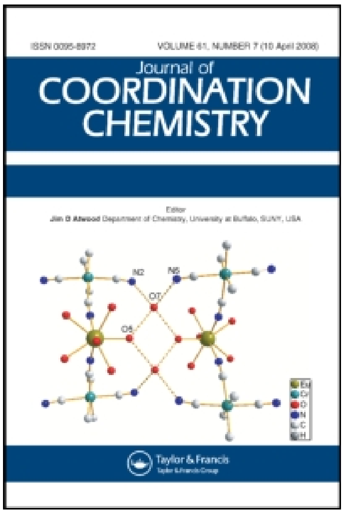

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OXOVANADIUM(IV) AND OXOVANADIUM(V) COMPLEXES WITH TRIDENTATE ONO DONOR LIGANDS

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OXOVANADIUM(IV) AND OXOVANADIUM(V) COMPLEXES WITH TRIDENTATE ONO DONOR LIGANDS

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A series of new coordination complexes of oxovanadium(IV) and oxovanadium(V) with tridentate ONO donor ligands are synthesized and characterized. The oxovanadium(IV) complexes are of the type: (i) VOL (H_2O), (ii) VOL $(py)_2$, (iii) VOL (ophen), (iv) VOL′·XH_2O and (v) VOL′ (ophen) (where LH_2 = 2-hydroxynaphthylidene-amino acid, a tridentate dibasic ligand with ONO donor atoms; py = pyridine; ophen = orthopenanthroline; $L'H_2$ = 2-hydroxynaphthylidene-orthoaminophenol). The oxovanadium(V) complexes are of the type: (i) $VO(OCH_3)L\cdot CH_3OH$ and (ii) $[VO(OH)L]_2$. The VOL (H_2O), VOL $(py)_2$, VOL (ophen) and VOL′ (ophen) complexes have normal magnetic moments (μ_{eff} = 1.70–1.74 BM) at room temperature. The VOL′·XH_2O complexes exhibit subnormal magnetic moments at room temperature and at lower temperatures. Electron spin resonance data of VOL′·XH_2O are reported. The oxovanadium(V) complexes are diamagnetic. Electrolytic conductance measurements indicate they are nonelectrolytes. Electronic spectra, infrared spectra and molecular weight data are reported.

INTRODUCTION

Recently there has been considerable interest in the synthesis and anomalous magnetic properties of oxovanadium(IV) complexes.[1–4] Some of these complexes were prepared from Schiff bases containing ONO or ONS donor sites.[1,2,4] The Schiff bases derived from 2-hydroxynaphthaldehyde and α-amino acids or orthoaminophenols have ONO donor atoms and we thought it worthwhile to synthesize subnormal oxovanadium(IV) complexes from these ligands. The corresponding subnormal copper(II) complexes have recently been reported.[5,6] In this paper we report the synthesis and characterization of oxovanadium(IV and V) complexes of Schiff bases derived from (i) 2-hydroxynaphthaldehyde and α-amino acids and (ii) 2-hydroxynaphthaldehyde and orthoaminophenols. These Schiff bases are dibasic tridentate ONO donor ligands. Oxovanadium(IV and V) complexes of salicylideneaminoacids have been reported recently.[7,8]

RESULTS AND DISCUSSION

The complexes of the type $VOL\cdot H_2O$ (where LH_2 = 2-hydroxynaphthylidene-amino acid) were prepared by refluxing 95% ethanolic solutions of vanadyl dichloride and the tridentate Schiff base and isolating the separated green precipitates. Water is tightly held in these complexes and the compounds cannot be dehydrated by heating at 150°C for hours. The presence of water is also indicated from infrared data. A broad band around 3300 cm^{-1} can be attributed to the ν(OH) frequency of coordinated water. The electrolytic conductance measurements of the complexes in freshly prepared methanol solutions indicate that the complexes are essentially non-electrolyltes ($\Lambda_M = \sim 1.5$ ohm^{-1} cm^2 $mole^{-1}$). Magnetic moments ($\mu_{eff} = 1.70 - 1.74$ BM at ~300°K) of the complexes are very close to the spin only value expected for a $3d^1$ system (see Table II). Reactions of $VOL\cdot H_2O$ complexes with pyridine or orthophenanthroline lead to the isolation of $VOL(py)_2$ and VOL (ophen). These complexes exhibit magnetic moments very close to the spin only value. The $VOL(py)_2$ complexes are unstable and lose pyridine when set aside at room temperature. The complex VO(Hydrox: L-valine·H_2O obeys the Curie–Weiss law with a θ value of + 2.

