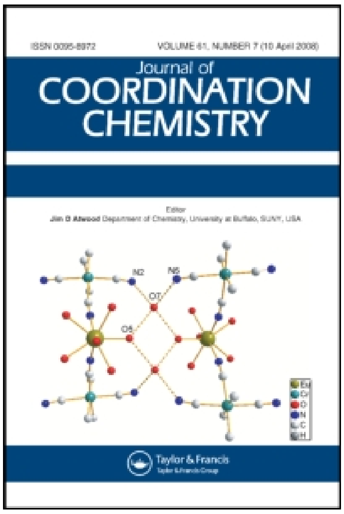

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THE MASS SPECTRA AND THE STEREOCHEMISTRY OF N,N′-BIS-(SALICYLIDENE)-1,1-(DIMETHYL)-ETHYLENEDIAMINO-OXOVANADIUM(IV)

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The oxovanadium(IV) complex of the ligand, N,N′-bis-(salicylidene)-1,1-(dimethyl)ethylenediamine, has been prepared. It has a magnetic moment of 1.76 B.M., which is almost invariant over a range of temperature. The electron paramagnetic resonance spectrum of the powder has been measured at 296° and 80°K, while that of the solution was measured at 296°K ($g_0 \approx 1.97$ and $A_0 \approx 90 \times 10^{-4}\,\mathrm{cm}^{-1}$). The magnetic moment of the complex agrees with that calculated from the paramagnetic resonance g values taken at 80°K. Furthermore, the complex has been characterized by mass spectra, infra-red, ultra-violet and visible spectra, conductivity, osmometry and polarimetry.

All evidence suggests that the complex is a tetragonal-pyramid.

INTRODUCTION

In previous papers we reported the stereochemical[1] and mass spectral studies[2] of the divalent metal complexes of the tetradentate salicylaldimine, N,N′-bis(salicylidene)-1,1-(dimethyl)-ethylenediamine. We have now extended these studies to the oxovanadium(IV) ion in which the geometry is different and which is asymmetric.

The oxovanadium(IV) salicylaldimine complexes with the formula $[\mathrm{OC_6H_4CH = NCH_2CR_1R_2N = CHC_6H_4O}]\mathrm{VO}$, ($R_1 = R_2 = H$; $R_1 = H$ and $R_2 = CH_3$) are green and assume nearly square-pyramid geometry, and their visible and electronic spin resonance spectra have been reported.[3] A similar complex with three methylene groups in the chain is orange and its x-ray structure showed that it is polymeric.[4] We have prepared[5] the complex $[\mathrm{OC_6H_4CH{=}NCH_2\ C(CH_3)_2N{=}CHC_6H_4O)VO}$, abbreviated as VO(sal$_2$-i-bn) and have deduced its stereochemistry by studying magnetic properties, mass spectra, electron paramagnetic resonance, infrared, ultraviolet and visible spectra, conductivity, osmometry and polarimetry.

EXPERIMENTAL

Preparation of N,N′-bis(salicylidene)-1,1-(dimethyl)-ethylenediamine-oxovanadium(IV). A hot solution of 5.93 g of the ligand (1) in 50 ml ethanol was added dropwise to a solution of 3.98 g of vanadyl sulphate dihydrate in 60 ml of 50% ethanol while the solution was stirred very vigorously under a blanket of nitrogen. It was found to be helpful to scratch the sides of the beaker to bring about precipitation. The solution and the dark green product which formed in it were allowed to stand for about 3 hours. The product was filtered and washed successively with small amounts of 50% ethanol and ether to remove any free uncomplexed ligand, and dried at 100°C under vacuum. The dried product was then recrystallized from chloroform as green crystals; yield, 4.48 g (61%), m.p. 233° (lit 230–231°).[5] The dried complex was found to be nonhydroscopic and stable in air. Anal.: Calcd. for $C_{18}H_{18}N_2O_3V$: C, 59.93; H, 5.09; N, 7.66. Found: C, 59.84; H, 5.02; N, 7.76.

