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SPECTROSCOPIC AND MAGNETIC PROPERTIES OF SCHIFF BASE COMPLEXES OF OXOVANADIUM(IV) DERIVED FROM 3-METHOXYSALICYLALDEHYDE AND ALIPHATIC DIAMINES

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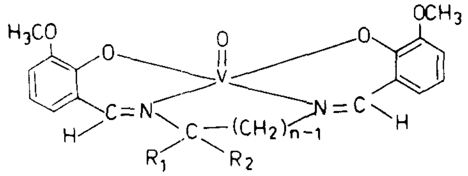
Abstract—Oxovanadium(IV) complexes of 3-methoxysalicylaldehyde and the Schiff base complexes $VO[OC_6H_3(OCH_3)CH{=}N\text{-}CR_1R_2\text{-}(CH_2)_{n-1}-N{=}CH(OCH_3)C_6H_3O]$ were $n = 2(R_1 = R_2 = H$ or $CH_3)$ and $n = 3$ to 10 $(R_1 = R_2 = H)$ have been prepared and characterised by elemental analysis, IR and electronic spectra and magnetic susceptibility measurements. Evidence is adduced that the conversion of the bis-aldehyde complex to the Schiff base complexes is accompanied by an inversion of the e_π^* and b_1^* energy levels. The ν (V = 0) frequency of 979–988 cm^{-1} observed for most of the complexes, except when $R_1 = R_2 = H$ and $n = 3$ where ν (V = 0) is 864 cm^{-1}, are normal for five-coordinate oxovanadium(IV) complexes. The magnetic moments at room temperature of the chelates fall in the range 1.72–1.83 B.M. and vary very slightly over the temperature range 320–80 K.

INTRODUCTION

Recently, we reported[1] the magnetic and spectral properties of V(IV)O Schiff base salicylaldimine complexes and speculated the possibility of the inversion of the ordering of the e_π^* and b_1^* energy levels. These studies now have been extended to bis(3-methoxy-salicylaldehyde)oxovanadium(IV) and its polymethylenediamine derivatives I in order to examine the effect of 3-methoxy substitution in the bonding and stereochemistry. The complexes investigated are being reported for the first time.



Compound	R_1	R_2	n	Abbreviation
1	H	H	2	VO(Omesal$_2$-en)
2	H	CH_3	2	VO(Omesal$_2$-pn)
3	CH_3	CH_3	2	VO(Omesal$_2$-Mepn)
4	H	H	3	VO Omesal$_2$-tn)
5	H	H	4	VO(Omesal$_2$-tm)
6	H	H	5	VO(Omesal$_2$-ptn)
7	H	H	6	VO Omesal$_2$-hxm)
8	H	H	7	VO(Omesal$_2$-hpm)
9	H	H	8	VO(Omesal$_2$-ocm)
10	H	H	9	VO(Omesal$_2$-nnm)
11	H	H	10	VO(Omesal$_2$-dcm)

The bis-aldehyde complex, $VO(Omesal)_2 \cdot H_2O$, is given number 0

EXPERIMENTAL

Preparation of bis(3-methoxysalicylaldehyde)oxovanadium(IV). An ethanolic solution of 0.2 mole of 3-methoxysalicylaldehyde was added dropwise to 0.1 mol of $VOSO_4.2H_2O$ dissolved in 300 cm^3 of 60% ethanol while stirring. The pH of the resultant solution was adjusted to 6 by addition of sodium acetate whereby a solid was precipitated. The product was filtered and washed consecutively with 50% ethanol and absolute ethanol.

Preparation of the Schiff base complexes. N,N′-bis(3-methoxysalicylidene)polymethylenediiminato - oxovanadium(IV).

Compounds 1–6 were isolated by the following procedure. A solution of 5.5–6.0 mmoles of the amine in absolute ethanol was added to a suspension of 5.0 mmoles of $VO(Omesal)_2.H_2O$ in about 100 cm^3 ethanol. The mixture was refluxed (slow heating) while stirring. For complexes 1–4 the reaction was complete in about 1 hr while VO(Omesal$_2$-tm) and VO(Omesal$_2$-ptn) required 8 and 16hr respectively. The products were filtered and soluble chelates (1–3) were recrystallised from chloroform while the insoluble complexes (4–6) were washed with ethanol and traces of soluble impurities removed by Soxhlet extraction.