The green $VOL\cdot H_2O$ complexes when dissolved in methanol gave reddish brown solutions from which brown complexes of the type $VO(OCH_3)L\cdot CH_3OH$ were isolated. The infrared spectra of these complexes exhibit a medium intense band around 3100 cm^{-1} due to coordinated

CH_3OH. The bands around 2800 cm^{-1} and 1050 cm^{-1} are indicative of a coordinated methoxy group.[8] These complexes are diamagnetic as expected for oxovanadium(V) complexes. The $VO(OCH_3)L \cdot CH_3OH$ complexes are monomeric in dilute chloroform solutions. The calculated molecular weight of $VO(OCH_3)$(Hydrox:DL-alanine)$\cdot CH_3OH$ is 361 and experimentally a value of 405 was found. The treatment of $VO(OCH_3)L \cdot CH_3OH$ with dichloromethane followed by *n*-hexane produces green precipitates of the complexes $[VO(OH)L]_2$. The infrared spectra of the complexes exhibit ν(OH) frequency around 3400 cm^{-1} .These complexes are non-electrolytes in nitromethane ($\Lambda_M = \sim 2$ ohm^{-1} cm^2 mole^{-1}). Molecular weight measurements in 1,2-dichloroethane indicate that the complexes are dimers. The calculated molecular weight of the complex [VO(OH)(Hydrox:DL-alanine)]$_2$ is 650. We obtained the following molecular weight measurement results: 710(50 mg/10ml) 800(100 mg/10ml), 880(150 mg/10ml). This concentration dependence

TABLE I

Analytical data of oxovanadium(IV), Oxovanadium(V), and copper(II) complexes[a]

Compound	Color	Stoichiometry		%C	%H	%N
VO(Hydrox: glycine) (H_2O)	green	$VC_{13}H_{11}NO_5$	Found	49.49	3.67	4.35
			Calcd.	50.00	3.52	4.48
Vo(Hydrox: DL-alanine) (H_2O)	green	$VC_{14}H_{13}NO_5$	Found	51.09	3.99	4.16
			Calcd.	51.53	3.98	4.29
VO(Hydrox: DL-phenylalanine) (H_2O)	green	$VC_{20}H_{17}NO_5$	Found	59.72	4.43	3.57
			Calcd.	59.70	4.23	3.48
VO(Hydrox: L-valine) (H_2O)	green	$VC_{16}H_{17}NO_5$	Found	54.54	4.91	3.99
			Calcd.	54.24	4.80	3.95
VO(Hydrox: glycine) $(Py)_2$	yellow	$VC_{23}H_{19}N_3O_4$	Found	61.30	3.89	9.13
			Calcd.	61.06	4.20	9.29
VO(Hydrox: DL-alanine) $(Py)_2$	yellow	$VC_{24}H_{21}N_3O_4$	Found	62.17	4.93	9.30
			Calcd.	61.80	4.51	9.01
VO(Hydrox: DL-phenylalanine) $(Py)_2$	yellow	$VC_{30}H_{25}N_3O_4$	Found	66.22	4.70	7.72
			Calcd.	66.42	4.61	7.75
VO(Hydrox: DL-phenylalanine) (ophen)	red	$VC_{32}H_{23}N_3O_4$	Found	67.88	4.27	7.25
			Calcd.	68.08	4.08	7.44
VO(Hydrox: orthoaminophenol) (H_2O)	brownish yellow	$VC_{17}H_{13}NO_4$	Found	58.55	3.38	4.07
			Calcd.	58.96	3.76	4.04
VO(Hydrox: 4-chloro-orthoaminophenol)	brownish yellow	$VC_{17}H_{10}NO_3Cl$	Found	56.37	2.80	3.97
			Calcd.	56.27	2.76	3.86
VO(Hydrox: 4-nitro-orthoaminophenol)	brownish yellow	$VC_{17}H_{10}N_2O_5$	Found	54.86	3.03	7.33
			Calcd.	54.69	2.68	7.50
VO(Hydrox: orthoaminophenol) (ophen)	red	$VC_{29}H_{19}N_3O_3$	Found	68.51	3.81	8.12
			Calcd.	68.50	3.74	8.26
VO(Sal: orthoaminophenol) (ophen)	red	$VC_{25}H_{17}N_3O_3$	Found	65.16	3.31	9.34
			Calcd.	65.50	3.71	9.17
$VO(OCH_3)$ (Hydrox: glycine)$\cdot CH_3OH$	brown	$VC_{15}H_{16}NO_6$	Found	51.30	3.99	3.84
			Calcd.	50.42	4.48	3.92
$VO(OCH_3)$ Hydrox: DL-alanine)$\cdot CH_3OH$	brown	$VC_{16}H_{18}NO_6$	Found	51.90	4.12	3.96
			Calcd.	51.75	4.85	3.77
$VO(OCH_3)$ (Hydrox:DL-phenylalanine)$\cdot CH_3OH$	brown	$VC_{22}H_{22}NO_6$	Found	59.11	5.18	3.11
			Calcd.	59.06	4.92	3.13
[VO(OH) (Hydrox: glycine)]$_2$	green	$(VC_{13}H_{10}NO_5)_2$	Found	49.65	3.39	4.60
			Calcd.	50.16	3.21	4.50
[VO(OH) (Hydrox: DL-alanine)]$_2$	green	$(VC_{14}H_{12}NO_5)_2$	Found	51.65	3.76	4.19
			Calcd.	51.69	3.69	4.30
Cu(Hydrox: orthoaminophenol)	greenish yellow	Cu $C_{17}H_{11}NO_2$	Found	62.99	3.31	4.42
			Calcd.	62.86	3.38	4.31