The complex is insoluble in water, carbon tetrachloride and ether, soluble in methanol, ethanol, benzene, toluene and dioxane and more soluble in acetone, chloroform, methylene chloride, pyridine, tetrahydrofuran, glacial acetic acid, acetonitrile, nitrobenzene, dimethylformamide, dimethylsulphoxide and nitromethane.

Physical Measurements. The magnetic, osmometric and spectroscopic methods used have been described elsewhere.[1] Low resolution mass spectra were recorded with an Atlas CH4 mass spectrometer, at 10 and 70 ev. The oxovanadium(IV) complex was introduced directly into the E–4B ion source through an oven inlet lock with a sample

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rod heated to 170°. The mass spectrum of the ligand is described elsewhere.[2] The conductance of a 2×10^{-3} M solution of the complex was measured in chloroform at 23°, and it was found to be a nonconductor. Resolution of the complex was attempted by shaking 25 ml of a benzene solution of the complex with powdered d-quartz for 15 min in the hope that one isomer would be adsorbed preferentially. However, the filtrate showed no rotation.

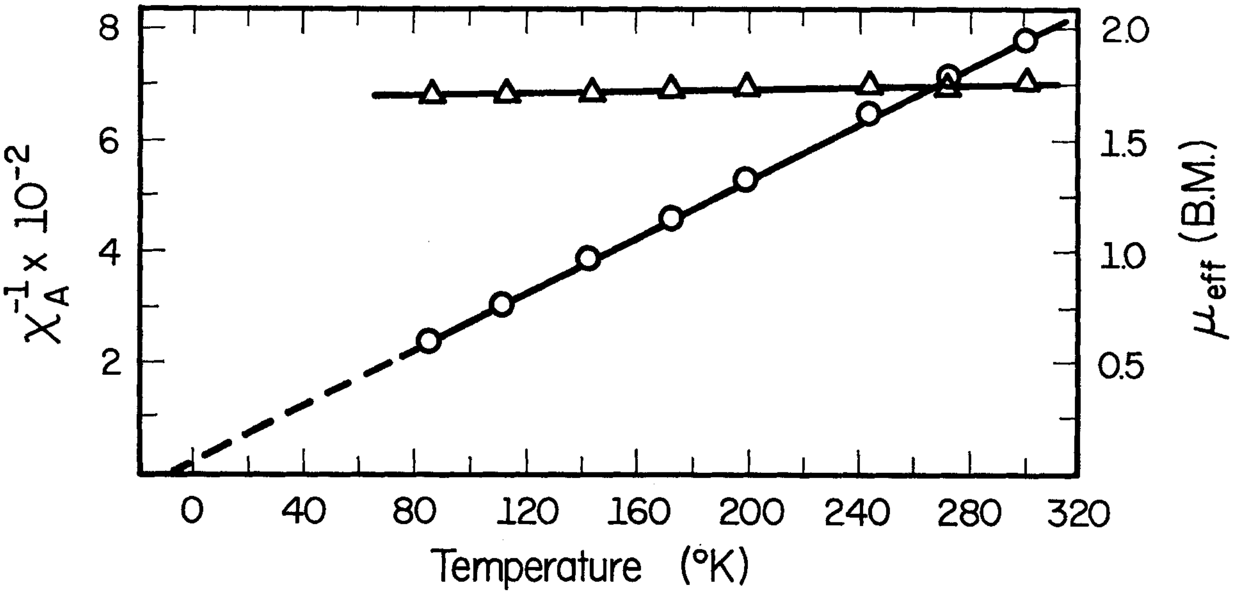


FIGURE 1 Variation with temperature of reciprocal molar susceptibility $\chi_A^{-1} \times 10^{-2}$ (O) and effective magnetic moment μ_{eff} (B.M.) (χ) of VO(sal$_2$-i-bn). Diamagnetic correction = -182×10^{-6}.

