8 B.M. [39]. ESR studies on oxovanadium(IV) acetate and its adducts with ethanol, acetic acid, ophen, dipy and α-picoline have appeared [38, 54]. Magnetic susceptibility data on some of these adducts and also on the thiourea adduct have been reported [55].

Still other organic acid complexes have been synthesized and exclusively studied by ESR measurements and single crystal X-ray structure determination. The complexes formed by quadridentate ligands *dl*-tartaric acid and *d*-tartaric acid have been the object of much work [51, 56—68]. Interest in these systems was stimulated by the report of the dimeric nature of these complexes as determined by single crystal X-ray [60, 62]. The tartrates $M_4[VO(tart)]_2 \cdot xH_2O$ ($M = Na^+, K^+, NH_4^+, Rb^+, N(CH_3)_4^+$ and $\frac{1}{2}Ba^{2+}$) are easily produced by reducing V_2O_5 with an excess of tartaric acid followed by addition of the base MOH [61]. The complexes $(NH_4)_4[VO(d\text{-tart})]_2 \cdot 2H_2O$ and $Na_4[VO(dl\text{-tart})]_2 \cdot 12H_2O$ are both binuclear in which two VO^{2+}



16 Structure of $[VO(dl\text{-tart})]_2^{4-}$ ion

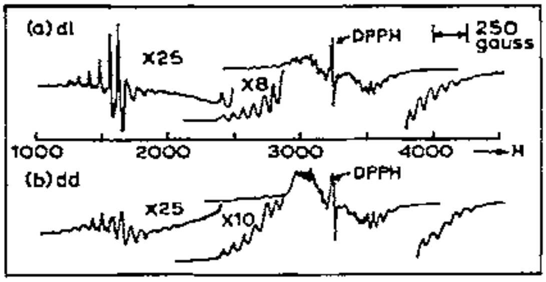


Fig. 2. X-Band ESR spectra of (a) $Na_4[(VO)_2(dl\text{-tart})_2]\cdot 12H_2O$ and (b) $Na_4[(VO)_2(d\text{-tart})_2]\cdot 6H_2O$ in ethylene glycol—water solution at 77°K. Reprinted with permission from J. Amer. Chem. Soc., 91 (1969) 4675. Copyright by the American Chemical Society.

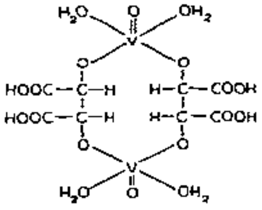
ions are bridged by tartrate groups. In $(NH_4)_4[VO(d\text{-tart})]_2\cdot 2H_2O$ the vanadium atom is situated in a distorted trigonal bipyramid coordination site with the vanadyl oxygen atom in the equatorial plane of the bipyramid [60]. On the other hand in $Na_4[VO(dl\text{-tart})]_2\cdot 12H_2O$ (structure 16) coordination of vanadium is a normal square pyramid [62]. The V=O and V—V distances in $Na_4[VO(dl\text{-tart})]_2\cdot 12H_2O$ and $(NH_4)_4[VO(d\text{-tart})]_2\cdot 2H_2O$ are 1.619, 4.082 and 1.60, 4.35 Å respectively (cf. Cu—Cu distance of 2.64 Å in copper(II) acetate monohydrate [69]). The lower V—V distance in the *dl*-tartrate complex is reflected in severe distortion from the usual square pyramidal structure. Osmometric molecular weight determinations and potentiometric titration indicate a dimeric structure for the complexes in solution [60]. The room temperature magnetic moments of these complexes are in the 1.7 B.M. region [51, 61]. Several papers have appeared on the solution and single crystal ESR of oxovanadium(IV) tartrates [63—68]. The important feature of the spectra (Fig. 2) of both oxovanadium(IV) *d*-tartrate and *dl*-tartrate chelates is the appearance of the half field spectra at ~1600 gauss due to the $\Delta M = 2$ transition. The hyperfine splittings of the half field spectra have been observed in the ethylene glycol—water frozen solution spectra and the splittings are 82.5 and 78.6 gauss for the *dl*- and *d*-tartrate complex respectively. The observation of a 15 line spectrum has been attributed to the electron exchange between two ^{51}V nuclei [65]. Dunhill and Symons [64] have observed pairs of satellite lines in the ESR spectra of oxovanadium tartrate in aqueous solution indicating the presence of a dimeric structure. A detailed analysis of ESR spectra of oxovanadium(IV) tartrates in aqueous solution at pH 2—9 has appeared [68]. The exchange energy has been calculated on the basis of analysis of satellite lines for the dimeric species in the pH ranges 2—3, 3—5 and at 9 and the J values are 5.62×10^{-2}, 1.07×10^{-1} and 2×10^{-1} cm^{-1} respectively [66—68]. Utilising the ESR g_{av} and D values (zero field splitting) the V—V distance (R) in these systems has been calculated according to the formula:

$$R^3 = \frac{0.65\, g_{\parallel}^2}{D}$$

R values at p*H* 2.8, 4.8 and 9 are 6.5, 5.2 and 4.2 Å respectively [68]. As the p*H* is lowered coordinated carboxyl groups become free and as a result the V—V distance increases. This is reflected in the decrease in *D* value with lowering of p*H*. The intensity of the $\Delta M = 2$ transition of VO—*d*-tartrate [68]

p*H*	$D \times 10^{-4}$ cm^{-1}	ν(V=O) cm^{-1}
9	335	958
4.8	180	978
2.8	88	988

also decreases as the p*H* is lowered. The V=O frequency increases with lowering of p*H* indicating a decrease in coordinating ability of the equatorial ligands. Structure (17) has been proposed for oxovanadium(IV) tartrate at p*H* 2.8 [68]. The electronic spectrum of the *dl*-tartrate complex contains three bands at 13600, 18700 and 23800 cm^{-1} and the *d*-tartrate complex four bands at 11000, 17000, 18700 and 25100 cm^{-1}. It is interesting to note that the electronic spectra of these dimers can be interpreted with the help of a monomer model [58, 60, 65]. This is also true for the spectra of other



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oxovanadium(IV) subnormal complexes [14, 18, 21, 23, 70]. This implies that magnetic exchange interaction does not appear to significantly affect the electronic spectra of these dimetallic complexes. Even the band at 27000 cm^{-1} in the spectrum of copper(II) acetate monohydrate which has been variously assigned, is now generally believed to be due to a symmetry forbidden ligand → metal charge transfer transition [71, 72].

The ESR spectra of DMF solutions of oxovanadium(IV) chelates of 1-hydroxycyclohexanecarboxylic acid and mandelic acid exhibit the half field spectra at ~1500 gauss due to the $\Delta M = 2$ transition. The V—V distance in the complexes is 3.6 Å which is comparable with the Cu—Cu separation in similar chelates of copper(II) [73].