[a] Abbreviations: Hydrox represents 2-hydroxynaphthaldehyde; Sal represents salicylaldehyde; Py = pyridine; and ophen = orthophenanthroline.

with dimeric structure was also found in the case of [VO(OH)(Hydrox:glycine)]$_2$. These complexes are also diamagnetic. The electronic spectra of [VO(OH)L]$_2$ complexes show a broad band around 15,500 cm^{-1} with high molar absorptivity ($\varepsilon \sim 600$ per vanadium). The VO(OCH$_3$)L·CH$_3$OH complexes exhibit a shoulder around 20,000 cm^{-1} ($\varepsilon = \sim 450$). These bands may be due to symmetry forbidden charge transfer bands.[7,8]

TABLE II

Room temperature magnetic susceptibility data of oxovanadium(IV), oxovanadium(V), and copper(II) complexes[a, b]

Complex	Temp (°K)	X_M^{Corr} 10^{-6} cgs	μ_{eff} (BM)
VO(Hydrox: glycine) (H$_2$O)	297	1261	1.74
VO(Hydrox: DL-alanine) (H$_2$O)	298	1204	1.70
VO(Hydrox: DL-phenylalanine) (H$_2$O)	298	1202	1.70
VO(Hydrox: L-valine) (H$_2$O)	297	1226	1.71
VO(Hydrox: glycine) (Py)$_2$	296	1251	1.73
VO(Hydrox: DL-alanine) (Py)$_2$	298	1205	1.70
VO(Hydrox: DL-phenylalanine) (Py)$_2$	297	1200	1.70
VO(Hydrox: DL-phenylalanine) (ophen)	297	1204	1.70
VO(Hydrox: orthoaminophenol) (H$_2$O)	297	991	1.54
VO(Hydrox: 4-chloro-orthoaminophenol)	295	872	1.44
VO(Hydrox: 4-nitro-orthoaminophenol)	294	758	1.34
VO(Hydrox: orthoaminophenol) (ophen)	298	1210	1.70
VO(Sal: orthoaminophenol) (ophen)	298	1200	1.70
VO(OCH$_3$) (Hydrox: glycine)·CH$_3$OH	297		diamag.
VO(OCH$_3$) (Hydrox: DL-alanine)·CH$_3$OH	297		diamag.
VO(OCH$_3$) (Hydrox: DL-phenylalanine)·CH$_3$OH	298		diamag.
[VO(OH) (Hydrox: glycine)]$_2$	297		diamag.
[VO(OH) (Hydrox: DL-alanine)]$_2$	298		diamag.
Cu(Hydrox: orthoaminophenol)	289	817[c]	1.38

[a] Magnetic moment was calculated using Curie equation: $\mu_{eff} = 2.84 (X_M^{Corr} \times T)^{1/2}$ BM.

