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MAGNETIC AND SPECTRAL PROPERTIES OF OXOVANADIUM(IV) COMPLEXES OF QUADRIDENTATE NAPHTHALDIMINE LIGANDS

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Oxovanadium(IV) complexes of 2-hydroxy-1-naphthaldehyde and the Schiff-base complexes [VO{OC₁₀H₈CH=N-CR¹R²-(CH₂)_{n-1}-N=CHC₁₀H₈O}] where n = 2 (R¹ = R² = H or CH₃) and n = 3-8 (R¹ = R² = H) along with the corresponding ligands have been synthesised and characterised by elemental analysis, i.r. and electronic spectral and magnetic susceptibility measurements. There is evidence that the conversion of the bis-napthaldehyde complex to the Schiff-base complexes is accompanied by an inversion of the e_{π}^* and b_1^* energy levels. Moreover, the introduction of a second phenyl ring results in a reduction of the in-plane ligand field. The v(V=O) frequencies suggest that the complexes are five-coordinate, except VO(naph₂-tn) which is likely to be six-coordinate and polymeric. Although the magnetic moments at room temperature for the complexes vary between 1.59 and 1.77 B.M. the variation of the moments with temperature is not appreciable.

INTRODUCTION

Although the magnetic and spectral properties of the oxovanadium(IV) Schiff-base complexes derived from salicylaldehyde and polymethylenediamines have very recently been reported,1 it appears from the literature that similar studies have not been made on the corresponding complexes of 2-hydroxy-1-naphthaldehyde. Moreover, there have been speculation about the possibility of the inversion of the ordering of the e_{π}^* and b_1^* energy levels² in such systems.¹ As the pK_a of 2-hydroxy-1-naphthaldehyde is lower than that of salicylaldehyde,³ one would expect that the oxovanadium(IV) complex of the naphthaldehyde would be more stable than that of salicylaldehyde⁴ and this provides an opportunity of following the stereochemical changes accompanying the conversion of the O₄ chromophore around V=O in the bis-aldehyde complex to O₂N₂ in the quadridentate Schiff-base complexes. Furthermore, it would be of interest to investigate the effect of the additional benzene ring on the stereochemistry of the oxovanadium(IV) Schiff-base complexes, I.



is given number 0.

EXPERIMENTAL

Preparation of ligands

The ligands were isolated by dropwise addition of

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Compound	Molecular formula	М.Р. (°С)	%C Found (Calc.)	%H Found (Calc.)	%N Found (Calc.)
H ₂ naph ₂ -en	$C_{24}H_{20}N_2O_2$	318ª	78.15	5.55	7.80
H ₂ naph ₂ -pn	$C_{25}H_{22}N_2O_2$	181.6	(78.24) 78.65 (78.51)	(5.47) 6.00 (5.80)	(7.60) 7.30 (7.32)
H ₂ naph ₂ -Mepn	$C_{26}H_{24}N_2O_2$	146.0	(78.51) 78.40 (78.76)	(5.80) 6.30 (6.10)	(7.32) 6.85 (7.07)
H ₂ naph ₂ -tn	$C_{25}H_{22}N_2O_2$	214.8	(78.70) 78.40 (78.51)	6.00	7.15
H2naph2-tm	$C_{26}H_{24}N_2O_2$	229.0	78.35	6.25	7.00
H2naph2-ptn	$C_{27}H_{26}N_2O_2$	157.7	79.00	(0.10) 6.40 (6.38)	7.50
H ₂ naph ₂ -hxm	$C_{28}H_{28}N_2O_2$	170.0	78.95	6.70	6.50
H ₂ naph ₂ -hpm	$C_{29}H_{30}N_2O_2$	141.3	(79.22) 79.20 (79.42)	6.70 (6.90)	6.40 (6.39)

TABLE I Analytical data for the Schiff-base ligands

^aDecomposition temperature.