The ESR spectra of an aqueous solution of oxovanadium(IV) citrate at p*H* 6—9 exhibit low field spectra at $g = 4.05$ due to the $\Delta M = 2$ transition indicating the formation of a dimeric oxovanadium(IV) citrate complex [63]. Oxovanadium(IV) citrate has been isolated and the compound exhibits a room temperature magnetic moment of 1.51 B.M. [51].

(iv) Oxovanadium(IV) porphyrins

Oxovanadium(IV) porphyrins occur in natural petroleum products and some of these are known to be involved in magnetic exchange [74]. Several reports have appeared describing the synthesis of oxovanadium(IV) porphyrins [75—79]. Oxovanadium(IV)-*meso*-porphyrindimethylester, -deuteroporphyrindimethylester and -diacetylporphyrindimethylester have room temperature magnetic moments in the range 0.69—1.2 B.M. [74]. Oxovanadium(IV)-protoporphyrin and -hematoporphyrin obey the Curie—Weiss law with magnetic moment of 1.8—1.9 B.M. and are not involved in magnetic exchange [80]. Oxovanadium(IV) porphyrins exhibit V=O frequency at 981 ± 4 cm^{-1} and show three electronic spectral bands at around 17400, 18700 and 24400 cm^{-1} [74]. The decrease in molar extinction coefficient with the increase in oxovanadium(IV) concentration and the temperature dependence of infrared bands indicate interaction between oxovanadium(IV) porphyrins [74, 81]. The ESR spectra of oxovanadium(IV)-deuteroporphyrindimethylester, -deuteroporphyrindibutylester and -protoporphyrindimethylester in chloroform solutions exhibit low field spectra [79] at ~1600 gauss due to the $\Delta M = 2$ transition which is diagnostic for the presence of dimeric species in solution. The V—V distance of the complexes is in the range 3.4—3.5 Å which is comparable with that for the copper(II) analogs (Cu—Cu = 3.7—3.9 Å) [79].

(v) Miscellaneous complexes

The magnetic moments of the complexes VOX(oxine) (where X = Cl, Br, OH) are dependent on temperature [82]. The authors have suggested a polymeric structure for these complexes on the basis of magnetic data. However $VO(oxine)_2$ and $VO(thio\text{-}oxine)_2$ are believed to be magnetically dilute [82].

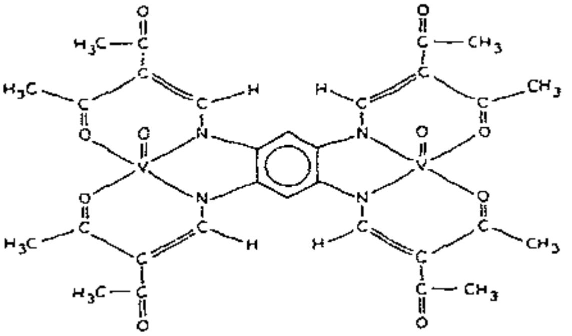
Aggarwal and Prasad have reported that the complex $VOCl_2$(acetylbenzoylhydrazine)$_2$ with a magnetic moment of 1.32 B.M. is involved in antiferromagnetic exchange [83a]. Presumably chlorine bridging is present in the complex. The oxovanadium(IV) complex of ethanolaminethiol displays a room temperature magnetic moment of 1.44 B.M. due to antiferromagnetic interaction [83b].

The adducts of the type $VOCl_2.2L.2H_2O$ (L = *m*-aminobenzoic acid or *p*-aminobenzoic acid) have room temperature magnetic moments in the range 1.28—1.40 B.M. but surprisingly the magnetic moments increase with lowering of temperature [51]. Although $VOCl_2.5NH_3$ has a room temperature magnetic moment of 1.62 B.M., the compound obeys the Curie—Weiss law with $\theta = +60°K$ [84].

Kalinnikov et al. [85] have reported that weak magnetic interaction exists in the compounds $M_2VOCl_4.nH_2O$ ($M = NH_4^+, K^+, Rb^+$ and Cs^+, $n = 0,1$). A small decrease in magnetic moment from 1.7 to 1.65 B.M. with lowering of temperature from 300 to 78°K is observed and J of the compounds is in the range -5 to -7 cm^{-1}. The authors believe that weak spin—spin exchange occurs throughout the entire crystal lattice of the compounds.

Oxovanadium(IV) sulphate has a polymeric structure [86] but has a magnetic moment of 1.7 B.M. at 300°K [50, 87]. The infrared spectral data of the complex indicate the presence of V=O···V bonding [50].

The variable temperature magnetic susceptibility data of the tetraaminobenzene bridged oxovanadium(IV) dimer (18) indicate the absence of magnetic exchange in the complex which has a V—V distance of 8.66 Å. However the corresponding copper(II) dimer having a Cu—Cu distance of 7.36 Å is involved in antiferromagnetic spin—spin exchange. Apparently in the oxovanadium(IV) complex the bridging nitrogen atoms are unable to propagate a spin polarization [88].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An unusual mixed valence compound of the formula $[(C_2H_5)_4N]_4[V_{10}O_{28}H_4]$ in which 8 vanadium atoms are in +5 state and 2 are in +4 state has been described by Heitner-Wirguin and Selbin [89]. The ESR spectrum of the compound exhibits a 15 line spectrum with hyperfine splittings of 51 gauss which is due to the coupling of two interacting ^{51}V nuclei. The room temperature magnetic moment of the complex (1.9 B.M.) is surprisingly high [89]. Variable temperature magnetic susceptibility data on the compound are not yet available.

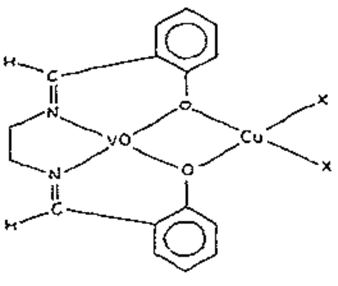
ESR has been used to detect a novel oxovanadium(IV) pyrophosphate trimer [90] in aqueous solution at pH 4—6. A 22 line spectrum was observed with intensity ratios (1:3:6:10:15:21:28:36:42:46:48:46:42:36:···) due to the interaction of one unpaired electron with 3 vanadium nuclei. The authors have isolated a compound of the formula $Na_6(VO)_3(P_2O_7)_3.18H_2O$ and the solution ESR spectrum of the compound also exhibits a 22 line spectrum. The ESR spectrum of the solid in glycerol—water solution at 103°K exhibits a low field component at ~1500 gauss due to the $\Delta M = 2$ transition. The compound possesses a room temperature magnetic moment of 3.6 B.M. indicating the presence of three electrons in the trimer. An independent Japanese [91] study has also reported a 22 line spectrum for the compound. These authors have measured magnetic susceptibilities of the complex at lower temperatures and report a J value of -30 cm^{-1}. Osmometric molecular weight determination supports the trimeric nature of the complex [91]. Spin polarization occurs through the π system of O—P—O in pyrophosphate.