[b] TIP = 50×10^{-6} cgs units.

[c] TIP = 60×10^{-6} cgs units.

The ν(V = O) frequencies of the oxovanadium(IV) and oxovanadium(V) complexes are presented in Table III. V = O frequencies of the VOL(py)$_2$ occur at lower frequencies in comparison to the VOL·H$_2$O. The shift ($\sim$40 cm^{-1}) of ν(= O) frequency suggest trans coordination of a pyridine molecule and is consistent with other pyridine complexes of oxovanadium(IV).[9] A shift (40 cm^{-1}) was also noticed in the case of VO(Hydrox:DL-phenylalanine) (ophen).

The spectral characteristics of the complexes are presented in Table 3. Consistent with other oxovanadium(IV) complexes,[9] the complexes reported in this study exhibit two or three bands in the 500–1200 mμ region. Recently Vanquickenborne and McGlynn[10] have presented a scheme for oxovanadium(IV) complexes and they have proposed the following ordering of vanadium d orbitals $d_{xy} < d_{xz}, d_{yz} < d_{x^2-y^2} < d_{z^2}$. According to this scheme the low energy band around 13,000 cm^{-1} is assigned to the $d_{xy} \rightarrow d_{xz}, d_{yz}$ transition and the high energy band around 19,000 cm^{-1} is assigned to the $d_{xy} \rightarrow d_{x^2-y}$ transition. The complexes exhibit one band around 25,000 cm^{-1} and this band is assigned to intraligand and/or charge transfer band due to the position and high intensity of the band. The free ligands also have bands in this region and this supports the above assignment. In coordinating solvent like pyridine the *d–d* bands are shifted and it seems likely that the oxovanadium(IV) complexes when dissolved in pyridine combine with one or two molecules of pyridine. The oxovanadium(IV) complexes reported in this study are low symmetry complexes and the splitting of the *d–d* bands were observed in some cases (see Table III) which is in line with other low symmetry oxovanadium(IV) complexes.[9]

We have synthesized oxovanadium(IV) complexes with other dibasic tridentate ONO donor ligands derived from 2-hydroxynaphthaldehyde and orthoaminophenol or substituted orthoaminophenol.

TABLE III

Electronic spectra and infrared spectral data of oxovanadium(IV), oxovanadium(V) and copper(II) Complexes[a]

Complex	$\nu(V=O)$ cm^{-1}	Medium	$\nu_{max}(\varepsilon)$ cm^{-1}
VO (Hydrox: glycine) (H_2O)	1000	Nujol	12900–13300, 18520, 24690
		Pyridine	12340(44), 13700(46), 19800(63), 25000(4700)
VO(Hydrox: DL-alanine) (H_2O)	1000	Nujol	13330, 18690, 24690
		Pyridine	12500(28), 13970(30), 18870(47), 25000(3000)
VO(Hydrox: DL-phenylalanine) (H_2O)	1000	Nujol	13790, 16000, 18520, 24100
		Pyridine	14080(26), 18870(51), 20200(52), 25000(9500)
VO(Hydrox: L-valine)(H_2O)	1000	Nujol	14080, 16390, 18520, 24100
		Pyridine	14080(26), 14925(27), 19230(51), 25000(7300)
VO(Hydrox: glycine) $(Py)_2$	955	Nujol	11900, 13790, 18520, 20000, 25000
		Pyridine	13160(43), 18870(68), 25000(6200)
VO(Hydrox: DL-alanine) $(Py)_2$	955	Nujol	11900, 12900, 18180, 25000
VO(Hydrox: DL-phenylalanine) (ophen)	960	Nujol	14080, 18870, 22730
VO(Sal: orthoaminophenol)	990	Nujol	12900 sh, 17850 sh
VO(Hydrox: orthoaminophenol) (H_2O)	1000	Nujol	14280 sh
VO(Hydrox: 4-chloro-orthoaminophenol)	990	Nujol	15380 sh
VO(Hydrox: 4-nitro-orthoaminophenol)	955	Nujol	16000 sh
VO(Hydrox: orthoaminophenol) (ophen)	960	Nujol	11900, 19800, 21270 sh
VO(Sal: orthoaminophenol) (ophen)	950	Nujol	11900, 17860 sh, 19610
$VO(OCH_3)$ (Hydrox: glycine)$\cdot CH_3OH$	975	$CHLl_3$	20000(520) sh
$VO(OCH_3)$ (Hydrox: DL-alanine)$\cdot CH_3OH$	970	$CHCl_3$	20000(440) sh
$VO(OCH_3)$ (Hydrox: DL-phenylalanine)$\cdot CH_3OH$	975	$CHCl_3$	20000(400) sh
[VO(OH) (Hydrox: glycine)]$_2$	960	Nujol	16260
		CH_2Cl_2	16390(530)
[VO(OH) (Hydrox: DL-alanine)]$_2$	980	Nujol	15380
		CH_2Cl_2	15500(615)
Cu(Hydrox: orthoaminophenol)	—	Nujol	16130 sh, 21050