N,N′-bis(3-methoxysalicylidene)ethylenediiminatooxovanadium(IV), VO(Omesal$_2$-en), was found to be air-sensitive and rapidly turned buff in chloroform. The dried complex slowly turned buff when exposed to air for about two hours. The green threadlike crystals obtained from chloroform, when dried in vacuo at room temperature analysed as VO(Omesal$_2$-en). $\frac{1}{2}CHCl_3$, presumably similar

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to Co(sal$_2$-en). $\frac{1}{2}$CHCl$_3$[2]. The chloroform was, however, lost when the crystals were dried in vacuo at 60°C for 8 hr. The brown crystals obtained from nitromethane analysed as VO(Omesal$_2$-en). $\frac{1}{2}$H$_2$O.O$_2$.

Using the above method for compounds (7–11) the reaction mixtures refluxed for up to 72 hr yielded less than 20% formation of the Schiff base complex. Consequently, compounds (7–11) were prepared by the method described previously[1].

All the complexes were dried in vacuo over CaCl$_2$/P$_2$O$_5$ and, where necessary, in a drying pistol at 60–100°C for 8 hr. These complexes are found to be relatively more soluble in organic solvents than their salicylaldimine analogues.

Elemental analyses for C, H, N and Cl were carried out by the Microanalytical Laboratory at the University of Leeds. Vanadium was estimated by converting the complexes to V$_2$O$_5$.

Physical measurements. The methods used for spectroscopic and magnetic measurements have been described elsewhere[1]. Molar masses of complexes soluble in chloroform were determined (using 5–15 mg of sample/1 cm^3 of CHCl$_3$) on the Hitachi Perkin-Elmer Molecular Weight Apparatus 115. VO(Omesal$_2$-Mepn) is monomeric whereas VO(Omesal$_2$-en) and VO(Omesal$_2$-pn) are probably associated with half a molecule of chloroform in the crystals.

The analytical data along with some physical properties of the complexes are presented in Table 1.

RESULTS AND DISCUSSION

The relevant IR band positions are tabulated in Table 2. The ν(C = N) in the complexes falls within the same range as in salicylaldimine analogues[1]. A band observed between 1550 and 1555 cm^{-1} which is at a slightly higher frequency than the corresponding band in the

Table 1. Analytical data of the oxovanadium(IV) complexes

Compound	Colour	M.P. (°C)	Yield (%)	% C Found (Calc.)	% H Found (Calc.)	% N Found (Calc.)	% V Found (Calc.)
VO(Omesal)$_2$.H$_2$O	green	145^c	74	49.55 (49.63)	4.30 (4.10)	-	13.00 (13.16)
VO(Omesal$_2$-en)	green	268.1	58	54.90 (54.97)	4.55 (4.61)	7.05 (7.12)	12.87 (12.95)
VO(Omesal$_2$-en).½CHCl$_3$ [a]	green	-	-	47.30 (49.05)	4.35 (4.12)	5.95 (6.18)	- -
VO(Omesal$_2$-en).½H$_2$O.O$_2$ [b]	brown	-	-	49.85 (49.82)	4.95 (4.41)	6.50 (6.45)	- -
VO(Omesal$_2$-pn)	green	243.0	62	56.25 (56.04)	4.95 (4.95)	6.70 (6.88)	12.32 (12.50)
VO(Omesal$_2$-Mepn)	green	225.5	60	57.55 (57.02)	5.10 (5.26)	6.55 (6.65)	11.90 (12.09)
VO(Omesal$_2$-tn)	yellow	299^c	94	55.80 (56.04)	4.85 (4.95)	6.75 (6.88)	11.97 (12.50)
VO(Omesal$_2$-tm)	grey-green	283^c	75	56.80 (57.02)	5.25 (5.26)	6.70 (6.65)	12.21 (12.09)
VO(Omesal$_2$-ptn)	grey-green	260^c	72	57.95 (57.94)	5.43 (5.56)	6.75 (6.43)	11.58 (11.70)
VO(Omesal$_2$-hxm)	grey-green	169^c	77	57.40 (58.81)	5.95 (5.83)	6.40 (6.23)	11.75 (11.33)
VO(Omesal$_2$-hpm)	grey-green	165^c	76	60.00 (59.62)	6.30 (6.09)	6.10 (6.04)	10.25 (10.99)
VO(Omesal$_2$-ocm)	grey-green	133^c	74	61.45 (60.36)	6.45 (6.33)	5.90 (5.87)	10.47 (10.67)
VO(Omesal$_2$-nnm)	grey-green	128^c	71	60.70 (61.08)	6.75 (6.56)	5.65 (5.70)	10.10 (10.36)
VO(Omesal$_2$-dcm)	grey-green	127^c	77	62.30 (61.77)	7.00 (6.78)	5.55 (5.54)	9.90 (10.08)

[a] %Cl 11.4 (11.7); [b] Brown crystals obtained from nitromethane; [c] Decompositon temperatures.