ESR measurements of DMF—H_2O solutions of the oxovanadium(IV) complex of 4,4′,4″,4‴-tetrasulfophthalocyanine provided evidence for dimer formation with the V—V distance 4.5 Å, which is comparable with the Cu—Cu distance of 4.3 Å in the corresponding copper(II) dimer [92]. Electronic spectral and kinetic studies on the dimeric complex have appeared [93].

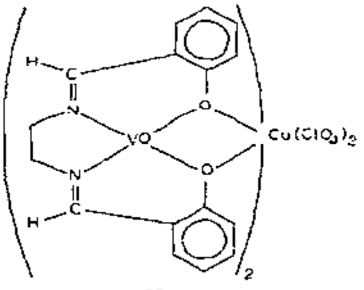
The oxovanadium(IV) complex of tetrakis(aminoethyl)methane exists in frozen aqueous glycol solution as a dinuclear complex as evidenced by the appearance of the triplet state ESR spectrum at ~1500 gauss due to the $\Delta M = 2$ transition. The V—V distance in the complex is 5.7 Å. The Cu—Cu distance in the corresponding dimeric copper(II) complex is also 5.7 Å [94].

Cavell et al. [95] have recently reported the presence of magnetic exchange in oxovanadium(IV) complexes of substituted dithiophosphinic acid. The complexes $[VO(S_2PX_2)_2]$ (X = F, CF_3) have anomalously high magnetic moments of 2.25 and 2.13 B.M. with $\theta = +17$ and $+10$ respectively. The authors believe that the high magnetic moments of the compounds arise due to the interactions between the molecules through the formation of V=O···V chains. The complexes exhibit the V=O frequency at 860—870 cm^{-1} indicating the presence of a V—O—V—O chain structure. This infrared band disappears in solution and the magnetic moments of the complexes in solution are close to 1.75 B.M. indicating the absence of magnetic exchange in solution. These complexes show inverse dependence of the magnetic susceptibility on the field strength (H). This is the first report of dependence of magnetic susceptibility on H in oxovanadium(IV) complexes. The magnetic moments of the complexes show slight increase with decrease in temperature. These results suggest the presence of ferromagnetic interaction in the complexes. However, molecular weight determinations by mass spectrometry indicate a monomeric nature for the complexes. The ESR spectra of the complexes exhibit high field spectra and half field spectra have not been observed. Magnetic studies down to helium temperature are needed to get conclusive proof of the presence of ferromagnetic exchange in these systems. These are not the only oxovanadium(IV) complexes which display higher magnetic moments. The other complexes which have unusually high magnetic moments are VO(3-hydroxy-1-*p*-nitrophenyl-3-phenyltriazene)$_2$ ($\mu_{eff} = 2.1$ B.M.) [96] and VO(*N*,*N*′-ethylenebis(*o*-hydroxyacetophenoneimine)) ($\mu_{eff} = 2.5$ B.M.) [97], the latter exhibiting the highest magnetic moment reported so far for a d^1 oxovanadium(IV) complex. Still other oxovanadium(IV) complexes which display high magnetic moments ~1.9 B.M. are known [2] and some of these magnetic moments have not been corrected for TIP contribution. The higher magnetic moment may be in part due to this factor. A need for detailed magnetic and ESR studies of these complexes is evident and such work is in progress in the reviewer's laboratory. A pertinent point worth mentioning is that some square pyramidal oxovanadium(IV) complexes exhibit room temperature magnetic moments of 1.4—1.6 B.M. and still obey the Curie—Weiss law with small positive θ values. Though a magnetic moment in the range 1.4—1.6 B.M. is characteristic of the subnormal complexes, magnetic exchange probably remains undetected in the temperature range 77—300°K usually studied. ESR may be tried in such cases in order to detect the presence of magnetic exchange.

One interesting series of compounds worth mentioning are the heteropolynuclear complexes containing the $d^1 VO^{2+}$ bridged to the $d^9 Cu^{2+}$ ion. The heterodinuclear complexes (19) have room temperature magnetic moments of 1.69—1.90 B.M. per complex molecule indicating the presence of strong antiferromagnetic interaction between the Cu^{2+} and VO^{2+} ions [98]. The heterotrinuclear complex (20) has a room temperature magnetic moment of 3.93 B.M. and the authors infer the absence of magnetic exchange in the complex. In the case of a trinuclear complex containing three atoms each with a spin of $\frac{1}{2}$ one expects a spin only moment of 3.0 B.M. in the absence of any exchange. This value will be somewhat higher than 3.0 B.M. because of the orbital contribution specially from the copper atom. The magnetic moment reported by the authors is indicative of the presence of magnetic exchange and variable temperature magnetic susceptibility data of the complex need to be recorded in order to ascertain if appreciable magnetic exchange is present in the complex. The infrared spectral data of the complexes (19 and 20) gave evidence for the polynuclear nature of the complexes.



19 X = Cl, Br



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C. COMPARISON WITH COPPER(II) COMPLEXES AND CONCLUDING REMARKS

The oxovanadium(IV) and copper(II) ions resemble each other magnetically in having one unpaired electron in their complexes. A comparison of magnetic data of both oxovanadium(IV) and copper(II) complexes of the same ligand may provide information for the evaluation of the magnetic exchange pathway operating in these systems. Comparison of the symmetries of the unpaired electrons and their overlap in these systems (d_{xy}—d_{xy} overlap in oxovanadium(IV) complexes and $d_{x^2-y^2}$ (orbitals of bridging atom) — $d_{x^2-y^2}$ overlap in copper(II) complexes) leads to the prediction that the antiferromagnetic exchange would occur to a greater extent in the oxovanadium-

TABLE 1

Magnetic data of subnormal oxovanadium(IV) complexes[a,b,c]

