The Stereochemistry of Oxovanadium(IV) Complexes derived from Salicylaldehyde and Polymethylenediamines

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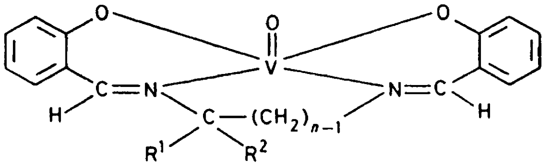
Several Schiff-base complexes of oxovanadium(IV), $[VO\{OC_6H_4CH=N-CR^1R^2(CH_2)_{n-1}-N=CHC_6H_4O\}]$ where $n = 2$ (R^1 and R^2 = H or CH_3) and n = 3—10 ($R^1 = R^2$ = H), have been isolated and their spectroscopic and magnetic properties have been investigated. The ν(V=O) stretching vibration frequencies fall in the range 861—994 cm^{-1}. Minimum and maximum d_π–p_π overlaps in V=O were observed in (4; $R^1 = R^2$ = H, n = 3) and (7; $R^1 = R^2$ = H, n = 6) respectively. The electronic spectra in chloroform and pyridine and in the solid state indicate the possibility of an inversion of the ordering of energies of the $e_\pi{}^*$ and $b_1{}^*$ levels; consequently a diversity of geometries were observed as the methylene chain length increased. The effective magnetic moments at room temperature of the complexes are between 1.64 and 1.81 B.M.; however, the θ values are relatively small.

IN contrast to the considerable attention paid to β-diketonates[1] and bidentate and tridentate Schiff-base complexes[2] of oxovanadium(IV), only little progress has been made in studies involving oxovanadium(IV) complexes of quadridentate Schiff-base ligands.

The oxovanadium(IV) salicylaldimine complexes $[VO\{OC_6H_4CH=N-CR^1R^2(CH_2)_{n-1}-N=CHC_6H_4O\}]$ [$n = 2$; (1; $R^1 = R^2 = H$), (2; $R^1 = H$, $R^2 = CH_3$), (3; $R^1 = R^2 = CH_3$)] are green, and their spectroscopic and magnetic properties suggest that they have tetragonal-pyramidal structures.[3] A corresponding complex (4; $R^1 = R^2 = H$, $n = 3$) is orange-yellow and its *X*-ray structure shows that it is polymeric, having a distorted octahedral geometry.[4] Similar complexes involving derivatives of salicylaldehyde and trimethylenediamines were found to be orange-yellow and presumably polymeric.[5]



Compound	R^1	R^2	n
(1)	H	H	2
(2)	H	CH_3	2
(3)	CH_3	CH_3	2
(4)	H	H	3
(5)	H	H	4
(6)	H	H	5
(7)	H	H	6
(8)	H	H	7
(9)	H	H	8
(10)	H	H	9
(11)	H	H	10

A square-pyramidal geometry has often been assumed for five-co-ordinate oxovanadium(IV) complexes.[1] Theoretical models developed[6,7] around this regular geometry have been found partially satisfactory for interpreting magnetic and spectral properties of some oxovanadium(IV) complexes, especially the ' low-symmetry ' complexes.[8] Consequently, the quadridentate complexes reported in this work are expected to exhibit a variety of stereochemistries and molecular complexity.[9]

Our interest in this molecular ion, therefore, was to use it as a paramagnetic and spectroscopic probe to monitor changes in stereochemistry in a series of quadridentate Schiff-base complexes. It was hoped that some degree of measurable perturbation of the oxovanadium(IV) entity would result when Schiff-base ligands formed from salicylaldehyde and polymethylenediamines co-ordinate to the molecular ion.

EXPERIMENTAL

All chemicals and solvents were of the reagent grade or purer and were used without further purification. The solvents for spectroscopic measurements were purified by standard methods and deoxygenated prior to use. Commercial 1,2-diaminopropane was purified by drying over K[OH] and distilled under an atmosphere of nitrogen; salicylaldehyde was carefully distilled under reduced pressure.

The ligands, *NN'*-bis(salicylidene)polymethylenediamines, were prepared by the method of Hariharan and Urbach.[9] Complexes (1)—(4) were prepared by the method of Patel and Bailar[3] except that compound (4) was recrystallised from pyridine. In the isolation of the higher members of the series, methanol was employed as the solvent. The use of an aqueous ethanolic solution either for $[VO][SO_4]\cdot 2H_2O$ or for washing the products was found to be unsuitable, perhaps due to hydrolysis and/or hydration of the products.

