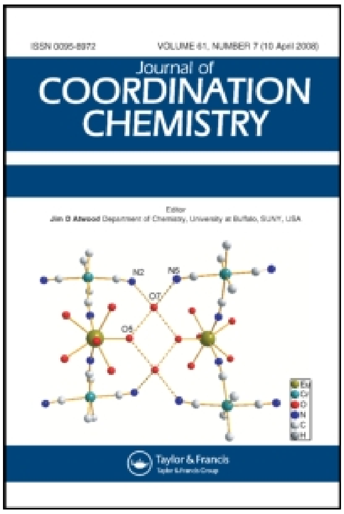

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THE STEREOCHEMISTRY AND MASS SPECTRA OF OXOVANADIUM(IV) COMPLEXES OF *N,N'*-BIS(3-ETHOXYSALICYLIDENE) TRIMETHYLENEDIIMINE AND *N,N'*-BIS(7-METHYLSALICYIDENE)TRIMETHYLENEDIIMINE

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THE STEREOCHEMISTRY AND MASS SPECTRA OF OXOVANADIUM(IV) COMPLEXES OF *N,N'*-BIS(3-ETHOXYSALICYLIDENE) TRIMETHYLENEDIIMINE AND *N,N'*-BIS(7-METHYLSALICYIDENE)TRIMETHYLENEDIIMINE

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Oxovanadium(IV) complexes, $VO[A\text{-}C_6H_4ORC{=}N\text{-}(CH_2)_3\text{-}N{=}CROH_4C_6\text{-}A]$, (where A = $3\text{-}OC_2H_5$, R=H and A=H, R=$7\text{-}CH_3$) have been prepared and characterised. The studies showed that the complexes are polymeric in the solid state and exhibit distorted octahedral geometry, but break down to five-coordinate monomers in chloroform and in the gas phase.

Keywords: Vanadium, Schiff-base, polymers, structure, mass-spectra

INTRODUCTION

Although the majority of complexes of oxovanadium(IV) are blue or bluish green[1,2] previous reports[3-5] on some tetradentate oxovanadium(IV) complexes involving salicylaldehyde or substituted salicylaldehydes and trimethylene diamines showed that some complexes are orange-yellow, polymeric and exhibit distorted octahedral geometry. The unusual colour that has been reported[6] for some bidentate Schiff-base complexes of oxovanadium(IV) was associated with the effect of electron-withdrawing groups in the aromatic rings and the metal geometry was found to be that of a distorted trigonal bipyramid. However, our recent studies[5,7,8] on oxovanadium(IV) schiff-base complexes with N_2O_2 chromophores showed that the substituent in the aromatic ring (for the trimethylene derivatives) does not alter the stereochemistry of the complexes.

It seemed therefore desirable to extend this study to salicylaldiimines in which electron-releasing substituents are placed on the aromatic ring VO(OEtsal$_2$-tn), (1), and on the azomethine carbon VO(7-Mesal$_2$-tn), (2) for the trimethylene derivatives. It was anticipated that the 7-methyl substituent might inhibit planarity and thus alter the general stereochemical pattern observed so far for this class of ligands. Furthermore, while the ethoxy group in (1) enriches the ring, the 7-methyl group in (2) enriches the azomethine fragment which should therefore not only enhance the in-plane σ-interactions but also should have some effect on the fragmentation pattern of complex (2). Moreover, the mass spectra of Schiff-base complexes of oxovanadium(IV) have received little attention.[9]

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EXPERIMENTAL

Preparation of Complexes

VO(OEtsal$_2$-tn). The isolation of the preformed ligand was not successful. A hot methanolic solution of ethoxysalicyaldelyde (6 mmol) and trimethylenediamine (3 mmol) was added to a hot methanolic solution of $VOSO_4 \cdot 2H_2O$ (3 mmol) and buffered with excess triethylamine (14 mmol). The mixture was refluxed for 40 min. The yellow product obtained after cooling was filtered and washed copiously with methanol. It was then digested thrice with methanol and dried over P_2O_5. Yield: 71%, Decomposition temperature: 290°. Analysis: C, 57.70; H, 5.65; N, 6.15; V, 11.90%; Expected for $C_{21}H_{24}N_2O_5V$: C, 57.90; H, 5.56; N, 6.43; V, 11.70%.