Table 2. Some relevant IR frequencies for the oxovanadium(IV) complexes–VO(Omesal$_2$-A)

A = -	en	pn	Mepn	tn	tm	ptn	hxm	hpm	ocm	nnm	dcm	Tentative assignments
	1620vs	1615vs	1610vs	1620vs	1620vs	1620vs	1620vs	1620vs	1618vs	1618vs	1618vs	ν(C=N)
1605vs												ν(C=O)
1547s	1550s	1550s	1550s	1548s	1555s	1555s	1553m	1555m	1552m	1552m	1552m	ν(C=C)
	1468m	1470m	1469m	1466m	1470m	1470m	1469m	1470m	1468m	1468m	1468m	-CH$_2$- deformation
	1439vs	1441s	1440s	1442m	1452m	1451m	1450m	1451m	1450m	1450m	1450w	
	1398m	1400m	1400m	1400m	1401m	1400m	1400m	1400m	1399m	1399m	1399w	ν(C-N)
1326s	1296vs	1298vs	1300vs	1314vs	1308vs	1308vs	1305vs	1307m	1306s	1305s	1305vs	ν(C-O)phenolic
1248s	1250s	1245m	1249m	1242s	1250s	1250s	1248s	1248s	1248s	1248s	1248s	δ(C-H)
1076s	1083vs	1081m	1081m	1077s	1084s	1081s	1082m	1082m	1080m	1081m	1081m	ν(C-O) methoxy
965vs	988s	982vs	985vs		987vs	979vs	981s	981s	980s	980s	980vs	ν(V=O)
				864vs								V-O-V
570m	570m	570m	573m	565m	584m	586m	587w	590w	589w	590w	590m	ν(V-O)
	460s	445s	486s	472m	462m	461m	466m		460m	464w	460m	ν(V-N)
	455m		455m	443m				440m				
399m	380m	378m	377m	396m	364m	370w	370w	360w	360w	365w	362m	ν(V-O)

vs = very strong, s = strong, m = medium, w = weak

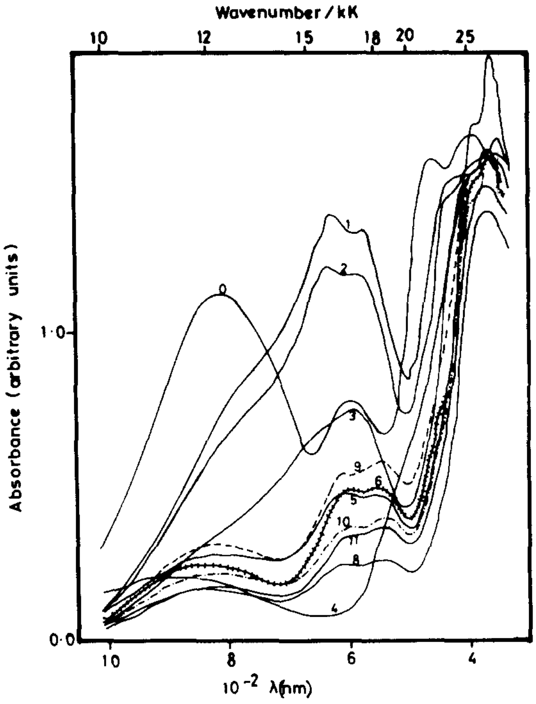

Fig. 1. Reflectance spectra.

salicylaldimine series is assigned to ν(C = C) aromatic. This increase is expected when an electron-releasing group is attached to an aromatic ring. The splitting of -CH$_2$- deformation modes between 1440 and 1470 cm^{-1} is likely due to interchain forces[3] in the polymethylene bridges. The ν(V = O) frequency of VO(Omesal)$_2$. H$_2$O is considerably lower compared to an unperturbed V=O[4] similar to the value (965 cm^{-1}) reported for VO(sal)$_2$.H$_2$O[5] and VO(acac)$_2$.py[6]. Moreover, the presence of a strong band at 3340 cm^{-1} suggests that the complex is likely to be six-coordinate. The trend in the ν(V – O) frequencies in the Schiff base complexes follows the order observed for the salicylaldimine series[1]; however, the ν(V – N) and ν(V – O) frequencies are higher indicating an increase in the in-plane σ-interaction and hence in covalency[7].