Complex	T°K	χ_A' (corr) 10^{-6} cgsu	μ_{eff} B.M.	$-J$ cm^{-1}	Ref.
VO(sal—*o*-aminophenol)	299	934	1.48	125	10
VO(5-Cl-sal—*o*-aminophenol)	296	1090	1.54	90	10
VO(5-Br-sal—*o*-aminophenol)	299	967	1.50	115	10
VO(5-CH_3-sal—*o*-aminophenol)	294	966	1.46	118	10
VO(5-NO_2-sal—*o*-aminophenol)	298	801	1.30	218	10
VO(sal—4-chloro-*o*-aminophenol)	294	959	1.47	120	10
VO(5-Cl-sal—4-chloro-*o*-aminophenol)	297	989	1.52	132	10
VO(hydrox—*o*-aminophenol)	297	991	1.54	151	14
	298	1468	1.84		17
	295	1339	1.78		16
VO(hydrox—4-chloro-*o*-aminophenol)	295	872	1.44	182	14
	298	977	1.48	49	17
	295	963	1.51		16
VO(hydrox—4-nitro-*o*-aminophenol)	294	758	1.34	201	14
VO(hydrox—4-phenyl-*o*-aminophenol)	295	907	1.47		16
	295	956	1.46	58	17
VO(hydrox—5-nitro-*o*-aminophenol)	296	868	1.44		16
	294	990	1.49	54	17
VO(3-hydroxythiophene-2-aldehyde-*o*-aminophenol)	296	979	1.53	139	22a
VO(dibenzoylmethane-*o*-aminophenol).H_2O	295	325	0.87		9a
VO(5-Cl-sal—*o*-aminothiophenol).H_2O	296	698	1.29		18
VO(5-Br-sal—*o*-aminothiophenol)	300	750	1.34		18
VO(5-NO_2-sal—*o*-aminothiophenol)	297	675	1.27		18
VO(hydrox—*o*-aminothiophenol).H_2O	297	971	1.52		18
VO(sal—ethanolamine)	296	844	1.41	215	21
	292	684	1.27	264	22
VO(5-Cl-sal—ethanolamine)	295	669	1.26	330	21
VO(5-Br-sal—ethanolamine)	294	686	1.27	321	21
VO(5-NO_2-sal—ethonalamine)	294	597	1.19	339	21
VO(3-NO_2-sal—ethanolamine)	293	373	0.94	486	21
VO(5-methoxy-sal—ethanolamine)	295	578	1.17	398	21
VO(3-methoxy-sal—ethanolamine)	297	336	0.89	519	21
VO(hydrox—ethanolamine)	295	756	1.34	281	23
	294	674	1.26	290	22
VO(sal—propanolamine)	296	985	1.53	141	21
	291	1100	1.61	102	22
VO(5-Cl-sal—propanolamine)	294	982	1.52	153	21
	295	963	1.51	142	22
VO(5-Br-sal—propanolamine)	293	938	1.48	166	21
	292	1025	1.56	131	22
VO(5-NO_2-sal—propanolamine)	293	769	1.34	294	21
VO(3-NO_2-sal—propanolamine)	293	1006	1.54	147	21
VO(5-methoxy-sal—propanolamine)	294	1053	1.58	117	21
VO(3-methoxy-sal—propanolamine)	294	1004	1.54	137	21

TABLE 1 (continued)

Complex	T°K	χ_A' (corr) 10^{-6} cgsu	μ_{eff} B.M.	$-J$ cm^{-1}	Ref.
VO(hydrox—propanolamine)	295	957	1.51	147	23
	290	850	1.41		22
VO(sal—isopropanolamine)	303	495^c	1.10		26
	294	429	1.01		27
VO(3-methoxy-sal—isopropanolamine)	295	290	0.83		27
VO(hydrox—isopropanolamine)	294	684	1.27		27
VO(sal—2-amino-2-methylpropanol)	303	434^c	1.03		26
VO(hydrox—2-amino-2-methylpropanol)	294	1002	1.54		27
VO(sal—thiosemicarbazone).1.5H_2O	293	677	1.27		28
VO(5-Cl-sal—thiosemicarbazone).H_2O	291	624	1.21		28
VO(5-Br-sal—thiosemicarbazone).H_2O	293	751	1.33		28
VO(acetic acid)$_2$	294	651	1.24	166	38
	292	600	1.19		39
VO(phenylacetic acid)$_2$	299	652	1.19	172	50
	293	662	1.25		39
VO(diphenylacetic acid)$_2$	292	592	1.18		39
VO(thioacetic acid)$_2$	294	803^c	1.38		36
VO(monochloroacetic acid)$_2$	295	364^c	0.93		52
	292	568	1.16		39
VO(dichloroacetic acid)$_2$	295	605^c	1.20		52
	291	572	1.16		39
VO(trichloroacetic acid)$_2$	295	646^c	1.24		52
VO(monobromoacetic acid)$_2$	295	678^c	1.27		52
VO(dibromoacetic acid)$_2$	295	657^c	1.25		52
VO(tribromoacetic acid)$_2$	295	437^c	1.02		52
VO(trimethylacetic acid)$_2$	293	628	1.22		39
VO(propionic acid)$_2$	295	711	1.24	169	50
VO(2,2-dimethylpropionic acid)$_2$	RT		1.3/1.4		49
VO(*n*-butyric acid)$_2$	301	707	1.25	166	50
	292	616	1.20		39
VO(isobutyric acid)$_2$	297	800	1.33	159	50
	292	637	1.23		39
VO(isovaleric acid)$_2$	296	703	1.23	161	50
	294	671	1.26		39
VO(hexanoic acid)$_2$	293	664	1.25	190	39
VO(heptanoic acid)$_2$	294	637	1.23		39
VO(octanoic acid)$_2$	293	658	1.25		39
VO(nonanoic acid)$_2$	292	665	1.25	190	39
VO(cinnamic acid)$_2$	291	725	1.30	180	39
VO(benzoic acid)$_2$	294	798	1.32	180	50
	293	797	1.38		39
VO(*o*-iodobenzoic acid)$_2$	293	662	1.25	180	39
VO(*m*-chlorobenzoic acid)$_2$	302	732	1.33	155	50
VO(succinic acid)	291	635	1.22		39
VO(glutaric acid)	291	707	1.29	190	39
VO(trihydroxyglutaric acid).0.5H_2O	291	1051^c	1.57		51

TABLE 1 (continued)

Complex	T°K	$\chi_{A'}$ (corr) 10^{-6} cgsu	μ_{eff} B.M.	$-J$ cm^{-1}	Ref.
VO(adipic acid)	291	643	1.23		39
Na_4[VO(*d*-tartaric acid)]$_2$.7H_2O	296	1282^c	1.75		61
$(NH_4)_4$[VO(tartaric acid)]$_2$	291	1231^c	1.70		51
Na_4[VO(*dl*-tartaric acid)]$_2$.11H_2O	296	1239^c	1.72		61
[(VO)$_3$(citric acid)$_2$].4H_2O	292	968^c	1.51		51
VO(difluorodithiophosphinic acid)$_2$	293.3	2287	2.25		95
VO(bis(trifluoromethyl)dithiophosphinic acid)$_2$	293.3	1998	2.13		95
VO(*meso*-porphyrindimethylester)	RT	566^c	1.17		74
VO(deuteroporphyrindimethylester)	RT	197^c	0.69		74
VO(diacetylporphyrindimethylester)	RT	595^c	1.2		74
$Na_6(VO)_3(P_2O_7)_3.18H_2O$	RT	5357^c	3.6^d	30	90, 91
$VOCl_2$.(*m*-aminobenzoic acid)$_2$.2H_2O	291	698^c	1.28		51
$VOCl_2$(*p*-aminobenzoic acid)$_2$.2H_2O	293	829^c	1.40		51
$VOCl_2$(acetylbenzoylhydrazine)$_2$	RT	720^c	1.32		83a
VO(ethanolaminethiol)$_2$	RT	980^c	1.54		83b
VO(salen)$CuCl_2.H_2O$	RT	1492^c	1.90^d		98
VO(salen)$CuBr_2$	RT	1180^c	1.69^d		98

[a] Unless otherwise mentioned the magnetic moment reported is per metal ion.

