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Magnetic Properties of Oxovanadium(IV) Complexes with Bidentate ON Donor Schiff Bases*

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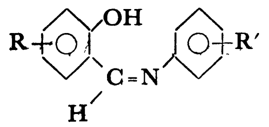
Synopsis. The magnetic properties of oxovanadium(IV) complexes of Schiff bases(I) are reported. Contrary to an earlier report that these complexes are involved in magnetic exchange, the complexes are found to be magnetically dilute. The complexes display μ_{eff} in the range 1.68—1.71 B. M. at 78—297 K with $\theta = 2$—4 K, and exhibit 8 line ESR spectra.

The $3d^1$ oxovanadium(IV) ion belongs to $s = 1/2$ system and the coupling of two $s = 1/2$ spins of interacting pair of oxovanadium(IV) ions may lead to both antiferromagnetic and ferromagnetic spin-spin coupling. Many terdentate dibasic ONO or ONS donor Schiff base ligands have been utilized for the syntheses of dimeric or polymeric oxovanadium(IV) complexes with antiferromagnetic properties.[1] The terdentate dibasic character of these ligands force the oxovanadium(IV) ion to dimerise or polymerise leading to complexes with subnormal magnetic properties. The oxovanadium(IV) complexes of the bidentate monobasic, terdentate monobasic, quadridentate dibasic Schiff bases are usually magnetically dilute.[2] On the other hand, the copper(II) complexes of terdentate monobasic and quadridentate dibasic Schiff bases are usually involved in magnetic exchange.[3,4] Although most copper(II) complexes with bidentate monobasic Schiff bases are magnetically dilute, several examples of copper(II) complexes of bidentate monobasic Schiff bases involved in magnetic exchange are known.[3,4] This difference in magnetic properties has been attributed to the presence of out-of-plane magnetic interaction in copper(II) complexes. The absence of such out-of plane magnetic interaction in oxovanadium(IV) complexes is due to the non-participation of the vanadyl oxygen atom in magnetic exchange.[1] A recent cryomagnetic study[5] of an oxovanadium(IV) Schiff base complex containing a V=O···V=O··· chain indicates that the vanadyl oxygen bridges (*ca.* 170° exchange) do not contribute to the antiferromagnetic interaction due to the intraionic exchange *via* $\sigma(O_{p_z}-V_{d_{z^2}})$ or $\pi(O_{p_x,p_y}-V_{d_{xz},d_{yz}})$ pathway. In the above light one may expect that the oxovanadium(IV) complexes with bidentate monobasic Schiff bases will not exhibit the behaviour of antiferromagnetic exchange. However, the oxovanadium(IV) complexes of ON donor bidentate monobasic Schiff bases(I) have been reported to possess a magnetic moment of 1.54 B.M. at 297 K indicating the presence of antiferromagnetic exchange in these complexes.[6] Kuge and Yamada[7] have also prepared the oxovanadium(IV) complex of I ($R = C_4H_4$, $R' = H$) but they believe the complex to be magnetically dilute. Due to this disagreement between these two groups of workers, it was of interest to repeat the work. We report here the detailed magnetic(78—297 K), ESR and molecular weight measurements on the complexes.



I. $R = H, C_4H_4$;
$R' = H, Cl, SO_2NH_2$.

Experimental

The oxovanadium(IV) complexes of I were prepared according to the method of Dutta and Sengupta.[6] However, the complexes were not recrystallised, and the complexes without recrystallisation gave satisfactory elemental analyses.

The magnetic susceptibilities of the complexes were determined by the Gouy method using mercury(II) tetrathiocyanatocobaltate(II) as the standard. Diamagnetic corrections of the metal and ligand atoms were calculated using a standard source.[8] The magnetic susceptibilities were corrected for the temperature independent paramagnetism using a value of 40×10^{-6} cgs unit. Electron spin resonance spectra were obtained with a Varian V-4502-12 X-band spectrometer using 100-kHz modulation and a 9-inch electromagnet. A minute polycrystalline sample of diphenylpicrylhydrazil (Aldrich Chemical Co., U. S. A.) free radical was used as a *g*-marker in a dual channel cavity and the frequency was monitored with the help of a frequency meter. Molecular weight measurements were made in $CHCl_3$ using a Hewlett-Packard Mechrolab Model 301 A Vapor Pressure Osmometer operating at 37 °C and calibrated with benzil.

Results and Discussion

The magnetic susceptibities and magnetic moment data of the complexes are presented in Table 1. The room temperature magnetic moments(1.69—1.71 B.M.) of the complexes are close to the spin-only value of 1.73 B.M. expected for a d^1 system. The magnetic data of the complexes indicate that the magnetic moments of the complexes remain almost constant in the temperature range 78—297 K. The complexes obey the Curie-Weiss law** with Weiss constant, θ in the range +2 to +4 K. A typical plot of reciprocal magnetic susceptibility *versus* temperature is given in Fig. 1. Thus the magnetic susceptibility data indicate the absence of magnetic exchange in

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* ON represents oxygen and nitrogen donor bidentate Schiff bases(I).