Preparation of [NN'-Bis(salicylidene)(polymethylenediiminato)]oxovanadium(IV) *Complexes* (5)—(11) (n = 4—10).—The salt $[VO][SO_4]\cdot 2H_2O$ (6 mmol) was dissolved in hot methanol (200 cm^3) and a mixture of NEt_3 (14 mmol) and the ligand (6 mmol) dissolved in a suitable volume of MeOH was added with stirring over about 10 min. The mixture was kept hot (60—70 °C) and stirred for about 30—45 min. The reaction mixture was left to cool and the products were filtered off. The complexes were washed and digested twice with warm methanol. The complexes were either insoluble in chloroform or interacted with the solvent. Attempts to recrystallise them from pyridine were also not successful. The removal of final traces of soluble impurities was therefore achieved by Soxhlet extraction using methanol. The final products were dried in a vacuum desiccator over $CaCl_2$–P_2O_5 and finally (where necessary) at 60—100 °C in a

TABLE 1

Analytical [a] and magnetic [b] data for the complexes

Compound	Colour	M.p./°C	M	Analysis (%) C	H	N	V	μ_e/B.M. 299 K	85 K	θ/K
(1)	Green	274.7	333 [d] (333)	57.4 (57.7)	4.3 (4.2)	8.3 (8.4)	15.0 (15.3)	1.75	1.72	8
(2)	Green	219.8	357 [d] (347)	58.9 (58.8)	4.6 (4.6)	8.2 (8.1)	14.3 (14.7)	1.75	1.71	8
(3)	Green	231.5	369 [d] (361)	59.9 (59.8)	5.1 (5.0)	7.9 (7.8)	14.0 (14.1)	1.76	1.71	9
(4)	Orange-yellow	315 [c]	347 [e] (347)	58.7 (58.8)	4.7 (4.6)	8.0 (8.1)	14.7 (14.7)	1.81	1.78	8
(5)	Greyish green	275 [c]	361 [e] (361)	60.2 (59.8)	5.1 (5.0)	7.8 (7.8)	13.0 (14.1)	1.72	1.69	6
(6)	Ash-green	164 [c]		61.0 (60.8)	5.5 (5.4)	7.8 (7.5)	13.3 (13.6)	1.74	1.70	9
(7)	Ash-green	268 [c]		60.9 (61.7)	5.9 (5.7)	7.3 (7.2)	13.4 (13.1)	1.71	1.55	[f]
(8)	Grey	125 [c]		63.0 (62.5)	6.1 (6.0)	7.3 (6.9)	12.4 (12.6)	1.64	1.59	11
(9)	Grey	122 [c]		63.3 (63.3)	6.5 (6.3)	6.9 (6.7)	11.9 (12.2)	1.67	1.60	14
(10)	Dark grey	140 [c]	1 318 [d] (431)	64.2 (64.0)	7.0 (6.5)	6.4 (6.5)	11.6 (11.8)	[g]		
(11)	Grey	112 [c]		65.0 (64.7)	7.0 (6.8)	6.5 (6.3)	11.0 (11.4)	1.77	1.67	19

[a] Calculated values are given in parentheses. [b] The moments are calculated from the expression $\mu_e = 2.828(\chi_A \cdot T)^{\frac{1}{2}}$ and the Curie–Weiss law $\chi_A^{-1} \propto (C + \theta)$. χ_A = Molar magnetic susceptibility, C = Curie constant; 1 B.M. = 0.927×10^{-23} A m^2. [c] Decomposition temperature. [d] Molar masses determined in chloroform solution. [e] Molar masses extracted from mass spectra. [f] See Figure 4. [g] Unsuitable for packing.

drying pistol over P_2O_5. The analytical results, along with colours, melting or decomposition temperatures, and molar masses for the complexes are given in Table 1.

Complexes (1)—(3) were soluble in chloroform and pyridine; complex (4) dissolved in these solvents only when it was left in an ultrasonic bath for about 30 min to give bright bluish green and orange-yellow solutions respectively; complexes (5)—(7) were insoluble in chloroform but moderately soluble in pyridine, and (8)—(11) interacted with chloroform at concentrations greater than 2×10^{-4} mol dm^{-3} to give flocculent precipitates but dissolved readily in pyridine.

