Schiff Base Oxovanadium(IV) Complexes with Subnormal Magnetic Moments

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It was reported previously that N-(hydroxyalkyl)-salicylideneimines (Formula I, abbreviated as X–SAL. Y–OH) formed magnetically subnormal copper(II) complexes, which were concluded to have a binuclear structure with exchange coupling between the two copper(II) ions.^{1,2)} Through the hole-formalism, the oxovanadium(IV) ion with a d^1 configuration is known to be somewhat similar to the copper(II) ion with a d^9 configuration. However, no report is available on the corresponding oxovanadium(IV) complexes. The present communication deals with preparation of new Schiff base complexes with oxovanadium(IV) having subnormal magnetic moments.

Oxovanadium(IV) complexes of the type VO (X-SAL, Y-O) were obtained as crystals by the following method. To an ethanolic solution of VOCl₂ (0.01 mol) was added the preformed

Schiff base, N-(hydroxyalkyl)salicylideneimine (0.015 mol), and the resulting solution was stirred at room temperature for a few hours. Microcrystals, which deposited in the solution, were filtered off, and washed with ethanol several times.

Analytical data, which are shown in Table 1, agree with the formula given above. The magnetic moments for these complexes, as shown in Table 1, are much smaller than the spin-only moment for the d^1 system. The subnormal magnetic moments are considered to be due to an exchange interaction between vanadium(IV) ions. It is most likely that these oxovanadium(IV) complexes have a binuclear structure similar to that of the corresponding copper(II) complexes. 1-3) A similar binuclear structure was proposed previously for oxovanadium(IV) complexes with 5substituted N-(2-hydroxyphenol)salicylideneimines, which were also reported to nave subnormal magnetic moments.4,5) The electronic spectra of these complexes differ significantly from those of the complexes of the type VO(X-SAL. alkyl)2, which involve no interaction between vanadium(IV)

Table 1. Analytical data of complexes of the type VO(X-SAL. Y-O)

x	Y	Calcd, %			Found, %			
		$\widehat{\mathbf{C}}$	H	N	$\widehat{\mathbf{c}}$	Ĥ	N	μ
Н	$(CH_2)_2$	46.98	3.94	6.09	46.45	4.33	6.01	1.06
Н	$(CH_2)_3$	48.99	4.94	5.71	49.14	4.95	5.74	1.36
$3\text{-CH}_3\mathrm{O}$	$(CH_2)_3$	48.19	4.78	5.11	48.01	4.78	4.82	0.87

μ: magnetic moment at room temperature in B. M.

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