The diffuse reflectance spectra of VO(Omesal)$_2$.H$_2$O and the Schiff base complexes are given in Fig. 1 and the band positions are tabulated in Table 3. The most intense band at 12.27 kK and a medium intensity band at 17.00 kK observed for VO(Omesal)$_2$.H$_2$O have been assigned to $b_2(d_{xy}) \rightarrow e_\pi^*(d_{xz}, d_{yz})$ and $b_2(d_{xy}) \rightarrow b_1^*(d_{x^2-y^2})$ transitions[8]. The reflectance spectra of the Schiff base complexes are, however, different from that of VO(Omesal)$_2$.H$_2$O where the band at 15–17 kK is the most intense and the band at 11–13 kK reduces to either a shoulder (complexes 1–3) or a broad low-intensity band (complexes 4–11). Measurements in chloroform solutions retain this trend as borne out by maximum molar absorptivity of the band at 15–17 kK. It therefore seems that the e_π^* and the b_1^* levels have been inverted[4,9] in the Schiff base complexes. In the reflectance spectra, the band at 15–17 kK splits into two closely spaced maxima in complexes 1 and 2. This separation is interpreted as arising from the removal of the degeneracy of the e_π^* levels as a result of greater deviation from regular geometry[10]. The absence of this band in the spectra of VO(Omesal$_2$-tn) and VO(sal$_2$-tn)[1, 11] suggests that VO(Omesal$_2$-tn) is likely to be polymeric with V–O–V linkages having a distorted octahedral geometry[12]. The third band appears either as a weak shoulder at 19–20 kK or is enveloped under an intense charge-transfer band at 25–30 kK in VO(Omesal)$_2$.H$_2$O and complexes (1–4). However, this band appears well-defined at 18–19.5 kK in complexes (5–11).

The solution spectra, (Fig. 2) and the minor shifts in band maxima (Table 3) indicate some solvent dependence on going from a non-coordinating to a coordinating solvent. Like the salicylaldimine series, these Schiff base complexes from six-coordinate species in pydridine solution and consequently the orietation of the alkyl bridge is equatorial[13].

Considering the band maxima and molar absorptivities

Table 3. Electronic spectral data of the oxovanadium(IV) complexes

Compound	State	Band maxima in kK $(\varepsilon/m^2\ mol^{-1})$			
		$b_2 \to b_1^*$	$b_2 \to e_\pi^*$	$b_2 \to a_1^*$	C.T
VO(Omesal)$_2$·H$_2$O	R	17.04	12.27	21.83	25.64
	C	b	b	~20.20^a	
	P	b	b	b	
VO(Omesal$_2$-en)	R	13.33^a	15.87 17.39	20.41^a	24.39, 28.17
	C	10.98(10)	15.53(62)	-	- -
	P	c	16.63(20)	-	- -
VO(Omesal$_2$-pn)	R	13.25^a	15.75 17.09	21.50^a	23.26^a,27.40
	C		15.18(145)		
	P	13.34(9)	16.42(22)		
VO(Omesal$_2$-Mepn)	R	11.98^a	16.89		25.64, 27.03
	C	c	16.08(29)		
	P	13.18(8)	16.57(17)		
VO(Omesal$_2$-tn)	R	11.36	-	19.23^a	26.32, 28.57
	C		14.15(435)	22.6^a(267)	
	P	13.18(9)	-	18.63(12)	
VO(Omesal$_2$-tm)^c	R	12.42	16.53	18.18	25.64, 27.62
VO(Omesal$_2$-ptn)^c	R	11.83	16.81	18.28	25.97, 27.40
VO(Omesal$_2$-hxm)	R	11.93	16.70	18.50	27.40
VO(Omesal$_2$-hpm)	R	11.90	16.53	18.52	27.03
	C	c	~16.80		
	P	13.29(8)		19.37(8)	
VO(Omesal$_2$-ocm)	R	11.76	16.45	18.35	27.25
	C	c	~16.72		
	P	b	b	b	
VO(Omesal$_2$-nnm)	R	12.20	16.81	18.52	25.97, 27.25
	C	c	16.94(115)		
	P	14.0(6)		19.39(7)	
VO(Omesal$_2$-dcm)	R	12.17	16.47	18.62	27.03
	C		16.61(121)		
	P	b	b	b	

R = reflectance, C = chloroform solution,

P = pyridine solution, C.T = charge transfer

a = shoulder, b = a flat broad unresolved spectrum,

c = a broad tail, likely to contain a low-intensity band.