[b] RT = room temperature. For abbreviations of ligands see p. 309.

[c] When the magnetic moment is given by the author but magnetic susceptibility is missing, $\chi_{A'}$ (corr) was calculated using the Curie equation: $\mu_{eff} = 2.84\ (\chi_{A'}\ (\text{corr}) \times T)^{1/2}$. For such calculation at RT, the temperature 300°K was used in the above equation.

[d] Magnetic moment per complex molecule.

(IV) complexes in comparison to the corresponding copper(II) complexes [10]. This prediction holds good in case of the oxovanadium(IV) and copper(II) complexes of the ligands sal—orthoaminophenol [10, 12] and sal—orthoaminothiophenol [18, 99]. On the other hand in complexes with the ligands sal—propanolamine [21, 100], hydrox—orthoaminophenol [14] and sal—thiosemicarbazone [28], the copper(II) complexes are more involved in antiferromagnetic exchange than the corresponding oxovanadium(IV) complexes. It is the present reviewer's view that such comparison is reasonable if the structures of the oxovanadium(IV) and copper(II) complexes of the same ligand are similar. If the structures of the oxovanadium(IV) and copper(II) complexes are not similar, the extent of magnetic interaction may be quite different. It is interesting to note that the copper(II) complexes of the ligands sal—ethanolamine [6], sal—isopropanolamine [101] and sal—2-amino-2-methylpropanol [101] are involved in ferromagnetic exchange whereas the corresponding oxovanadium(IV) complexes are involved in antiferromagnetic type of spin—spin exchange [26, 27]. In the absence of the single crystal X-ray crystallographic data on the oxovanadium(IV) and copper(II) complexes of

TABLE 2

ESR data on spin coupled oxovanadium(IV) complexes

Complex	Medium	$g_{\parallel}$	$g_{\perp}$	g_{av}	$A \times 10^{-4}$ cm^{-1}	$B \times 10^{-4}$ cm^{-1}	D cm^{-1}	R(Å)	Ref.
VO(sal—*o*-aminophenol)	solid			1.99					15
VO(hydrox—*o*-aminophenol)	solid	1.92	1.99	1.97			0.0568	3.48[a]	14
VO(hydrox—4-chloro-*o*-aminophenol)	solid	1.92	1.99	1.97			0.0561	3.50[a]	14
VO(hydrox—4-nitro-*o*-aminophenol)	solid			1.98					14
VO(sal—ethanolamine)	solid	1.92	2.02	1.99			0.053	3.56[a]	21
VO(5-Br-sal—ethanolamine)	solid	1.94	2.01	1.99			0.049	3.68[a]	21
VO(hydrox—ethanolamine)	solid	1.92	2.02	1.99			0.057	3.48[a]	23
VO(sal—propanolamine)	solid			1.99					21
VO(hydrox—propanolamine)	solid			1.99					23
VO(acetic acid)$_2$	solid			1.962					38
VO(phenylacetic acid)$_2$	solid			1.95					50
VO(propionic acid)$_2$	solid			1.96					50
VO(*n*-butyric acid)$_2$	solid			1.96					50
VO(isobutyric acid)$_2$	solid			1.95					50
VO(isovaleric acid)$_2$	solid			1.95					50
VO(benzoic acid)$_2$	solid			1.95					50
VO(*m*-chlorobenzoic acid)$_2$	solid			1.96					50
Na_4[VO(*dl*-tartaric acid)]$_2 \cdot 12H_2O$	ethylene-glycol—water	1.953	1.982	1.972	72.3	21.3	0.0334[c]	4.08[d]	65
Na_4[VO(*d*-tartaric acid)]$_2 \cdot 6H_2O$	ethylene-glycol—water	1.950	1.984	1.973	73.2	24.6	0.0335	4.35[d]	65, 60
VO(1-hydroxycyclohexane-carboxylic acid)	DMF—triethyl-amine	1.99	1.95	1.96[b]	175	6	0.055	3.6	73
VO(deuteroporphyrindimethyl-ester)	$CHCl_3$	1.95	1.99	1.98[b]	160	50		3.4	79

TABLE 2 (continued)

VO(deuteroporphyrindibutylester)	$CHCl_3$	1.95	1.98	1.97[b]	160	54		3.5	79
VO(protoporphyrindimethylester)	$CHCl_3$	1.95	1.98	1.97[b]	160	50		3.5	79
VO(4,4',4'',4'''-tetrasulphopthalocyanine)	DMF—water	1.96	1.99	1.98[b]	140	60	0.028	4.5	92
VO(tetrakis(aminomethyl)methane)	glycol—water	1.98	1.96	1.97[b]	220	80		5.7	94
$Na_6[(VO)_3(P_2O_7)_3] \cdot 18H_2O$	aq. soln.			1.964					90
VO(difluorodithiophosphinic acid)$_2$	glass			1.974					96
VO(bis(trifluoromethyl)dithiophosphinic acid)$_2$	glass			1.985					96
	solid			2.3					95
VO(salen)$CuCl_2 \cdot H_2O$	solid			2.096					98
VO(salen)$CuBr_2$	solid			2.086					98

[a] Calculated using the formula $R^3 = 0.65\, g_\parallel^2/D$.
[b] Calculated using the formula $g_{av} = \frac{1}{3}(g_\parallel + 2g_\perp)$.
[c] Single crystal data: 0.0338 cm^{-1}.
[d] Single crystal data.
For abbreviations of ligands see p. 309.

