Magnetic & Spectral Properties of Oxovanadium(IV) Complexes with Tridentate Dibasic ONO Donor Schiff Bases Derived from Isopropanolamine & Substituted Salicylaldehydes*

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Oxovanadium(IV) complexes of tridentate dibasic ONO donor Schiff bases derived from salicylaldehyde, 5-chlorosalicylaldehyde, 3,5-dichlorosalicylaldehyde, 5-bromosalicylaldehyde, 3-methoxysalicylaldehyde, 2-hydroxynaphthaldehyde and isopropanolamine have been synthesized and characterized by elemental analysis, infrared, electronic and ESR spectra, and magnetic susceptibility measurements from 83 to 297°K. They are insoluble in common solvents and decompose above 250°C without melting. Subnormal magnetic moments (μ_{eff} = 0·81-1·27 BM at room temperature) have been observed for all the complexes. The effective magnetic moments of the complexes decrease significantly as the temperature is lowered indicating the presence of antiferromagnetic exchange in the complexes. The exchange integral ($-J$) of these oxovanadium(IV) complexes are in the range 350-470 cm^{-1}. The ESR spectra of the complexes exhibit the half-field spectra around 1600 gauss due to the $\Delta M_s = \pm 2$ transition suggesting the presence of triplet state ($S = 1$) in these complexes. On the basis of magnetic susceptibility and ESR data a dimeric structure with singlet ground state ($S = 0$) has been proposed for these complexes. The V = O stretching frequencies of the complexes occur around 980 cm^{-1}.

THE spin-spin coupled oxovanadium(IV) complexes have been prepared utilizing the ligands containing OO, ON, OS, SS, ONO, ONS and OOO donor sites[1]. Most of these magnetically condensed oxovanadium(IV) complexes are non-crystalline powders precluding their structure determination by single crystal X-ray. Only in one system, viz. [VO(tartaric acid)]$_2^{4+}$ the structures have been determined by X-ray[2-4]. We report in this paper the synthesis of several oxovanadium(IV) complexes with tridentate dibasic ONO donor Schiff bases derived from salicylaldehyde, 5-chlorosalicylaldehyde, 3,5-dichlorosalicylaldehyde, 5-bromosalicylaldehyde, 3-methoxysalicylaldehyde, 2-hydroxynaphthaldehyde and isopropanolamine (2-amino-1-propanol). The complexes (I) have been characterized by elemental analysis, infrared, electronic and ESR spectra, and magnetic susceptibility measurements. Rao and Rastogi[5] have reported only the room temperature magnetic moment of VO (sal-isopropanolamine). We have investigated the magnetic properties of the complexes (I) in detail with a view to finding out the bridging atoms from the magnetic data.

I, R=H, 5−Cl; 5−Br; 3, 5− DICHLORO;
3−OCH₃; 5,6−BENZO
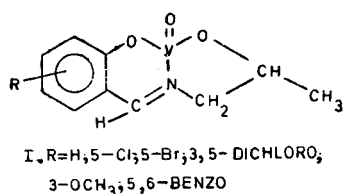
Materials and Methods

The chemicals oxovanadium(IV) chloride (K and K Laboratories, USA), isopropanolamine and 2-hydroxynaphthaldehyde (Fluka AG, Switzerland), 3-methoxysalicylaldehyde (Koch-Light) and salicylaldehyde (reagent grade, Sarabhai Merck) were used.

Vanadium was determined by decomposing the complexes with conc. H_2SO_4 and HNO_3 and finally igniting to V_2O_5. Infrared spectra (KBr) were recorded on a Perkin-Elmer model 21 infrared spectrophotometer. Reflectance spectra were recorded on a Cary model 14 or Bausch and Lomb Spectronic 505 recording spectrophotometer. Electron spin resonance spectra were recorded on a Varian V-4502-12 X-band spectrophotometer using 100-kc modulation and a 9 inch electromagnet equipped with a gauss meter and a frequency meter. A polycrystalline sample of diphenylpicrylhydrazil free radical was used as a g marker. The magnetic susceptibilities were determined by the Gouy method using $Hg[Co(NCS)_4]$ as the standard. The temperature variation was done using a modified cryostat similar in design to that described by Figgis and Nyholm[6]. Diamagnetic corrections of the metal and ligand atoms were calculated using a standard source[7].

The complexes were prepared by the following general procedure:

Salicylaldehyde or substituted salicylaldehyde (·001 mole) and isopropanolamine (0·75 g, 0·01 mole) were refluxed in 50-100 ml ethanol for 30 min. to give yellow solution of the condensed Schiff base. Sodium acetate (1·64 g, 0·02 mole) was added to a solution of oxovanadium(IV) chloride (0·01 mole)

in water (30 ml) and the mixture was stirred for two min. To the oxovanadium(IV) acetate solution the Schiff base solution was added drop by drop with stirring and the mixture was refluxed for 12 hr while stirring magnetically. The separated grey to green precipitate was suction filtered, washed thoroughly with ethanol and dried under vacuum at room temperature; yield 60%. The compounds are not soluble in common solvents.