Table 4. Variation of magnetic moments ($\mu_{eff.}$* B.M.) with temperature

Compound / T(K)	0	1	2	3	4	5	6
320	1.77	1.72	1.76	1.72	1.83	1.73	1.74
300	1.77	1.72	1.75	1.72	1.82	1.73	1.74
280	1.76	1.72	1.75	1.71	1.82	1.72	1.73
260	1.76	1.72	1.75	1.71	1.82	1.72	1.73
240	1.75	1.72	1.75	1.71	1.82	1.72	1.73
220	1.75	1.72	1.75	1.71	1.81	1.72	1.73
200	1.75	1.71	1.74	1.70	1.81	1.71	1.73
180	1.74	1.71	1.74	1.70	1.80	1.71	1.72
160	1.73	1.71	1.74	1.69	1.80	1.70	1.71
140	1.73	1.71	1.73	1.68	1.79	1.69	1.71
120	1.71	1.70	1.72	1.67	1.79	1.69	1.70
100	1.70	1.69	1.71	1.67	1.77	1.67	1.69
85	1.68	1.68	1.70	1.64	1.76	1.65	1.68
θ	12	5	7	12	8	11	9
$-\chi_L \times 10^6$ ($cm^3 mol^{-1}$)	214	220	231	243	231	243	255

* Calculated from $\mu_{eff.}$ = 2.828 $(\chi_A.T)^{½}$ and the Curie-Weiss law $\chi_A^{-1} \propto (T+\theta)$.

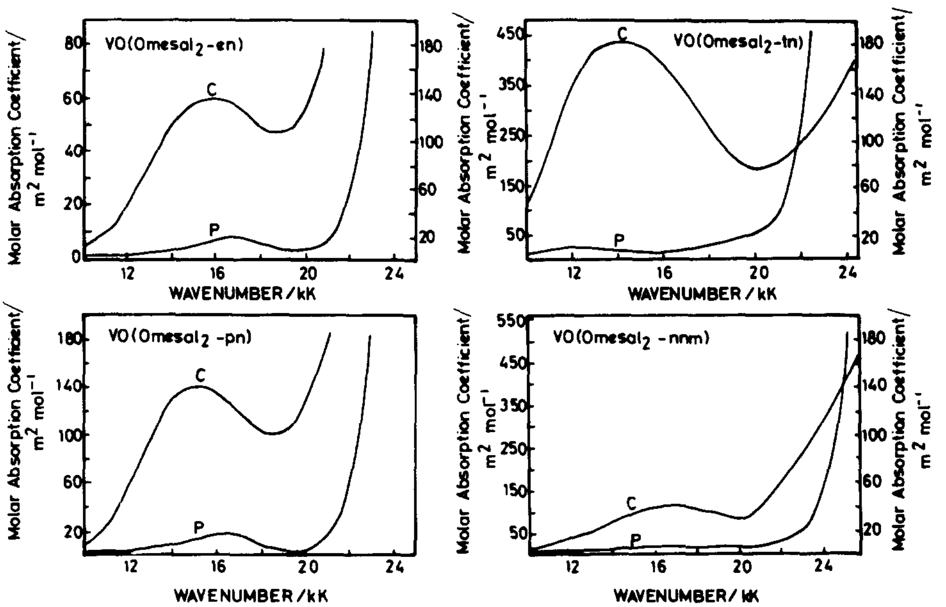

Fig. 2. Electronic spectra of VO(Omesal$_2$-en), VO(Omesal$_2$-pn), VO(Omesal$_2$-tn) and VO(Omesal$_2$-nnm) in chloroform (C) and pyridine (P).

the spectral data (Table 3) can be reasonably interpreted with the aid of the energy level diagrams presented in Fig. 3. The energies of the three *d–d* transitions are slightly lower in this series than in the salicylaldimine series[1] suggesting that the introduction of the methoxy group results in a reduction in the in-plane and axial ligand fields, which is consistent with increase in σ-interaction between V and the donor atoms[7].

The magnetic moments at 300 K (1.72–1.82 B.M.) are normal for a d^1-oxovanadium(IV) system and the complexes obey the Curie–Weiss Law (Table 4). However, the large θ values observed for VO(Omesal)$_2$.H$_2$O, VO(Omesal$_2$-Mepn) and VO(Omesal$_2$-tm) indicate some weak magnetic interaction.

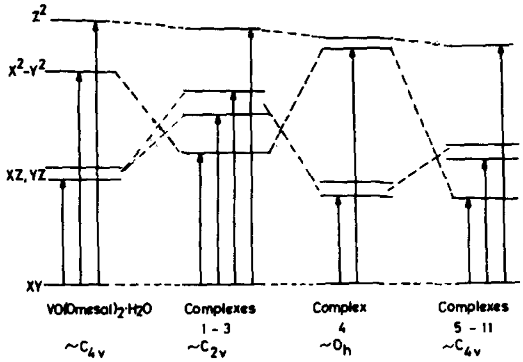

Fig. 3. Changes in the ordering of the *d* orbitals in oxovanadium (IV) complexes (not to the scale).

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