TABLE 3

Electronic spectral data of subnormal oxovanadium(IV) complexes[a, b]

Complex	Medium	Band I	Band II	Band III	Band IV	Band V	Ref.
VO(sal—*o*-aminophenol)	nujol	12900 sh	17850 sh				14
VO(hydrox—*o*-aminophenol)	nujol	14280 sh					14
VO(hydrox—4-chloro-*o*-aminophenol)	nujol	15380 sh					14
VO(hydrox—4-nitro-*o*-aminophenol)	nujol	16000 sh					14
VO(5-Cl-sal—*o*-aminothiophenol) · H_2O	nujol	13300 sh					18
VO(5-NO_2-sal—*o*-aminothiophenol)	nujol	14900 sh					18
VO(5-Br-sal—*o*-aminothiophenol)	nujol	18200 sh					18
VO(hydrox—*o*-aminothiophenol) · H_2O	nujol	20000					18
VO(sal—ethanolamine)	nujol	14200 sh	16600 sh	19200	26400		21
VO(5-Cl-sal—ethanolamine)	nujol	14000 sh	15000 sh	19700	25300		21
	solid	9000	10500	15000	19000	25000	70
VO(5-Br-sal—ethanolamine)	nujol	13400 sh	15100 sh	19800	24400		21
	methanol	11500(47)	13100(83)	15650(265)	20500(320)	25000(3500)	70
VO(5-NO_2-sal—ethanolamine)	nujol	12900 sh	18200 sh	20300 sh	27000		21
VO(3-NO_2-sal—ethanolamine)	nujol	13700 sh	16100 sh	19000	27000		21
VO(5-methoxy-sal—ethanolamine)	nujol	13150 sh	16900 sh	19500 sh	24400		21
VO(3-methoxy-sal—ethanolamine)	nujol	13700 sh	17000 sh	19600	26600		21
VO(hydrox—ethanolamine)	nujol	14300 sh	16000 sh	19230	23800		23
VO(sal—propanolamine)	nujol	13700 sh	16100	18700	26400		21
VO(5-Cl-sal—propanolamine)	nujol	14200 sh	15100	18400	27000		21
VO(5-Br-sal—propanolamine)	nujol	13400 sh	15100	18300	26600		21
VO(5-NO_2-sal—propanolamine)	nujol	15000 sh	16800 sh	19700 sh	27400		21
VO(3-NO_2-sal—propanolamine)	nujol	13500 sh	16800 sh	18900 sh	25600		21
VO(5-methoxy-sal—propanolamine)	nujol	13400	16200	18500	24400		21
VO(3-methoxy-sal—propanolamine)	nujol	13800 sh	16250	18700	25300		21
VO(hydrox—propanolamine)	nujol	13300 sh	15870 sh	19000	24400		23
VO(sal—isopropanolamine)	reflectance	15390	18180				26
VO(sal—2-amino-2-methylpropanol)	reflectance	15390	18500				26

TABLE 3 (continued)

VO(acetic acid)$_2$	solid	10730	17795	26315		38
VO(phenylacetic acid)$_2$	solid	10000	17400	26200		50
VO(propionic acid)$_2$	solid	10300	17500	26700		50
VO(*n*-butyric acid)$_2$	solid	10000	17400	26300		60
VO(isobutyric acid)$_2$	solid	9700	17500	27600		50
VO(isovaleric acid)$_2$	solid	9600	17200	27000		50
VO(benzoic acid)$_2$	solid	10300	17900	25600		60
VO(*m*-chlorobenzoic acid)$_2$	solid	10200	17600	25800		50
Na_4[VO(*dl*-tartrate)]$_2 \cdot 12H_2O$	aq. soln.	13600	18700	23800		65
Na_4[VO(*d*-tartrate)]$_2 \cdot 6H_2O$	aq. soln.	11100	17000	18700	25100	65
$VOCl_2$(acetylbenzoylhydrazine)$_2$	methanol	14280	16000	24360		83a
VO(5-Br-sal—aniline)$_2$	solid	10300	17500	26700		32
VO(ethanolaminethiol)$_2$	solid	17400	19100			83b

[a] Figures in the parentheses indicate ϵ.

[b] sh = shoulder.

For abbreviations of ligands see p. 309.

the same ligand it is not meaningful to compare the degree of magnetic interaction in complexes of these two metal ions. There are many copper(II) complexes of uni- bi- and quadridentate ligands which are involved in magnetic exchange but the corresponding oxovanadium(IV) complexes are magnetically dilute. The out-of-plane magnetic interaction is quite significant in copper(II) complexes but not important in oxovanadium(IV) complexes presumably due to non-participation of the vanadyl oxygen bridge in antiferromagnetic interaction.

It is now generally believed that magnetic exchange in many copper(II) complexes occurs via superexchange through the bridging atoms. Magnetic studies on the oxovanadium(IV) complexes of tridentate dibasic ligands reveal the presence of direct V—V exchange through σ overlap of the d_{xy} orbitals of the adjacent vanadium atoms. On the other hand the magnetic interaction in oxovanadium(IV) carboxylates is believed to be due to the superexchange though carboxylate bridges and direct V—V interaction. However, there is definite need for X-ray structural and variable temperature magnetic data of some more oxovanadium(IV) complexes involved in magnetic exchange in order to learn more about magnetic exchange pathways. So far no unequivocal example of an oxovanadium(IV) complex possessing a triplet ground state has been reported and chemists should give efforts to synthesize and characterize such complexes. In conclusion it appears that the chemistry of magnetically condensed oxovanadium(IV) complexes is quite interesting and presents possibilities for further fruitful investigation.

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ADDENDUM

Since this review was submitted a number of significant papers have appeared. The following are called to the reader's attention:

An electron spin resonance study of metal ion separations in dimeric vanadyl (dl)- and (dd)-tartrates, A.D. Toy, T.D. Smith and J.R. Pilbrow, Aust. J. Chem., 27 (1974) 1.

Electron spin resonance study of paramagnetic ion pair systems with non-parallel alignment of their axes, S.G. Carr, T.D. Smith and J.R. Pilbrow, J. Chem. Soc. Faraday II, (1974) 497.

Magnetic susceptibility and electron paramagnetic resonance of new vanadyl chelates with anomalous magnetic properties, G.M. Klesova, L.V. Mosina, V.V. Zelentsov, Yu.V. Yablokov and V.I. Spinsyn, Zh. Neorg. Khim., 19 (1974) 1155; C.A., 81 (1974) 31190 p.

Magnetic exchange between V^{IV}—V^{IV} in some binuclear VO^{II} chelates of 1,3,5-triketones, R.L. Lintvedt and J. Mack, American Chemical Society 6th Central Regional Meeting, Detroit, April 21—24, 1974.

Substituent effect on magnetism of dimeric VO^{II} chelates of Schiff bases, H. Okawa, I. Ando and S. Kida, Bull. Chem. Soc. Jap., 47 (1974) 3041.

ESR study of VO^{II} polyaminocarboxylates in aqueous solutions, T.D. Smith, J.F. Boas and J.R. Pilbrow, Aust. J. Chem., 27 (1974) 2535.