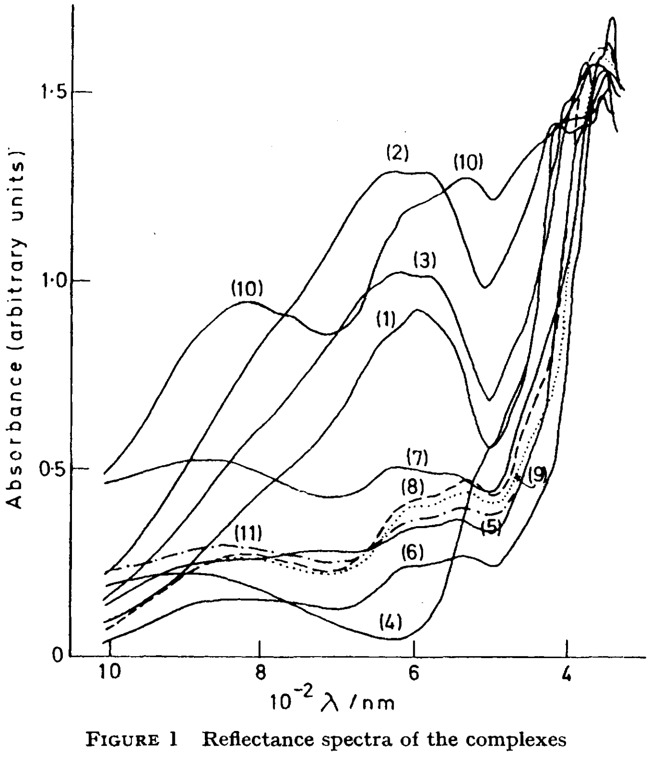


FIGURE 1 Reflectance spectra of the complexes

Physical Measurements.—The i.r. spectra were recorded on a Perkin-Elmer 457 spectrophotometer in the 250—4 000 cm^{-1} range, 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 diffuse-reflectance electronic spectra were measured in the range 10 000—29 850 cm^{-1} on an SP 500 spectrophotometer using LiF as a reference. The electronic spectra in chloroform and pyridine solution (10^{-4}—10^{-3} mol dm^{-3}) were recorded on an Applied Physics Cary 14H spectrophotometer. The magnetic susceptibility measurements in the temperature range 80—320 K were carried out on a Gouy balance and diamagnetic corrections for the ligands were calculated using the Pascal constants.[10]

RESULTS AND DISCUSSION

The C=N stretching vibrations in the ligands are located in the region 1 620—1 630 cm^{-1} and are shifted to lower wavenumbers upon chelation [except (4; $R^1 = R^2 = H$, $n = 3$)] indicating that the azomethine N atom is involved in the V–N bond formation.[11,12] The ν(V=O) frequencies are normal,[13] except for complex (4), being located at 861 cm^{-1} in agreement with Mathew *et al.*[4] and Farmer and Urbach.[5] The maximum ν(V=O) (994 cm^{-1}), recorded for (7; $R^1 = R^2 = H$, $n = 6$), suggests that considerable d_π–p_π overlap between V and O is achieved in the hexamethylene chain. Two ν(V=O) frequencies, 981 and 959 cm^{-1}, observed for (5; $R^1 = R^2 = H$, $n = 4$)

indicate the existence of V=O in two different environments.

Although the assignments of the electronic spectra of the oxovanadium(IV) ion are still not settled[1] there seems to be more evidence favouring the ordering proposed by Ballhausen and Gray:[6] $b_2(d_{xy}) < e_\pi^*(d_{xz}, d_{yz}) < b_1^*(d_{x^2-y^2}) < a_1^*(d_{z^2})$. The spectral data are provided in Table 3, while some of the spectra are illustrated in Figures 1—3.

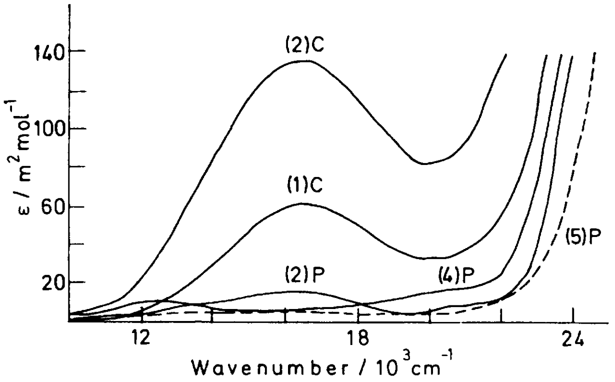


FIGURE 2 Electronic spectra of chloroform (C) and pyridine (P) solutions of complexes (1), (2), (4), and (5)

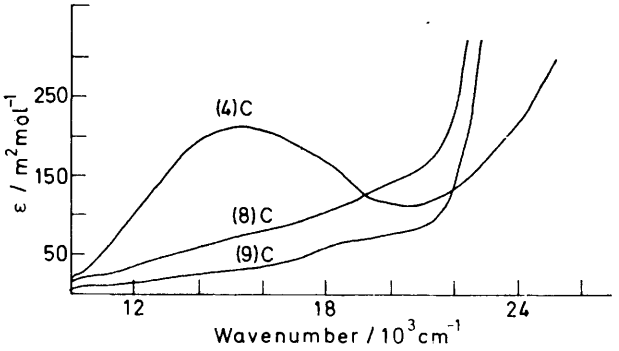


FIGURE 3 Electronic spectra of chloroform (C) solutions of complexes (4), (8), and (9)