VO(7-Mesal$_2$-tn). This was prepared according to the method of Farmer and Urbach.[10] Yield: 20%. Decomposition temperature: 237°. Analysis: C, 60.20; H, 5.45; N, 7.40; V, 13.52%; Expected for $C_{19}H_{20}N_2O_3V$: C, 60.80; H, 5.37; N, 7.49; V, 13.57%.

Physical Measurements

The methods used for i.r. and electronic spectral measurements have been described elsewhere.[5] The room temperature magnetic susceptibility measurements were carried out by the Gouy method, using $Hg[Co(NCS)_4]$ as calibrant. The mass spectra were recorded with an AEI MS 902 double focussion spectrometer at 10eV and 70eV, employing direct sample introduction techniques at 90–200°. The spectrometer was coupled to a Carrick computer interface.

RESULTS AND DISCUSSION

Infra-red Spectra

The relevant i.r. frequencies and their tentative assignments are presented in Table I. The ν(C=N) for complex (1) falls within the range reported[3–5,7,9] for similar complexes with auxochromes in the salicylaldehyde ring. However, ν(C=N) in complex (2) is found to be low both in the ligand (1610 cm^{-1}) and in the complex (1599 cm^{-1}). It reveals that a significant distortion in the C=N bond in (2) could hinder effective lateral overlap between C-pπ and N-pπ orbitals. The significantly low value in H_2-7-Mesal$_2$tn could have arisen from increased electron density on the azomethine nitrogen atom which would strengthen H-bonding between it and the phenolic hydroxy group.

The ν(*V*=O) frequencies in both complexes are consistent with polymeric systems involving V=O... V=O bridges. The relatively low value observed for (2) is in agreement with Farmer and Urbach.[9] It seems that the increased electron density relayed from the 7-methyl group to V (*via* azomethine N) either reduces the V-O electrostatic interaction or reduces the pπ-dπ overlap in O=V. Despite the low ν(*V*=O) frequency, which signifies a stronger V=O... V=O linkage, complex (2) is rather unstable (decomposing readily in chloroform solution and having a relatively low decomposition temperature).

Electronic Spectra

The spectral data are presented in Table II. The diffuse reflectance spectra exhibit a single broad band at ~11.0kK with an additional shoulder at ~20.0kK similar to the spectra reported[3–5,8,9] for six-coordinate and polymeric distorted octahedral VO^{2+} complexes and they are assigned to $b_2 \rightarrow e_\pi^*$ and $b_2 \rightarrow a_1^*$ transitions[7,11] respectively. The

TABLE I
Relevant i.r. spectral data for the complexes

VO(OEtsal$_2$-tn)	VO(7-Mesal$_2$-tn)[a]	Tentative assignment
1626 vs	1599 vs	ν(C=N)
	(1610 vs)	
1600 sh	1587 sh	
	(1570 sh)	
1551 vs	1538 vs	ν(C=C)
	(1499 m)	
1468 m 1447 m } vs	1468 w .1439 s } vs	ν(C-C) + -CH$_2$-deformation
	(1445 m)	
1400 m		C-O (ethoxy)
1315 m	1340 m 1335 w } vs	C-O (phenolic)
	(1306 m)	
1244 ms 1227 wm } vs	1240 m (1230 m)	δ(C-H)
862 vs	854 vs	V-O-V
530 w 450 m, br	546 w, br 437 m, br	ν(V-N)
349 w, br 319 w, br 287 w 273 w	357 w 342 m 330 m 290 w 234 w	ν(V-O) + M-L vibrations

[a]Frequencies due to the free ligand in parentheses; vs = very strong, s = strong, m = medium, ms = medium strong, w = weak, wm = weak medium, br = broad, sh = shoulder