REFERENCES

1 M. Kato, H.B. Jonassen and J.C. Fanning, Chem. Rev., 64 (1964) 99.
2 J. Selbin, Chem. Rev., 65 (1965) 153.
3 J. Selbin, Coord. Chem. Rev., 1 (1966) 293.
4 B.N. Figgis, Introduction to Ligand Fields, Wiley, 1966, p. 266.
5 M. Inoue and M. Kubo, Inorg. Chem., 9 (1970) 2310.
6 A. Syamal and L.J. Theriot, J. Coord. Chem., 2 (1973) 241.
7 B. Bleaney and K.D. Bowers, Proc. Roy. Soc. Ser. A, 214 (1952) 451.
8 V.V. Zelentsov, Dokl. Akad. Nauk. SSSR, 139 (1961) 1110; C.A., 56 (1962) 1442 c.
9 (a). V.V. Zelentsov, Russ. J. Inorg. Chem., 7 (1962) 670.
(b). V.V. Zelentsov, Zh. Strukt. Khim., 5 (1964) 714; C.A., 62 (1965) 3515 a.
10 A.P. Ginsberg, E. Koubeck and H.J. Williams, Inorg. Chem., 5 (1966) 1656.
11 G.A. Barclay and B.F. Hoskins, J. Chem. Soc., (1965) 1979.
12 A.P. Ginsberg, R.C. Sherwood and E. Koubek, J. Inorg. Nucl. Chem., 29 (1967) 353.
13 C.M. Harris, B.F. Hoskins and R.L. Martin, J. Chem. Soc., (1959) 3728; S. Gupta, K.C. Kalia and A. Chakravarty, Inorg. Chem., 10 (1971) 1534; A.K. Majumdar and S.C. Saha, J. Indian Chem. Soc., 50 (1973) 697.
14 A. Syamal and L.J. Theriot, J. Coord. Chem., 2 (1973) 193.
15 A. Syamal, unpublished results.
16 G.O. Carlisle and D.A. Crutchfield, Inorg. Nucl. Chem. Lett., 8 (1972) 443.
17 G.O. Carlisle, D.A. Crutchfield and M.D. McKnight, J. Chem. Soc. Dalton, (1973) 1703.
16 C.C. Lee, A. Syamal and L.J. Theriot, Inorg. Chem., 10 (1971) 1669.
19 S.N. Poddar, K. Dey, J. Haldar and S.C. Nathsarkar, J. Indian Chem. Soc., 47 (1970) 743.
20 Y. Kuge and S. Yamada, Bull. Chem. Soc. Japan, 43 (1971) 3972.
21 A. Syamal, E.F. Carey and L.J. Theriot, Inorg. Chem., 12 (1973) 245.
22 (a). G.M. Klesova, V.V. Zelentsov and V.I. Spitsyn, Dokl. Akad. Nauk. SSSR, 208 (1973) 642; C.A., 78 (1973) 116937 a.
(b). I.Y. Kasparova and V.V. Zelentsov, Dokl. Akad. Nauk. SSSR, 173 (1967) 127; C.A., 67 (1967) 27322 b.
23 A. Syamal, Indian J. Chem., 11 (1973) 363.
24 L.G. Vanquickenborne and S.P. McGlynn, Theor. Chim. Acta, 9 (1968) 390.
25 S. Yamada and Y. Kuge, Bull. Chem. Soc. Jap., 42 (1969) 152.
26 G.N. Rao and S.C. Rustagi, Indian J. Chem., 11 (1973) 1181.
27 A. Syamal and K.S. Kale, unpublished results.
28 M.D. Revenko and N.V. Gerbeleu, Russ. J. Inorg. Chem., 17 (1972) 529; N.V. Gerbeleu and M.D. Revenko, Zh. Neorg. Khim., 18 (1973) 2397; C.A., 79 (1973) 132408 e.

29 L.J. Theriot, G.O. Carlisle and H.J. Hu, J. Inorg. Nucl. Chem., 31 (1969) 3303.
30 J.J.R. Frausto da Silva, R. Wooton and R.D. Gillard, J. Chem. Soc. A, (1970) 3369.
31 R.L. Dutta and G.P. Sengupta, J. Indian Chem. Soc., 44 (1967) 738; J. Indian Chem. Soc., 48 (1971) 33.
32 Y. Kuge and S. Yamada, Bull. Chem. Soc. Japan., 45 (1972) 799.
33 A. Syamal, unpublished results.
34 H.J. Seifert, Z. Anorg. Allg. Chem., 317 (1962) 123.
35 R.C. Paul, S. Bhatia and A. Kumar, Inorg. Synth., 13 (1972) 181.
36 V.V. Zelentsov, V.T. Kalinnikov and M.N. Volkov, Zh. Strukt. Khim., 6 (1965) 647; C.A., 64 (1966) 1472 b.
37 D.R. Dakternieks, C.M. Harris, P.J. Milham, B.S. Morris and E. Sinn, Inorg. Nucl. Chem. Lett., 5 (1969) 97.
38 A.T. Casey and J.R. Thackeray, Aust. J. Chem., 22 (1969) 2549.
39 V.T. Kalinnikov, V.V. Zelentsov, O.N. Kuzmicheva and T.G. Aminov, Russ. J. Inorg. Chem., 15 (1970) 341.
40 D.M.L. Goodgame and S.V. Waggett, Inorg. Chim. Acta, 5 (1971) 155.
41 M. Mathew, A.J. Carty and G.J. Palenik, J. Amer. Chem. Soc., 92 (1970) 3197.
42 V.V. Zelentsov and V.T. Kalinnikov, Dokl. Akad. Nauk. SSSR, 155 (1964) 395; C.A., 60 (1964) 15284 b.
43 V.T. Kalinnikov, V.V. Zelentsov, M.N. Volkov and S.M. Shostakovskii, Dokl. Akad. Nauk. SSSR, 159 (1964) 882; C.A., 62 (1965) 9941 c.
44 V.V. Zelentsov, V.T. Kalinnikov and M.N. Volkov, Zh. Neorg. Khim., 10 (1965) 1506; C.A., 63 (1965) 6455 b.
45 V.T. Kalinnikov, V.V. Zelentsov and M.N. Volkov, Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol., 9 (1965) 728; C.A., 66 (1967) 98851 a.
46 V.T. Kalinnikov, V.V. Zelentsov and M.N. Volkov, Zh. Strukt. Khim., 8 (1967) 63; C.A., 66 (1967) 120340 v.
47 V.T. Kalinnikov and T.G. Aminov, Dokl. Akad. Nauk. SSSR, 177 (1967) 633; C.A., 68 (1968) 82464 v.
48 V.T. Kalinnikov and V.V. Zelentsov. Zh. Neorg. Khim., 12 (1967) 3404; C.A., 68 (1968) 82690 r.
49 B.G. Bennett and D. Nicholls, J. Inorg. Nucl. Chem., 34 (1972) 673.
50 A.T. Casey, B.S. Morris, E. Sinn and J.R. Thackeray, Aust. J. Chem., 25 (1972) 1195.
51 V.T. Kalinnikov, V.V. Zelentsov, O.D. Ubozhenko and T.G. Aminov, Dokl. Akad. Nauk. SSSR, 206 (1972) 627; C.A., 78 (1973) 21723.
52 J.P. Walter, M. Dartiguenave and Y. Dartiguenave, J. Inorg. Nucl. Chem., 35 (1973) 3207.
53 C.J. Ballhausen and H.B. Gray, Inorg. Chem., 1 (1962) 111.
54 G.M. Larin, V.T. Kalinnikov, V.V. Zelentsov and M.E. Dyatkina, Teor. Eksp. Khim., 6 (1970) 213; C.A., 73 (1970) 93451 t.
55 V.T. Kalinnikov, V.V. Zelentsov, O.D. Ubozhenko and T.G. Aminov, Dokl. Akad. Nauk. SSSR, 187 (1969) 1089.
56 G.J.B. Conn, U.S. Pat. (1963) 3076830; C.A., 58 (1963) 12375 c.
57 K.M. Jones and E. Larsen, Acta Chem. Scand., 19 (1965) 1210.
58 J. Selbin and L. Morpurgo, J. Inorg. Nucl. Chem., 27 (1965) 673.
59 J.H. Dunlop, D.F. Evans, R.D. Gillard and G. Wilkinson, J. Chem. Soc. A, (1968) 2189.
60 J.G. Forrest and C.K. Prout, J. Chem. Soc. A, (1967) 1312.
61 R.E. Tapscott and R.L. Belford, Inorg. Chem., 6 (1967) 735.
62 R.E. Tapscott, R.L. Belford and I.C. Paul, Inorg. Chem., 7 (1968) 356.
63 R.H. Dunhill and T.D. Smith, J. Chem. Soc. A, (1968) 2189.
64 R.H. Dunhill and M.C.R. Symons, Mol. Phys., 15 (1968) 105.