Results and Discussion

The analytical data summarized in Table 1 show 1:1 (metal-ligand) stoichiometry for the complexes. The absence of anion of original metal salt in the resulting complexes indicates the liberation of protons of the two —OH groups of the ligands. The absence of ν(OH) stretching vibration in the IR spectra of the complexes indicates that they do not contain any water molecule and the ligands are dibasic in character. The tridentate dibasic behaviour of the ligands force the oxovanadium(IV) ion to dimerize or polymerize. This is reflected in the insolubility of the complexes in water and common non-polar organic solvents and the decomposition of the complexes above 250° without melting. The ESR and magnetic susceptibility data also support this.

The IR spectra of the complexes exhibit a strong band in the region 965-995 cm⁻¹ characteristic of νV = O. In the case of VO (3-methoxysal-isopropanolamine) the splitting of ν(V = O) occurs (975, 985 cm⁻¹) and this splitting may be attributed to unit cell group splitting or to a crystal packing effect[8]. In oxovanadium(IV) complexes consisting of infinite linear chains of molecules linked by ...V—O—V—O... bonds the ν V = O occurs[9] at much lower frequency than the usual range[10] of 960 ± 50 cm⁻¹. The occurrence of ν V = O at 965-995 cm⁻¹ in the complexes do not support a linear chain structure. The bands around 1620 cm⁻¹ can be attributed to the coordinated ν C=N[11] involving coordination through the nitrogen atom of the azomethine group since free C=N stretch is known to appear at around 1640 cm⁻¹ in aromatic Schiff bases[12,13].

The electronic spectral data of the complexes exhibit two to three d-d bands around 14000, 16000 and 20000 cm⁻¹ assigned on the basis Vanquickenborne and McGlynn scheme[14] 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. It is noteworthy that the electronic spectral bands of these complexes can be interpreted with reason-

able certainty using the above monomer model[14] thus indicating that the magnetic interaction have negligible effect on the electronic spectra of these complexes. So far any band characteristic of VO(II)-VO(II) interaction has not been observed in oxovanadium(IV) complexes.

The magnetic susceptibilities and magnetic moments of the complexes are presented in Table 3. The complexes do not exhibit any dependence on magnetic field strength indicating the absence of ferromagnetic interaction. The magnetic moments of the complexes decrease considerably as the temperature is lowered showing the presence of antiferromagnetic spin-spin coupling in the complexes. The exchange integral (J) of the complexes has been calculated by fitting the magnetic data to the dimer susceptibility equation[15]:

$$\chi_M = \frac{g^2 N \beta^2}{3kT} \left[1 + \frac{1}{3} \exp\left(-J/kT\right) \right]^{-1} + N_a$$

where χ_M is the susceptibility per g-atom of vanadium, g is the gyromagnetic ratio (= 1·99 from ESR measurements of the complexes) and N_a is the temperature independent paramagnetism term (= 50 × 10⁻⁶ cgs units). The exchange integral (—J in cm⁻¹) values of VO(sal-isopropanolamine), VO(3-methoxysal-isopropanolmine), VO(5-chlorosal-isopropanolamine), VO(3,5-dichlorosal-isopropanolamine) and VO(5-bromosal-isopropanolamine) are 369,385, 470, 450 and 350 respectively. On the basis of our earlier studies[16] and the above magnetic results we suggest that the aminoalcoholic oxygen atoms and not the phenolic oxygen atoms attached to the benzene ring are the bridging atoms in the complexs VO (X-sal-ethanolamine) and VO (X-sal-propanolamine). In case the phenolic oxygen atoms are the bridging atoms one does not expect such difference in magnetic properties in these two series of complexes as the electronic environment

TABLE 2 — REFLECTANCE ELECTRONIC SPECTRAL DATA OF OXOVANADIUM(IV) COMPLEXES WITH SCHIFF BASES

Complex	νmax	(cm⁻¹)
VO(sal-isopropanolamine)	14250, 20700	16850
VO(5-chlorosal-isopropanolamine)	16000	19000
VO(3,5-dichlorosal-isopropanolamine)	15600	18800
VO(5-bromosal-isopropanolamine)	16000	19000
VO(3-methoxysal-isopropanolamine)	14300	21100
VO(hydroxy-isopropanolamine)	14300	20500

TABLE 1 — ANALYTICAL DATA OF OXOVANADIUM(IV) COMPLEXES WITH SCHIFF BASES[a]

Complex	Formula	Calc. (%)				Found (%)			
		C	H	N	V	C	H	N	V
VO(sal-isopropanolamine)	VC₁₀H₁₁NO₃	49·18	4·51	5·74	20·90	50·0	5·0	5·7	20·7
VO(5-chlorosal-isopropanolamine)	VC₁₀H₁₀NO₃Cl	43·09	3·59	5·03	18·31	42·8	3·7	5·0	18·2
VO(5-bromosal-isopropanolamine)	VC₁₀H₁₀NO₃Br	37·15	3·09	4·33	15·79	35·8	3·7	4·4	15·9
VO(3,5-dichlorosal-isopropanolamine)	VC₁₀H₉NO₃Cl₂	38·34	2·87	4·47	16·29	38·6	3·5	4·8	16·1
VO(3-methyoxysal-isopropanolamine)	VC₁₁H₁₃NO₄	48·17	4·74	5·11	18·60	48·1	5·3	5·4	18·5
VO(hydroxy-isopropanolamine)	VC₁₄H₁₃NO₃	57·14	4·42	4·76	17·34	56·6	4·8	5·1	17·1

(a) Abbreviations: sal = salicylaldehyde and hydroxy = 2-hydroxy-1-naphthaldehyde.