0.05 mol of the aliphatic diamines (Aldrich) in 40 cm³ methanol to a warm 80 cm³ methanolic solution of 0.1 mol of 2-hydroxy-1-naphthaldehyde while stirring. The reaction mixture was refluxed for 15 min. and yellow crystals of Schiff-bases separated while cooling except those of octamethylene diamine and methyl-propylene derivatives. H₂naph₂-ocm formed an oily product while H₂naph₂-Mepn was precipitated by the addition of petroleum ether. The products were recrystallised from methanol. The analytical data for the ligands are given in Table I. They were found to be relatively less soluble in organic solvents and possess higher melting points compared with those of the corresponding salicylaldimine and 3-methoxysalicyl-aldimine Schiff-bases.⁵

Preparation of bis(naphthaldehyde)oxovanadium(IV) monohydrate

34.4 g (0.2 mol) of 2-hydroxy-1-naphthaldehyde was added in bits to a solution of 20.0 g (0.1 mol) of VOSO₄·2H₂O dissolved in 800 cm³ of 60% ethanol while stirring. The pH of the resultant mixture was adjusted to 6 by addition of an aqueous solution of sodium acetate whereby the complex was precipitated. The product was filtered, washed with 40% ethanol and digested thrice with 60% ethanol. It was finally washed twice with absolute ethanol and dried in vacuo over $CaCl_2-P_2O_5$, and finally at 100° in a drying pistol over P_2O_5 for 8 h.

Preparation of N, N'-bis(naphthalidene)(polymethylenediiminato)oxovanadium(IV) complexes

Complexes (1)–(5), and (7) were obtained by refluxing a suspension of VO(naph)₂·H₂O in ethanol with ethanolic solutions of the appropriate amines in mole ratio 2 : 1. Complexes (6), (8), and (9) were isolated by the reaction of equimolar (6 mmol) methanolic solutions of VOSO₄·2H₂O with preformed Schiff-bases buffered with triethylamine (14 mmol).¹ All the reactions required refluxing for 1 h except complexes (5) and (7) which required 2 h and 18 h respectively.

Physical measurements

Elemental analysis was performed by the Microanalytical Laboratories of the Universities of Ibadan and Leeds. Vanadium was estimated as vanadium(V) oxide. Melting points were determined using the Reichert Austria Instrument equipped with a digital thermometer. The analytical results along with colours, melting points and yields are presented in Table II. The i.r. spectra were recorded on a Perkin-Elmer 457 Grating Infrared spectrophotometer in the range 250–4000 cm⁻¹, using pressed KBr discs, and a Grubb-Parsons DM4 spectrophotometer equipped with a CsI prism was also used for recording the spectra in Nujol mulls in the range 200–500 cm⁻¹. The frequencies are believed to be accurate within ± 2 cm⁻¹. The diffuse-reflectance electronic spectra were

		tical results	of the oxe		ompiexes		
Compound	Colour	М.Р. (°С)	Yield (%)	%C Found (Calc.)	%H Found (Calc.)	%N Found (Calc.)	%V Found (Calc.)
VO(naph) ₂ ·H ₂ O	green	226 ^a	90	62.35	3.80		11.81
				(61.84)	(3.77)		(11.92)
VO(naph ₂ -en)	light-green	310 ^a	70	66.65	4.25	6.70	11.50
				(66.52)	(4.19)	(6.46)	(11.75)
VO(naph ₂ -pn)	light-green	270 ^a	70	67.35	4.75	6.30	11.26
				(67.12)	(4.51)	(6.26)	(11.39)
VO(naph ₂ -Mepn)	green	278.8	66	67.60	4.95	6.25	10.90
	U			(67.68)	(4.81)	(6.07)	(11.02)
VO(naph ₂ -tn)	orange-vellow	292.0	95	66.95	4 .60	6.25	<u>`11.39</u> ´
	0,			(67.12)	(4.51)	(6.26)	(11.39)
VO(naph ₂ -tm)	light-green	246 ^a	80	`67.00 ´	` 5.00 [´]	6.25	`10.66 ´
· · · · · · · · · · · · · · · · · · ·	8 8			(67.68)	(4.81)	(6.07)	(11.02)
VO(naph ₂ -ptn)·H ₂ O	light-green	224 ^a	82	65.50	5.15	5.45	10.52
- (- <u>-</u> <u>-</u> <u>-</u> <u>-</u> <u>-</u> <u>-</u> <u>-</u> <u>-</u> <u>-</u> <u></u>	0 0			(65.72)	(5.31)	(5.68)	(10.32)
VO(naphhxm)	light-green	247 ^a	82	68.55	5.60	5.70	10.25
· · · · · · · · · · · · · · · · · · ·		- · ·		(68.71)	(5.35)	(5.72)	(10.41)
VO(naph ₂ -hpm)	light-green	210 ^a	83	69.80	5.75	5.60	10.35
				(69.18)	(5.61)	(5.56)	(10.12)
VO(naph_ocm)·H ₂ O	grevish-green	162 ^a	80	67.95	5.90	5.80	9.41)
	6-0,100 groon	100		(67.28)	(6.02)	(5.23)	(9.51)