65 R.L. Belford, N.D. Chasteen, H. So and R.E. Tapscott, J. Amer. Chem. Soc., 91 (1969) 4675.
66 P.G. James and G.R. Luckhurst, Mol. Phys., 18 (1970) 141.
67 L.C. Dickinson, R.H. Dunhill and M.C.R. Symons, J. Chem. Soc., A (1970) 922.
68 A. Hasegawa, Y. Yamada and M. Miura, Bull. Chem. Soc. Jap., 44 (1971) 3335.
69 J.N. Van Niekerk and F.R.L. Schoening, Acta Crystallogr., 6 (1953) 227.
70 I.Y.a. Kasparova and V.V. Zelentsov, Zh. Strukt. Khim., 9 (1968) 532; C.A. 69 (1968) 111629 f.
71 L. Dubicki and R.L. Martin, Inorg. Chem., 5 (1966) 2203.
72 A.K. Gregson, R.L. Martin and S. Mitra, Proc. Roy. Soc. Ser. A, 320 (1971) 473.
73 T.D. Smith, T. Lund, J.R. Pilbrow and J.H. Price, J. Chem. Soc. A, (1971) 2936.
74 E. Higginbotham and P. Hambright, Inorg. Nucl. Chem. Lett., 8 (1972) 747.
75 J.E. Falk, Porphyrins and Metalloporphyrins, Elsevier, Amsterdam, 1964.
76 J.G. Erdman, V.G. Ramsey, N.W. Kalenda and W.E. Hanson, J. Amer. Chem. Soc., 78 (1956) 5844.
77 J.T. Horeczy, B.N. Hill, A.E. Walters, H.G. Schutze and W.H. Bonner, Anal. Chem., 27 (1955) 1899.
78 K. Ueno and A.E. Martell, J. Phys. Chem., 60 (1956) 934.
79 P.D.W. Boyd, T.D. Smith, J.H. Price and J.R. Pilbrow, J. Chem. Phys., 56 (1972) 1253.
80 P. Hambright, A.N. Thorpe and C.C. Alexander, J. Inorg. Nucl. Chem., 30 (1968) 3139.
81 F.E. Dickson and L. Petrakis, J. Phys. Chem., 74 (1970) 2850.
82 G.M. Klesova, V.V. Zelentsov and V.I. Spitsyn, Zh. Obshch. Khim., 43 (1973) 454; C.A., 79 (1973) 12978 u.
83 (a) R.C. Aggarwal and B. Prasad, Indian J. Chem., 10 (1972) 1182.
(b) A. Hodge, K. Nordquest and E.L. Blinn, Inorg. Chim. Acta, 6 (1972) 491.
84 L.V. Kobets, L.P. Dmitrieva, N.I. Vorob'ev and V.V. Pechkovskii, Dokl. Akad. Nauk. Belorusskoi SSR, 15 (1971) 713; C.A., 75 (1971) 135052 n.
85 V.T. Kalinnikov, A.I. Morozov, V.G. Lebedev, O.D. Ubozhenko and M.N. Volkov, Zh. Neorg. Khim., 17 (1972) 675; C.A., 77 (1972) 11888 m.
86 P. Kierkegaard and J.M. Longo, Acta. Chem. Scand., 19 (1965) 1906.
87 J. Roch, C.R. Acad. Sci., 249 (1959) 56.
88 E.F. Hasty, T.J. Colburn and D.N. Hendrickson, Inorg. Chem., 12 (1973) 2414.
89 C. Heitner-Wirguin and J. Selbin, J. Inorg. Nucl. Chem., 30 (1968) 3181.
90 C.C. Parker, R.R. Reeder, L.B. Richards and R.H. Rieger, J. Amer. Chem. Soc., 92 (1970) 5230.
91 A. Hasegawa, Y. Yamada and M. Miura, Bull. Chem. Soc. Jap., 42 (1969) 846.
92 P.D.W. Boyd and T.D. Smith, J. Chem. Soc. Dalton, (1972) 839.
93 R.D. Farina, D.J. Halko and J.H. Swinehart, J. Phys. Chem., 76 (1972) 2343.
94 S.G. Carr, P.D.W. Boyd and T.D. Smith, J. Chem. Soc. Dalton, (1972) 1491.
95 R.G. Cavell, E.D. Day, W. Byers and P.M. Watkins, Inorg. Chem., 11 (1972) 1591.
96 R.L. Dutta and S. Lahiry, J. Indian Chem. Soc., 40 (1963) 857.
97 S.N. Poddar, K. Dey and S.C. Nathsarkar, J. Indian Chem. Soc., 40 (1963) 489.
98 J. Selbin and L. Ganguly, Inorg. Nucl. Chem. Lett., 5 (1969) 815.
99 K. Ison and E. Kokot, Aust. J. Chem., 23 (1970) 661.
100 M. Kato, Y. Muto, H.B. Jonassen, K. Imai and A. Harano, Bull. Chem. Soc. Jap., 41 (1968) 1864.
101 T. Tokii, Y. Muto, M. Kato, K. Imai and H.B. Jonassen, J. Inorg. Nucl. Chem., 34 (1972) 3377.