[a] Abbreviation: sh = shoulder.

These complexes possess subnormal magnetic properties ($\mu_{eff} = 1.34$—1.58 BM at ~297°K). We studied the magnetic properties of the complexes at lower temperatures (see Table IV). The magnetic data supports the presence of antiferromagnetic exchange in the complexes. Zelentsov[1] and Ginsberg *et al.*[2] also noticed subnormal magnetic behaviour of oxovanadium(IV) complexes derived from salicylaldehyde and orthoaminophenol. Recently we reported antiferromagnetic behaviour of oxovanadium(IV) complexes with salicylaldehyde or 2-hydroxynaphthaldehyde and orthoaminothiophenol.[4]

Electron spin resonance of VO(Hydrox: 4-nitro-orthoaminophenol) in polycrystalline sample reveals only one line with $g = 1.98 \pm .01$ at room temperature. At liquid nitrogen temperature this compound exhibits also a single line spectra with $g = 1.98$ and no hyperfine splittings were observed. The half-field line due to $\Delta M_s = 2$ transition could not be located in this compound at room temperature and at liquid nitrogen temperature. The ESR spectra of VO(Hydrox:orthoaminophenol)$\cdot H_2O$ and VO(Hydrox:4-chloro-orthoaminophenol) show two parallel lines (H_{z_1} and H_{z_2}), two perpendicular lines ($H\perp_1$ and $H\perp_2$), and a broad line around 1600 G due to $\Delta M_s = 2$ transition. The ESR spectra were analysed according to standard procedure.[11,12] The magnetic parameters of these complexes are as follows:

Compound	$g_{\parallel}$	$g_{\perp}$	g_{av}	D cm^{-1}	J cm^{-1}
VO(Hydrox:orthoaminophenol)·H_2O	1.92±.01	1.99±.01	1.97	0.0568	151
VO(Hydrox: 4-chloro-orthoaminophenol)	1.92±.01	1.99±.01	1.97	0.0561	182
Vo(Hydrox: 4-nitro-orthoaminophenol)	—	—	1.98	—	201

It is to be noted that $g_{\perp} > g_{\parallel}$ and D in our complexes are greater than that of vanadyl tartrate.[13] The ESR spectra of VO(Hydrox:orthoaminophenol)·H_2O and VO(Hydrox: 4-chloro-orthoaminophenol) in polycrystalline samples show hyperfine splittings at liquid nitrogen temperature. Due to the overlap of parallel and perpendicular lines A and B values could not be determined accurately. The complexes being insoluble in common solvents the ESR spectra could not be recorded in solution. The half-field spectra show hyperfine splittings at liquid nitrogen temperature and as a result the expected 15 lines could be observed. The hyperfine splittings of the half-field lines of 82.5 G. Belford *et al.*[13] observed hyperfine splittings of half-field lines of 82.5 G in vanadyl dl-tartrate complex. The appearance of half-field lines supports the presence of triplet state in these complexes. Using the ESR g_{av} values the singlet-triplet exchange integral, J was calculated using Bleaney and Bowers equation.[14] J of the complexes is presented along with the ESR parameters. A comparison of J values with the corresponding salicylaldehyde analogs[2] (for VO(Sal:orthoaminophenol), $J = 125\,\text{cm}^{-1}$) indicates that magnetic exchange is slightly greater in VO(Hydrox:orthoaminophenol)·H_2O. J values of our complexes are in the order $H < Cl < NO_2$. Ginsberg *et al.*[2]