TABLE II Analytical results of the oxovanadium(IV) complexes

^aDecomposition temperatures.

measured in the range 335–1000 nm on an SP 500 spectrophotometer using LiF as a reference, while the solution electronic spectra in chloroform and pyridine $(10^{-3}-10^{-4} \text{ mol dm}^{-3})$ were recorded on an Applied Physics Cary 14H spectrophotometer. The magnetic susceptibility measurements were carried out by the Gouy method over the temperature range 84–320K using a Newport Instruments Gouy balance. The samples were packed into flat-bottomed silica tubes and were sealed via graded seals under vacuum. The samples were free from ferromagnetic impurities and the diamagnetic corrections were calculated from tables of Pascal's constants.

RESULTS AND DISCUSSION

The relevant i.r. band positions are given in Table III. The ν (C=O) mode shifts from 1645 cm⁻¹ in the 2hydroxy-1-naphthaldehyde to 1596 cm⁻¹ in VO(naph₂· H₂O, indicating that the carbonyl oxygen is involved in bonding to V. The band in the range 1620–1638 cm⁻¹ in the Schiff-base ligands which shifts to 1600–1620 cm⁻¹ in the complexes is assigned to ν (C=N). This observation suggests the weakening of the C=N bond due to coordination of the azomethine N to V. The splitting of this band suggests that the two azomethine groups may be more distorted below and above the horizontal plane than in the salicylaldimine analogues.¹ The v(C=C) stretching frequency (1538–1548 cm⁻¹) is not significantly changed from the ligands (1540 cm⁻¹). However, the position of this band is lower than in the corresponding bands in the salicylaldimines.¹ The $-CH_2$ — deformation modes are expected at 1450–1503 cm⁻¹ but it seems there is a considerable coupling with C—C modes.⁶ On the basis of previous assignments^{1,6–8} the band at 1301 cm⁻¹ in the complexes has been assigned to v(C-O).

The v(V=O) mode in VO(sal)₂·H₂O⁴ which is at 965 cm⁻¹ is found to be normal⁹ (980 cm⁻¹) in VO(naph)₂·H₂O suggesting that the water is present as lattice water¹⁰ and the complex itself is five-coordinate. In the Schiff-base complexes v(V=O) vibrations are sharp and normal (975–980 cm⁻¹) except for complex (4) (R¹ = R² = H; n = 3), where a band at 860 cm⁻¹ is diagnostic for V—O—V polymerisation.^{11,12} The bands at 560–580 cm⁻¹ and 420–460 cm⁻¹, absent in VO(naph)₂·H₂O, are assigned to v(V-N) while the bands at 480–530 cm⁻¹ and 290–340 cm⁻¹ are assigned to (V—O) in both VO(naph)₂·H₂O and the Schiff-base complexes.

The electronic spectral band position along with molar absorptivities (where solution measurements were taken) and the diffuse-reflectance spectra of the complexes are given in Table IV and Fig. 1 respectively. The most intense band in VO(naph)₂·H₂O observed at 741 nm is assigned to $b_2(d_{xy}) \rightarrow e_{\pi}^*(d_{xy}, d_{yz})$.² Two relatively weak bands are also observed at 667–625 nm