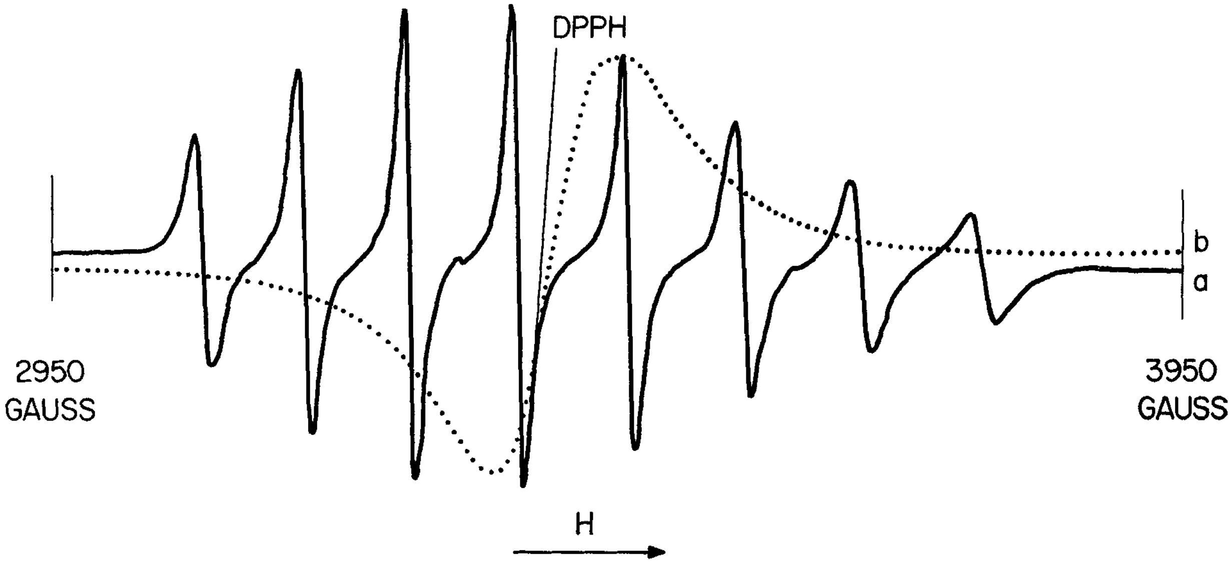


FIGURE 2(*a*) Electron paramagnetic resonance spectrum of VO(sal$_2$-i-bn) in chloroform at room temperature.
(*b*) Electron paramagnetic resonance spectrum of VO(sal$_2$-i-bn) powder at room temperature.

RESULTS AND DISCUSSION

Magnetism

The results of the magnetic measurements on VO(sal_2-i-bn) are given in Figure 1. The effective magnetic moment of the complex is 1.75 B.M. at 296°K and the θ value is 9°K. Our result is similar to that observed with square-pyramidal VO(sal_2en)[6] and VO(5-bromo-sal_2en)[7] complexes.

Electron Paramagnetic Resonance Spectra

The epr spectrum of VO(sal_2-i-bn) (2×10^{-3} M) in chloroform at room temperature (Figure 2*a*) is normal for tetragonal-pyramidal oxovanadium(IV) complexes; $g \approx 1.970$ and $A \approx 90 \times 10^{-4}\,cm^{-1}$. These parameters compare well with $< g > = 1.973$ and $A = 88.1 \times 10^{-4}\,cm^{-1}$ obtained from a single crystal study of VO^{2+} in bis(N-methylsalicylaldiminato)nickel(II).[8] Moreover, the results are in close agreement with the reported values $g = 1.974$; $A = 91 \times 10^{-4}\,cm^{-1}$ and $g = 1.973$; $A = 92 \times 10^{-4}\,cm^{-1}$ for VO(sal_2en) and VO(sal_2pn) complexes.[3,9] The powder spectrum is almost identical at liquid air and room temperature (Figure 2*b*) and is the usual slightly asymmetric broad line consistent with the g-value found for the solution and with the usual anisotropy ($g_{\parallel} \sim 1.95$, $g_{\perp} \sim 1.98$)[8,9] for tetragonal-pyramidal monomeric oxovanadium(IV) complexes. Using the solution g-value, we predict a magnetic moment $\mu_{calc.} = 1.70$ B.M., in satisfactory agreement with the bulk susceptibility measurements.