TABLE IV

Magnetic susceptibilities and magnetic moments of oxovanadium(IV) and copper(II) complexes from 78 to 297° K[a]

	VO(Hydrox: orthoaminophenol)·H_2O (J = 151)						
Temp (°K)	297	265	228	189	152	120	78
$\chi_M^{Corr}(10^{-6}\text{cgs})$	991	1055	1116	1252	1275	1353	1173
μ_{eff} (BM)	1.54	1.49	1.43	1.38	1.25	1.14	0.86
	VO(Hydrox: 4-chloro-orthoaminophenol) (J = 182)						
Temp (°K)	295	265	228	189	152	120	78
$\chi_M^{Corr}(10^{-6}\text{cgs})$	872	933	997	1117	1269	1172	932
μ_{eff} (BM)	1.44	1.41	1.35	1.30	1.22	1.06	0.76
	VO(Hydrox: 4-nitro-orthoaminophenol) (J = 201)						
Temp (°K)	294	265	228	189	152	120	
$\chi_M^{Corr}(10^{-6}\text{cgs})$	758	819	915	1095	1341	1681	
μ_{eff} (BM)	1.34	1.32	1.29	1.29	1.28	1.27	
	VO(Hydrox: L-valine) (H_2O) ($\theta = +2$)						
Temp (°K)	297	265	228	189	152	120	
$\chi_M^{Corr}(10^{-6}\text{cgs})$	1226	1367	1568	1980	2410	2970	
μ_{eff} (BM)	1.71	1.71	1.70	1.73	1.72	1.69	
	Cu(Hydrox: orthoaminophenol) (J = 301)						
Temp (°K)	289	265	228	189	152		
$\chi_M^{Corr}(10\text{–}_{6}\text{cgs})$	817	791	713	577	429		
μ_{eff} (BM)	1.38 (1.39[b])	1.30	1.14	0.94	0.72		

[a] TIP value of 50×10^{-6} cgs unit was used for all oxovanadium(IV) complexes. TIP value of 60×10^{-6} cgs units was used. for the copper(II) complex.

[b] Taken from ref. 5 for comparison.

also noticed higher J value for VO(Sal:4-nitro-orthoaminophenol). However the data indicates that J is relatively unaffected by the substituents and this result is in line with the work of Ginsberg *et al.*[2] We also prepared one copper(II) complex, Cu(Hydrox:orthoaminophenol) and recorded its magnetic susceptibilities at several temperatures (see Table IV). This copper(II) complex is also involved in antiferromagnetic exchange and a calculation of J using Bleaney and Bowers equation gives a value of 301 cm^{-1} ($g = 2.07$ from ESR measurements, TIP $= 60 \times 10^{-6}$ cgs units). From a comparison of J values of VO(Hydrox:orthoaminophenol) and Cu(Hydrox: orthoaminophenol) it appears that the antiferromagnetic exchange occurs to a greater extent in the copper(II) complex.

This is also true in the case of oxovanadium(IV) and copper(II) complexes of the Schiff base derived from salicylaldeyde and propanolamine where the moments are 1.36 and 0.41 BM respectively at room temperature. Previous comparisons of magnetic data with the corresponding copper(II) complexes has led to the conclusion that antiferromagnetic exchange occurs to a greater extent in oxovandium(IV) complexes.[1,2,4]

The VOL′·XH_2O complexes are poorly soluble in common solvents and the electronic spectra of these complexes were recorded in nujol mulls. The electronic spectra of these subnormal complexes are very similar to the reported spectra of other oxovanadium(IV) complexes with subnormal magnetic properties[4]. The spectral bands are not well resolved and appear as shoulders. These bands are assigned to *d–d* transitions. VO(Sal: orthoaminophenol) or VO(Hydrox: orthoaminophenol) reacts with orthophenanthroline to form VO(Sal: orthoaminophenol)(ophen) or VO(Hydrox: orthoaminophenol)(ophen). These heterochelate complexes possess magnetic moments ($\mu_{eff} = 1.70$ BM) very close to spin only value. The electronic and infrared spectral bands are included in Table III.