					~~~~ L		· - · · · · · · · · · · · · · · · · · ·	1		
(0)	(1)	(2)	(3)	(4)	(5)	(9)	(1)	(8)	(6)	Tentative assignment
	1614 1600 vs (1638 vs)	1614 1600 (vs (1625vs)	1618 1602 ^{vs} (1620vs)	1615vs (1632vs)	1618 1601 (vs (1632vs)	$1620\ 1607\vspace{-1}{1607}vs$	1620 1605 ⁰ vs (1628vs)	$1616 \\ 1603 \\ v_{s} \\ (1634 v_{s})$	1616 1603 vs	v(C=N)
1596m 1534s	1538s	1540s	1540s	(1540s	1542s	1548s	1546s	1542s	1543s	v(C=0) v(C=C)
	(1240s) 1503m (1490m)	(1241m) 1505m (1490w)	(1540m) 1510m (1490w)	(1240m) 1500m (1488w)	(1505m) (1488w)	(m0401) 1501w (1490w)	(1509m) 1509m (1490w)	(1245m) 1505m (1490w)	1505m	-CH2-deformation
1452s	1450m (1447m)	(1440w)	(1440w)	(1442w)	(1453m (1438w)	1456m (1437w)	1456m (1445w)	(1453m (1445m)	1454m }	$\nu$ (CC) +CH ₂ - deformation
1422s 1407vs	1438m 1408m (1402m)	1428m 1410m (1400m)	1434m 1416w (1395w)	1430m 1410m (1399w)	1429m 1412m (1400w)	1432m 1416m (1398w)	1432m 1416m (1400w)	1430m 1414m (1400m)	1430m) 1412m	
1365sh	1389ш 1355ш (1350s)	1390m 1357m (1350m)	1393m 1359m (1350s)	1396sh 1360m (1360m)	1393w 1356m (1353m)	1391w 1360m (1350m)	1394vw 1360m (1360m)	1391w 1356m (1364m)	1357m 1357m	v(C-N)
1305m 1250m	1298s (1310w) 1247m	1300s (1314vw) 1248m	1301m (1320sh) 1250m	1302s (1310w) 1245m	1300s (1305m) 1249m	1303m (1305w) 1250m	1302s (1316w) 1250m	1301s (1311m) 1251m	1300s 1250m	<i>ь</i> (С−О) δ(С−Н)
1190s	(1256m) 1187m (1180m)	(1252w) 1190s (1182m)	(1250w) 1186s (1184w)	1187s (1180w)	(1254w) 1185m (1191m)	(1255w) 1189m (1178m)	(1250vw) 1188m (1179m)	(1258m) 1190m (1184m)	1188m	
980vs	989 982 vs	986vs	984vs	987 965 860vs	985vs	987s	987s	981s	983s	v_0-0-V
524m 479m	573s 528m 460w	571vs 522m 460m	579s 520m 462w	575m 533m 462m	560sh 520s	550w 524m 468s	552w 523m	260w 522m	522m )	(V-N) (V-V) (V-V)
410s	(455m) 420w 411w 390w	(448w) 420m 388w	(460w) 423m	420m 400m	420m	417m 400	421w	(440m) 422w 404w	420w 403w	+ $\nu$ (V-O) + Ligand vibrations
/	356m	350m	364m	364m			398m 351w		348w	
339 (w 325 ^{(w}	334m 308w	330w 310w	329vw	337w 320m			346 326w			
299w	301w 277w	275w	291w 276w	291m 273w						
a vs $\approx$ v _i b Corres	ery strong, s : ponding ligar	<pre>= strong, m = nd frequencies</pre>	<pre>: medium, w = s in parenthes</pre>	= weak. es.						

TABLE III Some relevant infrared frequencies^{a,b} for the oxovanadium(IV) complexes

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					Band IV	Band V
Compound	Medium ^a	Band I $b_2 \rightarrow b_1^*$	Band II $b_2 \rightarrow e_{\pi}^*$	Band III $b_2 \rightarrow a_1^*$	Charge	Transfer
(0)	R	610	740	510	395	350
	C ^b		630			
	Р	761(10)	557(23)			
(1)	R	800sh	630		385	
			595			
	С		639(116)			
	Р	762(23)	606(40)			
(2)	R	800sh	620		405	365
			600?			
	С		652(190)	478(157)		
	P	758(10)	621(20)			
(3)	R	800sh	645		405	362
			600sh			
	C		645(81)			
	Р		615(17)	511(9)		
(4)	R	890br		540sh	400	370
	C		795(161)		417(237)	
	Pc		558	494		
(5)	R	800	625	505	382	
(6)	R	806br	617	533	380	
(7)	R	815br	615	570	400	375
(8)	R	825	615	550	380	365
(9)	С		670(35)	525(61)		

TABLE IV
Electronic spectral data of oxovanadium(IV) complexes. Band maxima/nm $(\epsilon/m^2 \text{ mol}^{-1})$

 ${}^{a}R = reflectance; C = chloroform; P = pyridine.$ 

^bUnresolved spectrum sh = shoulder; br = broad.