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** The Curie-Weiss law is used in the form: $\chi_M^{corr} = \frac{C}{T-\theta}$.

Table 1. Magnetic susceptibilities and magnetic moments of oxovanadium(IV) Schiff base complexes[a,b,c)]

VO (hydrox-aniline)				VO (hydrox-*p*-chloroaniline)$_2$				VO (sal-salphanilamide)$_2$			
Temp (K)	χ_M^{corr} (10^{-6} cgs unit)	μ_{eff} (B. M.)	θ (K)	Temp (K)	χ_M^{corr} (10^{-6} cgs unit)	μ_{eff} (B. M.)	θ (K)	Temp (K)	χ_M^{corr} (10^{-6} cgs unit)	μ_{eff} (B. M.)	θ (K)
295	1198	1.69		297	1216	1.71		295	1215	1.70	
189	1851	1.68	+4	185	1936	1.70	+2	184	1930	1.69	+2
78	4472	1.68		80	4477	1.70		78	4542	1.69	

a) Abbreviations: hydrox = 2-hydroxy-1-naphthaldehyde and sal = salicylaldehyde. The effective magnetic moment was calculated using the Curie equation: $\mu_{eff}=2.84(\chi_M^{corr}\times T)^{1/2}$ B. M. b) TIP $=40\times10^{-6}$ cgs units. c) Although the magnetic susceptibilities were determined at seven temperatures (see Fig. 1), the data for only three temperatures are presented for brevity.

these complexes. We synthesized these three complexes by several independent experiments and measured magnetic susceptibilities separately, and found deviation in the magnetic moment seldom greater than ±2%.

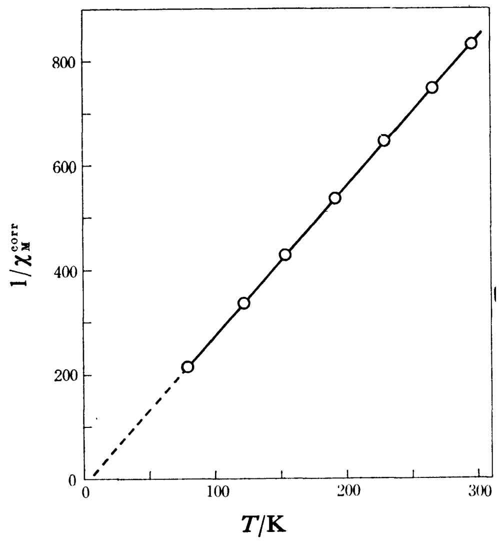

Fig. 1. The inverse magnetic susceptibility *vs.* temperature plot of VO(hydroxynaphthaldehyde-aniline)$_2$.

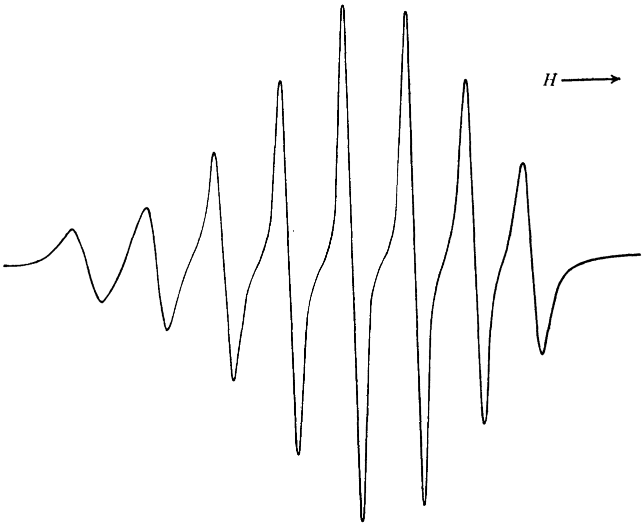

Fig. 2. The ESR spectrum of VO(hydroxynaphthaldehyde-aniline)$_2$ in chloroform.

We recorded the electeon spin resonace spectra of the complexes in dilute chloroform soution. The spectra of the complexes exhibit eight line spectra (^{51}V, $I=7/2$) with $g_{av}=1.98\pm0.01$ and average hyperfine splittings ⟨A⟩ around 100 gauss. A typical spectrum is presented in Fig. 2. The complexes do not exhibit any triplet state spectra (ΔMs $=\pm2$ transition) at around 1600 gauss. The ESR spectra of the complexes are typical of the spectra of magnetically dilute oxovanadium(IV) complexes.[2)] The osmometric molecular weight measurements in chloroform solutions indicate the monomeric nature of the complexes. Thus the magnetic, ESR, and molecular weight data of the complexes indicate the absence of magnetic exchange in these complexes and the magnetic moments reported by Dutta and Sengupta[6)] are in error. Our work agrees with the work of Kuge and Yamada[7)] and proves conclusively that the complexes are spin-doublet species. On the basis of the experimental evdence presented a monomeric square pyramidal structure is suggested to these complexes.

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