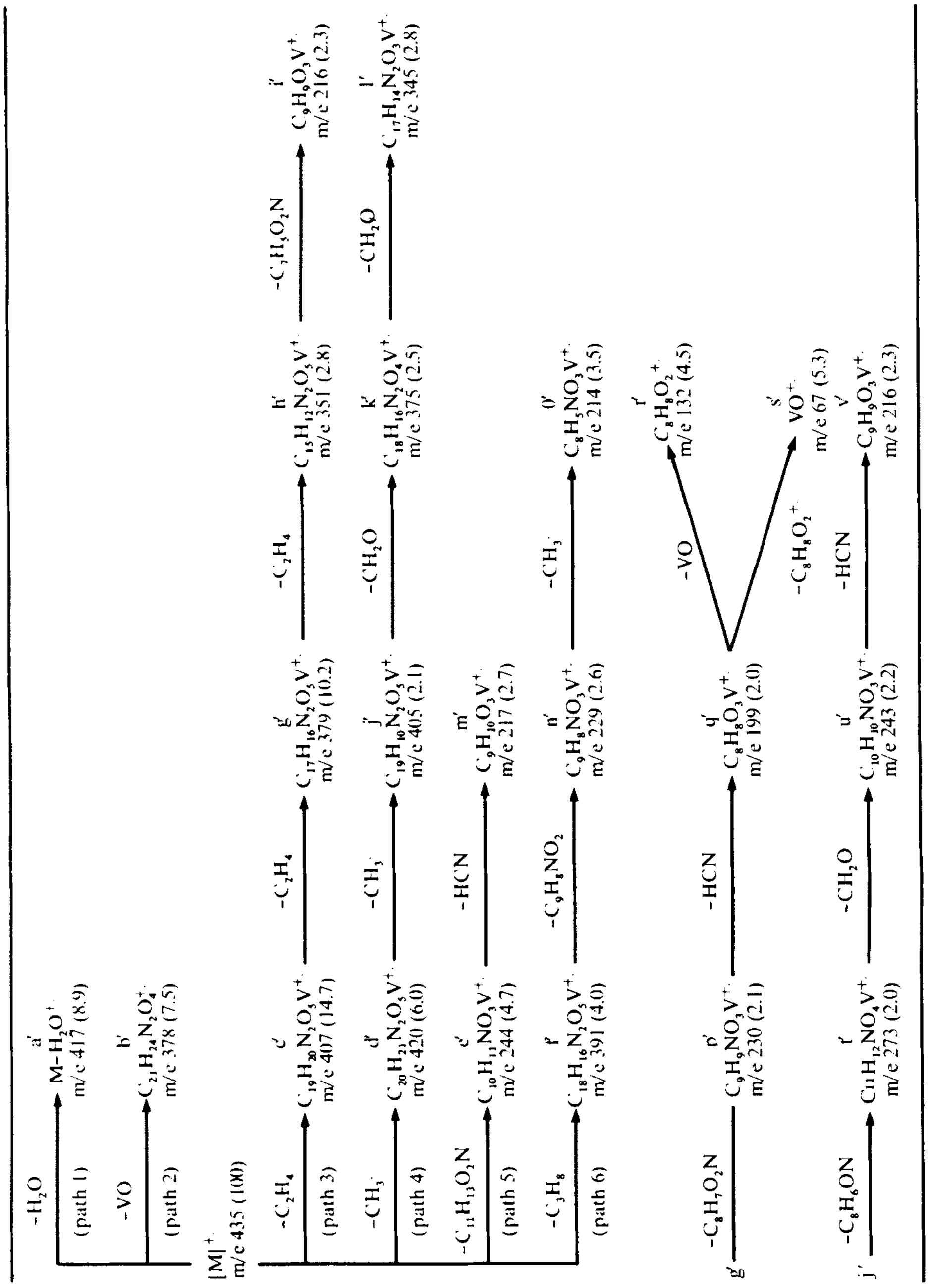
TABLE II
Electronic spectral data for the complexes.

		Band maxima/kK (ε/m^2 mol*)				
Compound	Medium	$b_2 \rightarrow e_\pi^*$	$b_2 \rightarrow b_1^*$	$b_2 \rightarrow a_1^*$	Charge Transfer	
VO(OEtsal$_2$-tn)	Solid	11.11		19.80[a]	26.67[a]	28.17
	CHCl$_3$		14.54(240)			
	pyridine	insoluble				
VO(7-Mesal$_2$-tn)	solid	11.36		20.62		28.17
	CHCl$_3$		14.34(195)	20.0(208)		
	pyridine	a flat spectrum		20.80[a](23)		