Although it might be possible to discuss small differences in bonding between this complex and other vanadyl systems, there is no evidence for large differences or for any unusual inter-molecular interactions.

Molecular Weight Determinations

The mass spectrum taken at 10 ev affords only the parent ion peak of the complex, which agrees exactly with the molecular weight of the monomer.

The osmometric molecular weight of the complex in chloroform solution (320) is approximately the calculated monomeric value (361).

Infrared Spectra

The significant infrared bands for Sal_2-i-bn and its oxovanadium(IV) complex are given in Table 1.

TABLE I

I. R. Spectral data for Sal_3-i-bn and its Oxovanadium(IV) complex.

Sal_2-i-bn	VO(sal_2-i-bn)	Assignments
Literature (5)		
1525(w)	1545(m)	C = N
	1302(m)	V — O
1278(s)		O — H
1100(m)	1110(w)	C — O
This work		
2850(wbr)		ν(OH····N bond)
1627(s)	1618(s)	ν(C = N)
1618(sh)	1603(sh)	ν(C = C) aromatic
1585(s)	1548(s)	
1501(s)		
1164(m)	1131(m)	ν(C − O)
1280(s)		δ(O — H in H bonded rings)
	987(s)	ν(V = O)

w = weak, s = sharp, m = medium, br = broad, sh = shoulder, v = very.