 $^{\circ}0.98 \times 10^{-3}$  mol dm⁻³ solution gave one band at 494 nm;  $0.17 \times 10^{-3}$  mol dm⁻³ solution gave an additional band at 558 nm.

along with a shoulder at 526-500 nm. The bands at 610 nm and 510 nm are assigned to  $b_2(d_{xx}) \rightarrow$  $b_1^*(d_{x^2-v^2})$  and  $b_2(d_{xv}) \rightarrow a_1^*(d_z^2)$  respectively. The observation of four likely d-d transitions may suggest a distortion of the square-pyramidal geometry around V in support of the i.r. results. The reflectance spectra of the Schiff-base complexes are, however, different from that of  $VO(naph)_2 \cdot H_2O$  where the most intense band shifts to 667-588 nm and the band at 770 cm⁻¹ reduces to either a shoulder [complexes (1)-(3)] or a broad low-intensity band [complexes (4)-(9)] at 910-770 nm. Similar trends are observed in cases where measurements were taken in chloroform solutions. These results support our earlier speculation¹ about the possibility of an inversion^{9,13} of the  $e_{\pi}^*$  and b₁* energy-levels in the quadridentate Schiff-base complexes. The weak splitting of Band II (667-588 nm) in the reflectance-spectra of complexes (1)-(3), and (5)-(9) is interpreted as arising from the removal of the degeneracy of the  $e_{\pi}^*$  levels⁹ as a result of lowering of symmetry of the complexes by the introduction of the alkyl bridge. The absence of this band in the spectra of (4), similar to VO(sal₂-tn),^{1,11,12} suggests that (4) is also

likely to be polymeric, with a distorted octahedral geometry.¹¹

Although the electronic spectra of the Schiff-base complexes are similar to those observed for corresponding complexes of the salicylaldimine series,¹ the energies of Bands I, II, and III tend to be lower in the present series. The lowering of the energies of the d-d transitions appears to be due to the introduction of the benzene ring into the salicylaldehyde and this observation is consistent with the effect of phenyl substitution observed in the  $\beta$ -ketimine complexes.¹⁴

The magnetic data for seven of the complexes are tabulated in Table V. The room temperature magnetic moments are 'normal'¹⁵ for VO(naph)₂·H₂O and complexes (1)-(3), and (7), higher for (4), and lower for (5). However, the variation of the moments with temperature is not appreciable and the compounds follow the Curie-Weisslaw giving small  $\theta$ -values. A  $\theta$ -value of -4K obtained for (4) indicates some very weak ferromagnetic interaction, similar to that reported for VO(sal₂-tn).^{16,17}

The magnetic moment at room temperature for (5) (1.59 B.M.) is very close to that reported for  $(VO)_2$ 



FIGURE 1 Reflectance spectra of the naphthaldimine complexes.

 $(triketone)_2$ ¹⁸ however, in the absence of anticipated direct V—V coupling the origin of the subnormal moment is unknown.

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Compound 7 0 2 3 4 5 **T(K)** 1 1.725 1.725 1.715 1.77 1.60 1.73 320.0 1.72 1.76 1.59 1.74 1.72 1.72 1.71 1.71 300.0 1.59 280.0 1.725 1.72 1.71 1.71 1.75 1.74 1.70 1.755 1.59 1.74 260.0 1.72 1.715 1.71 240.0 1.70 1.76 1.58 1.73 1.72 1.71 1.69 1.69 220.0 1.71 1.71 1.70 1.76 1.58 1.745 200.0 1.71 1.70 1.69 1.69 1.75 1.58 1.74 1.685 1.58 1.71 180.01.70 1.69 1.76 1.711.68 1.68 1.76 1.58 1.70 160.0 1.70 1.69 1.685 1.68 1.57 1.70 1.70 1.76 140.0 1.67 1.56 1.69 120.0 1.69 1.68 1.66 1.68 1.77 1.67 100.0 1.67 1.67 1.65 1.67 1.77 1.56 1.55 1.77 1.6784.0 1.685 1.67 1.65 1.65 9 -4 8 14  $\theta/K$ 7 10 13  $-\chi_L \times 10^6$  $(cm^3 mol^{-1})$ 257 268 292 238 245 257 268

TABLE V Variation of magnetic moments ( $\mu_{eff}^{a}/B.M.$ ) with temperature

^aThe moments are calculated from the expression  $\mu_e = 2.828(X_A \cdot T)^{1/2}$  and the Curie-Weiss law  $\chi_A^{-1} \propto (C + \theta)$ . X_A = Molar magnetic susceptibility, C = Curie constant, 1 B.M. =  $0.927 \times 10^{-23}$  Am².

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