Although we were able to prepare subnormal oxovanadium(IV) complexes with hydroxynaphthylidene-orthoaminophenols, oxovanadium(IV) complexes with subnormal magnetic properties could not be prepared from the Schiff bases derived from salicylaldehyde/hydroxynaphthaldehyde and α-amino acids. The aquo molecule in VOL·H_2O complexes could not be removed by heating at 150°C under vacuum. $VOL(py)_2$ complexes were prepared with an end in view that two pyridines may be removed on heating with the formation of dimeric or polymeric complexes. Complete removal of pyridine could be achieved by heating $VOL(py)_2$ at 150°C under vacuo. But at the same time the complexes underwent oxidation. The oxovanadium(IV) complexes with subnormal magnetic properties could not be prepared from these Schiff bases due to the apparent problem of oxidation.

EXPERIMENTAL SECTION

Chemicals Vanadyl dichloride was obtained from K & K Laboratories Inc. 2-Hydroxynaphthaldehyde, orthoaminophenol, 4-chloro-orthoaminophenol, and 4-nitro-orthoaminophenol were obtained from the Aldrich Chemical Co., Inc. Amino acids were the products of Nutritional Biochemical Corporation. Copper(II) acetate monohydrate was obtained from Mallinrodt Chemical Works.

Physical Measurements The electronic spectra were recorded using a Cary Model 14 recording spectrophotometer. Solid state spectra were obtained by mulling the complexes in nujol. Solution spectra were obtained using 1 cm matched quartz cells. A Perkin-Elmer Model 621 recording spectrometer was used to record the infrared spectra. Both KBr pellet and nujol mull techniques were employed. Electrolytic conductivities were determined on a Model RC 16 B2 Conductivity Bridge from Industrial Instruments, Inc. The conductivity cell with platinum electrodes was calibrated with aqueous potassium chloride solutions. Molecular weight measurements were obtained in 1,2-dichloroethane at 37°C with a Mechrolab Model 301A Vapor pressure osmometer calibrated with benzil. Several concentrations were used in the measurements. Magnetic susceptibilities at several temperatures were determined by the Gouy method. All the measurements were calibrated using $Hg[Co(NCS)_4]$ as a standard. Diamagnetic corrections for the metal and ligand atoms were computed using a standard source.[19] The accuracy and precision of the magnetic measurements were checked with the known suceptibilities of copper(II) acetate monohydrate. Electron spin resonance spectra were obtained with a Varian V–4502–12 X-band spectrophotometer using 100–KC modulation and a 9-in. electromagnet. Cylindircal quartz sample tubes and a Varian V–4533 cylindrical cavity were employed. For liquid nitrogen temperature a quartz dewar which fitted into the cavity was used. A small amount of powdered DPPH was used in some of the measurements.

Carbon, hydrogen, and nitrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee, C. F. Gieger, Ontario, California and the North Texas State University Analytical Services. The Analytical Data is presented in Table I.

Preparation of the Complexes

Aquo-2-hydroxynaphthylidene-glycine oxovanadium(IV). To a suspension of 0.75 g (0.01M) of glycine and 1.72 g (0.01 M) of 2-hydroxynaphthaldehyde in 30 ml 95% ethanol, and 95% ethanolic solution of vanadyl dichloride (0.01 M in 10 ml) was added and the mixture was refluxed for four hours. The separated green micro-crystals were suction filtered, washed thoroughly with 95% ethanol, and dried under vacuum. Yield = 40%.

Aquo-2-hydroxynaphthylidene-DL-alanine oxovanadium(IV) and aquo-2-hydroxynaphthylidene-DL-phenylalanine oxovanadium(IV) were prepared as green microcrystals utilizing similar procedure as above. Yield = 40%.