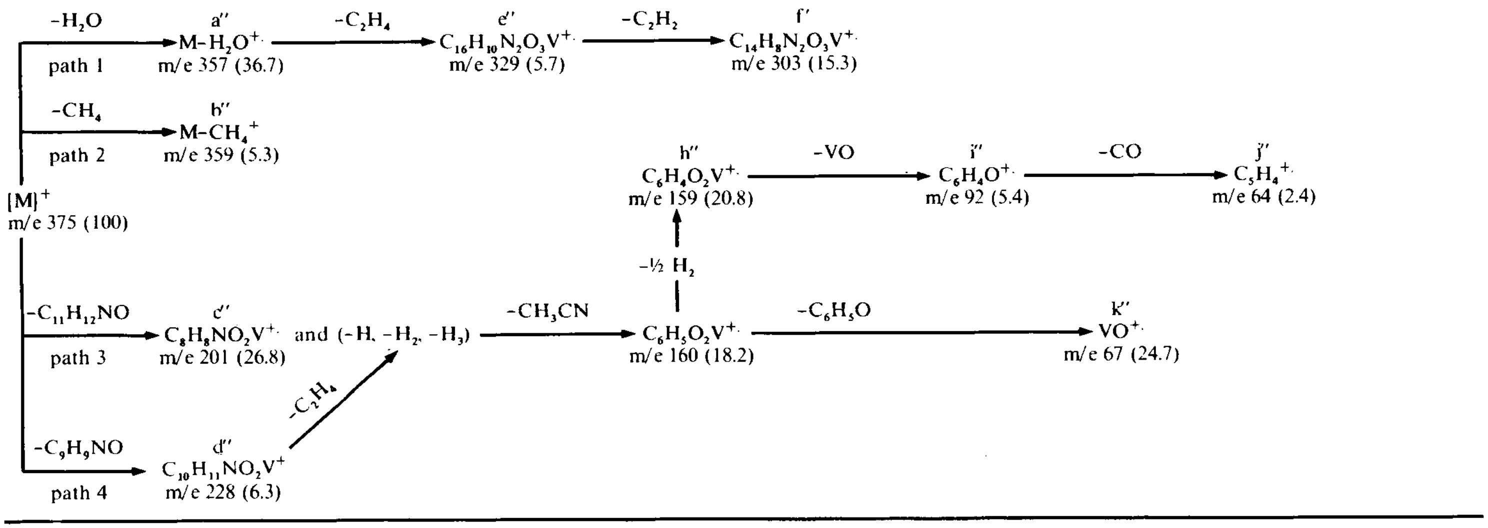
[a]Shoulder.

spectrum of (2) in pyridine, in which (1) is insoluble, is similar to the reflectance spectrum except that a very broad band covering 10–18kK replaces the low-energy band. Both complexes exhibit a band at 14–15kK in chloroform and this band is assigned to the $b_2 \rightarrow b_1^*$ transition. This very low frequency for the $b_2 \rightarrow b_1^*$ transition suggests a considerable reduction in the energy of the $b_1^*(d_{x^2-y^2})$ level such that in the solid it is close to the $e_\pi^*(d_{xy}, d_{yz})$ degenerate orbitals. However, in chloroform solution the complexes are five-coordinate (blue) and deviate from octahedral geometry such that the b_1^* level is raised but not to the extent which it assumes in a perfect square-pyramid. The higher extinction coefficients of the energies ($b_2 \rightarrow b_1^*$) indicate a significant increase in either covalency or $p\pi$-$d\pi$ O=V interaction on going from octahedral geometry to tetragonal geometry. The remaining higher energy bands in the

SCHEME I
Proposed fragmentation pattern of $VO(OEtsal_2\text{-}tn)$.



SCHEME II
Proposed fragmentation pattern of VO(7-Mesal$_2$-tn)



reflectance spectra are assigned to change-transfer bands. The room temperature magnetic moments for (1), 1.79 B.M. and (2), 1.80 B.M. are normal for the d^1-VO^{2+} system[12] and fall within the range reported for similar complexes.[4,5,7–9]

Mass Spectra

The mass spectra of the complexes (1) and (2) are summarized with the proposed fragmentation patterns for the major peaks in Schemes I and II. Although the complexes are polymeric, the parent ion afforded $M^{+\cdot}$ as a base peak and no higher masses were detected. The loss of water (path 1) was found in the spectra as reported previously[10] and M-H_2O occurs as a doubly changed ion.

In Scheme I, besides the above fragment, additional major fragments are derived from the molecular ion by exclusion of vanadium(II) oxide (path 2), loss of ethene (path 3), loss of a methyl radical (path 4), cleavage of C-C, C-V and N-V bonds (path 5) and loss of propane (path 6). Parent ions obtained from these paths undergo further framentation, as illustrated for ions g′ and j′.

In Scheme II, the fragmentation is less complex; the molecular ion has the possibility as in Scheme I of losing water (path 1), methane (path 2) and undergoing a C-C, O-V and N-V bond cleavage (path 3) but no loss of vanadium(II) oxide from M^+ was observed. Besides the above fragmentation pattern the molecular ion could suffer N-C, O-V and N-V bond cleavage (path 4), probably resulting in a cluster.

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