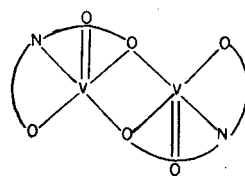TABLE 3 — MAGNETIC SUSCEPTIBILITY AND MAGNETIC MOMENT DATA OF SPIN-COUPLED OXOVANADIUM(IV) COMPLEXES[a],[b]

Temp. ($^\circ$K)	χ_M (10^{-6} cgs units)	μ_{eff} (BM)	Temp. ($^\circ$K)	χ_M (10^{-6} cgs units)	μ_{eff} (BM)
VO(sal-isopropanolamine)			VO(5-chlorosal-isopropa-nolamine)		
294	429	1·01	295	324	0·88
215	354	0·78	213	197	0·58
161	252	0·57	155	129	0·40
127	205	0·46	123	123	0·35
105	108	0·30			
VO(3,5-dichlorosal-isopropa-nolamine)			VO(5-bromosal-isopropa-nolamine)		
295	274	0·81	297	403	0·98
209	195	0·57	203	370	0·78
154	163	0·45	149	314	0·61
83	96	0·25	118	222	0·46
			83	258	0·42
VO(3-Me sal-isopropa-nolamine)			VO(hydroxy-isopropa-nolamine)		
295	290	0·83	294	684	1·27
216	258	0·67	214	633	1·05
159	217	0·53	158	548	0·84
127	188	0·44	127	466	0·71
104	188	0·40	115	362	0·58
95	92	0·26	105	308	0·51
			93	215	0·40

(a) Magnetic moment was calculated using Curie equation: $\mu_{eff} = 2\cdot84 \, (\chi_M \times T)^{1/2}$.

(b) Susceptibilities were corrected for TIP (50 $\times$ 10^{-6} cgs units).

II

Oxovanadium(IV) complexes with tridentate ligands will be apparently tetra-coordinated (see I). But the dibasic character of the tridentate ligands requires that the complexes would dimerize or polymerize to achieve the normal penta- or hexa-coordination. As the magnetic susceptibility data of the complexes obey the dimer susceptibility equation, we propose a dimeric structure (II) for these complexes in which the alcoholic oxygen atoms are the bridging atoms. The normal occurrence of v (V = O) frequency precludes a polymeric structure.

The magnetic exchange pathway in these complexes may be by either direct V-V exchange or by superexchange through the bridging oxygen atoms. The unpaired electron in square pyramidal oxovanadium(IV) complexes is in the d_{xy} orbital. This orbital has the proper symmetry for a σ overlap, leading to direct V-V exchange. The mixing of d_{xy} orbital with $d_{x^2-y^2}$ or d_{z^2} orbital will occur only in the excited state thus precluding the superexchange pathways through $d_{x^2-y^2}$ or d_{z^2} orbital. However, in the case of oxovanadium(IV) acetate the magnetic exchange pathways by both superexchange and direct exchange have been proposed[1,19,20].

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in the chelate ring around the bridge would be same in both the cases. J for VO (X-sal-isopropanolamine) complexes is significantly higher than those for VO (X-sal-propanolamine). The difference in magnetic properties in these complexes may be attributed to the chelate ring effect arising out of variation of number of carbon atoms in aminoalcohol part of the complexes. The complexes VO (X-sal-isopropanolamine) form five-membered chelate ring around vanadium in aminoalcohol part of the molecules. The marked difference in the extent of magnetic interaction in VO (X-sal-isopropanolamine) and VO (X-sal-propanolamine) complexes also supports that the aminoalcoholic oxygen atoms are the bridging atoms.

The ESR spectra of two of the complexes have been recorded in polycrystalline solids. The spectra of the complexes exhibit a band at $\sim$1600 gauss due to the $\Delta Ms = \pm 2$ transition indicating the presence of triplet state dimeric species. The high field spectra are comparable with the spectra of known spin-spin coupled oxovanadium(IV) complexes[16,17]. At liquid nitrogen temperature the high field spectra exhibit hyperfine splittings similar to that observed in oxovanadium(IV) tartrates[18]. Due to the overlap of parallel and perpendicular lines it was not possible to calculate A and B accurately. The ESR parameters, viz. $g_{||}$ and $g_\perp$ for both VO (sal-isopropanolamine) and VO (3-OMe sal-isopropanolamine) are 1·94 $\pm$ 0·02 and 2·01 $\pm$ 0·2 respectively with $g_{av} = 1\cdot99$.