Aquo-2-hydroxynaphthylidene-L-valine oxovanadium(IV). 2-Hydroxynaphthaldehyde (1.72 g. 0.01 M) and L-valine (1.16 g, 0.01 M) were suspended in 30 ml of 95% ethanol. To this an aqueous solution of sodium acetate trihydrate (2.72 g, 0.02 M in 17 ml) was added and refluxed for half an hour. To this mixture a 95% ethanolic solution of vanadyl dichloride (0.01 M in 5 ml) was added and refluxed for four hours. The separated green precipitates were filtered off, washed with 95% ethanol, and dried under vacuum. Yield = 40%.

Preparation of $[VO(OH)L]_2$ *complexes* The corresponding green $VOL(H_2O)$ complex was dissolved in methanol (5 g in 400 ml) and filtered. The filtrate was allowed to evaporate until dry while stirring with the help of a magnetic stirrer. The brownish product was then dissolved in a minimum amount of dichloromethane and filtered. To the filtrate *n*-hexane was added with stirring and green precipitates were obtained. The process of dissolution in dichloromethane and precipitation with *n*-hexane was repeated once more and the precipitates were filtered off and dried under vacuum for one hour.

Preparation of $VOL(py)_2$ *complexes* $VOL(H_2O)$ (3g) was dissolved in 50 ml of pyridine and the resulting solution was allowed to stand for two hours with occasional stirring. The separated brownish yellow precipitates were suction filtered, washed with 95% ethanol, and dried under vacuum. Yield = 65%

Preparation of VO(Hydrox: DL-phenylalanine) (ophen) 2-Hydroxynaphthaldehyde (1.72 g, 0.01 M) and DL-phenylalanine (1.65 g, 0.01 M) and DL-phenylalanine (1.65 g, 0.01 M) were taken up with 30 ml of 95% ethanol. To this mixture an ethanolic solution of vanadyl dichloride (0.01 M in 10 ml) was then added and refluxed for half an hour. An ethanolic solution of orthophenanthroline monohydrate (1.98 g, 0.01 M in 10 ml) was then added and the mixture was refluxed for four hours. The separated red precipitates were filtered off, washed with ethanol and dried under vacuum. Yield = 55%.

Preparation of $VO(OCH_3)L\cdot CH_3OH$ *complexes* The green complex with normal magnetic moment (5 g) was dissolved in 400 ml of anhydrous methanol and filtered. The filtrate was allowed to evaporate slowly in air overnight or longer. On reducing the volume to about one fourth of the original volume a brown product was obtained. These were dried under vacuum at room temperature.

Preparation of $VOL'\cdot H_2O$ *complexes* 2-Hydroxynaphthaldehyde (1.72 g, 0.01 M) and orthoaminophenol or substitued orthoaminophenol (0.01 M) were refluxed in 300 ml of absolute ethanol for half an hour. To this an ethanolic solution of vanadyl dichloride (0.01 M in 50 ml) was added and refluxed overnight. The separated yellow to brownish yellow precipitates were filtered off, washed with ethanol and dried under vacuum. Yield = 70%.

Preparation of VO(Sal: orthoaminophenol)(ophen) Salicylaldehyde (0.61 g, 0.005 M) and orthoaminophenol (0.54 g, 0.005 M) were refluxed in 50 ml 95% for half an hour. To this an ethanolic solution of vanadyl dichloride (0.005 M in 10 ml ethanol) was added and the mixture was refluxed for half an hour. An ethanolic solution of orthophenanthroline monohydrate (0.99 g, 0.005 M in 10 ml) was added and refluxed for four hours. The separated red microcrystals were filtered off, washed with ethanol, and dried under vacuum.

The complex VO(Hydrox:orthoaminophenol) (ophen) was prepared utilizing a similar procedure as described above.

Preparation of Cu(Hydrox: orthoaminophenol) The Schiff base was prepared by refluxing equimolar amounts of 2-hydroxynaphthaldehyde and orthoaminophenol in 95% ethanol. Schiff base (0.005 M)

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was dissolved in a minimum amount of hot methanol. This was added to an aqueous solution of copper(II) acetate monohydrate (0.005 M). The mixture was refluxed overnight. The separated greenish yellow precipitates were filtered hot, washed with methanol, and dried under vacuum. Yield = 80%.

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