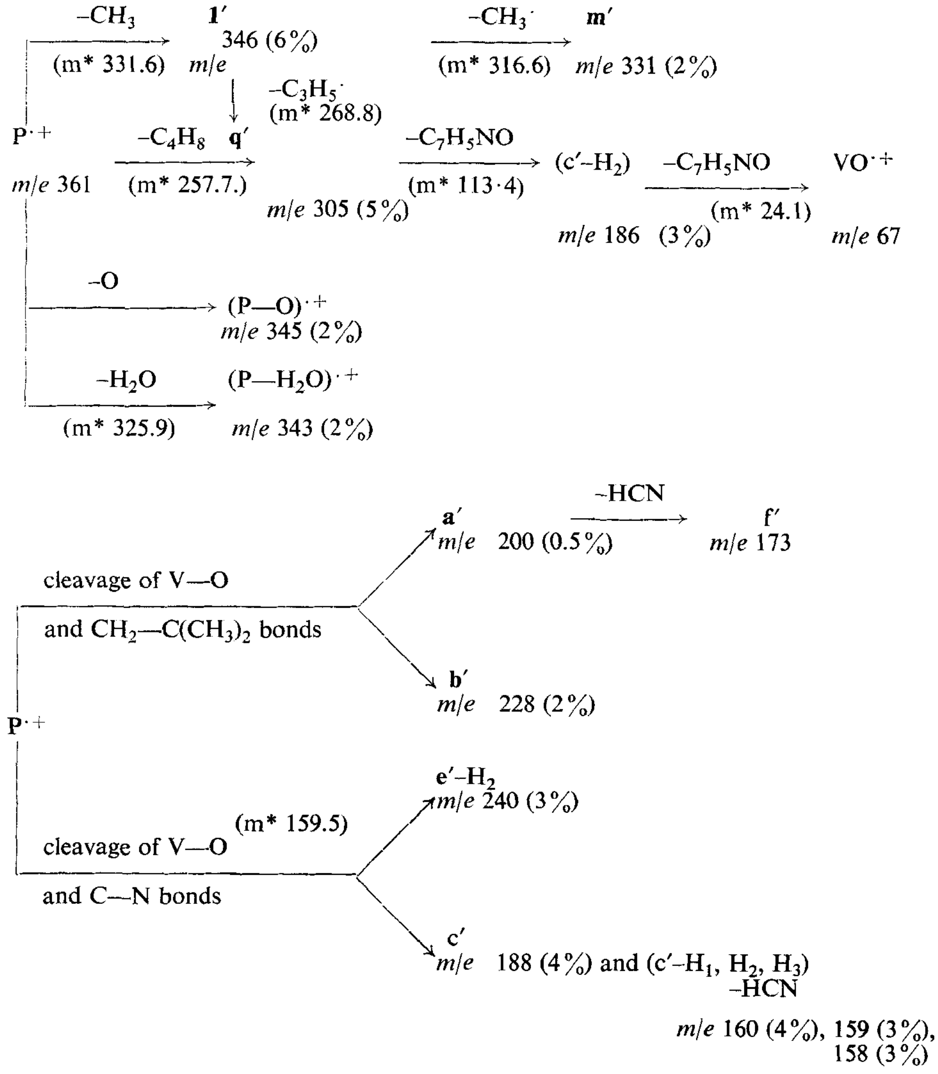
TABLE II

Ultra-violet and visible absorption maxima for Sal_2-i-bn and its oxovanadium(IV) derivative in KEL-F grease mull and in chloroform.

	$\nu_{max.}$ in mull, KK	$\nu_{max.}$ in chloroform, KK and $\epsilon_{max.}$ (in brackets)	Assignments
Sal_2-i-bn	38.8	38.6 (26,000)	aromatic band
	31.3	31.3 (8,800)	$\pi \rightarrow \pi^*$
	24.8	24.8 (257)	$n \rightarrow \pi^*$
VO(sal_2-i-bn)	47.6^{wsh}	—	aromatic or c.t.
	$\sim 41.3^{sh}$	$\sim 40.8^{sh}$ (43,000)	ligand band
	35.1	35.3 (25,000)	c.t.
	27.2	27.0 (8,900)	ligand and c.t.
	$\sim 21.5^{bsh}$	$\sim 21.5^{bsh}$ (90)	$dxy \rightarrow dz^2$
	17.1	17.0 (140)	$dxy \rightarrow dx^2\text{-}y^2$
	$\sim 15.4^{vwsh}$	$\sim 15.4^{vwsh}$ (70)	dxy → dxy, dyz

SCHEME I

Fragmentations of VO(sal$_2$-i-bn)



Ultra-violet and Visible spectra

The electronic spectra of VO(sal$_2$en) and VO(sal$_2$pn) have been studied previously.[3, 10] The ultra-violet and visible spectra of the free ligand (sal$_2$-i-bn) and its oxovanadium(IV) complex (in mulls and in chloroform) are given in Table 2. They follow the same pattern.[5]

The assignments of observed electronic bands for oxovanadium(IV) complexes have been a matter of controversy. However, the electronic spectra are assigned using proposed ordering of vanadium d orbitals by Vanquickenborne and McGlynn:[11] $xy < xz,yz < x^2 - y^2 < z^2$, and are consistent with those of the same type of complex.[3]

Mass spectral studies

The major peaks in the spectrum of VO(sal$_2$-i-bn) are those shown in Scheme 1. Most of the ions shown (those lettered) can be ascribed to fragmentations reported earlier for the divalent metal complexes of the same ligand.[2]

The parent ion peak ($p^{\cdot+}$) is the base peak (*m/e* 361), whose intensity accounts for 30% of Σ_{33}. The stability of the complex is sufficiently high that the doubly charged ion p^{++} is also found in the spectrum and the fragments *l′* $(P\text{-}CH_3)^{++}$, *m′* $(P\text{-}2CH_3)^{++}$, *q′* $(P\text{-}C_4H_8)^{++}$, $(P\text{-}O)^{\cdot +}$ and $(P\text{-}H_2O)^{\cdot +}$ all occur as doubly charged ions.

The first major fragmentation of the parent ion is the cleavage of a V—O bond and one of the C—N bonds. This leads to ion c′ at *m/e* 188 and peaks near it (c′—H,H_2,H_3). The alternative fragment from C–N cleavage results in ion (e′–H_2) at *m/e* 240, and the corresponding metastable ion is detected. It seems likely that ions (c′-H,H_2,H_3) lose HCN to give ions at *m/e* 160, 159 and 158, but the corresponding metastable ions are not found.

A less pronounced cleavage, of a V—O bond and a CH_2-$C(CH_3)_2$ bond gives less abundant ions **b**′(2%) and **a**′(0.5%).

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