For convenience the compounds are classified into three categories on the basis of their reflectance spectra: A, (1)—(3); B, (4); and C, (5)—(11). Complexes A are characterised by a band and a weak shoulder at 16 000—18 000 cm^{-1} and two low intensity shoulders at 12 000—13 000 and 21 000—22 000 cm^{-1} in agreement with previous reports.[3] The spectrum of (4) is very similar to that observed by Farmer and Urbach.[5] The compounds C show a broad band at 12 000—13 000 cm^{-1} [two bands for complex (5)] and two closely spaced maxima of nearly equal intensity at 16 000—17 000 and 18 000—19 000 cm^{-1} respectively. Contrary to expectation, the transition $b_2 \rightarrow b_1^*$ (band II, 16 000—17 000 cm^{-1}) has a greater intensity while $b_2 \rightarrow e_\pi^*$ (band I, 12 000—13 000 cm^{-1}) has a lower intensity suggesting that the energies of b_1^* and e_π^* have been inverted in the complexes. Some charge-transfer bands are also observed at 24 000—30 000 cm^{-1}.

The spectra in chloroform of complexes A gave only one band at 16 000—17 000 cm^{-1} and a weak shoulder at 12 000—15 000 cm^{-1}. The former band shifts to 15 490 cm^{-1} in complex (4) with a considerable increase in molar absorptivity. For $n = 7$—10 [compounds (8)—(11)] the spectra gave two poorly resolved bands at 14 000—22 000 cm^{-1} and a long 'tail' at 10 000—14 000 cm^{-1}. On dilution, the spectrum of (10; $R^1 = R^2 = H$, $n = 9$) gave one band at 15 230 cm^{-1} ($\varepsilon = 250$ m^2 mol^{-1}).

TABLE 2

Relevant i.r. bands (cm^{-1}) of the complexes

Compound	C=N [a]	V=O	V–N	V–O
(1)	1 620vs	990vs	550w	416w
	(1 633)		461s	348wm
(2)	1 619vs	989vs	550w	400w
	[b]		464s	350w
(3)	1 615vs	990vs	551w	405w
	(1 627)		462m	350wm
(4)	1 628vs	861vs	565w	404sh
	(1 629)		464ms	336m
(5)	1 620vs	981ms	556w	400w
	(1 630)	959s	458s	337m
(6)	1 618vs	981vs	566w	400w
	(1 629)		460s	337m
(7)	1 617vs	994vs	564w	400w
	(1 629)		458ms	339m
(8)	1 620vs	982vs	568w	405m
	(1 631)		460ms	334w
(9)	1 620vs	983vs	570w	405w
	(1 630)		463ms	335w
(10)	1 620vs	980vs	568w	400w
	(1 629)		455ms	332m
(11)	1 620vs	983vs	567w	405w
	(1 630)		460s	329w

[a] ν(C=N) for corresponding free ligands are given in parentheses. [b] Spectrum not taken.

vs = Very strong, ms = medium strong, m = medium, wm = weak medium, w = weak, sh = shoulder.

The spectra in pyridine of complexes A are similar to their corresponding reflectance spectra. However, a considerable reduction in molar absorptivities is observed on going from chloroform to pyridine. In the other complexes the spectra in pyridine are similar to the reflectance spectrum of (4).

The above spectral characteristics indicate that complexes A are five-co-ordinate square pyramids in the solid and in chloroform and the reduction in molar absorptivity in pyridine indicates a facile formation of six-co-ordinate species in solutions of the co-ordinating solvent.[14] The minor shifts in the band positions on going from chloroform to pyridine indicate that the weak solvent interaction is accompanied by an increase in in-plane ligand field in complexes (1) and (2) and a decrease in (3).[15] Compound (4) breaks down to five-co-ordinate monomers in chloroform but in pyridine remains six-co-ordinate. No structural change is indicated on going from solid to chloroform solution in complexes (8)—(11) ($n = 7$—10). The changes observed in the spectrum of (10) in chloroform on dilution suggest that the higher members ($n = 4$—10) are not likely to be simple monomers. The similarity in the spectra of the complexes for $n \geqslant 3$ in pyridine and the reflectance spectrum of (4) indicates that the higher

TABLE 3

Electronic spectral band positions [a]

Compound	Solvent [b]	Band I $b_2 \longrightarrow b_1^*$	Band II $b_2 \longrightarrow e^*$	Band III $b_2 \longrightarrow a_1^*$	Band IV C.T.	Band V C.T.
(1)	R	13.30 [c]	15.87 [c]	21.98 [c]	25.00	
			16.81			
	C	13.45(24)	16.75(65)			
	P	14.99(12)	16.79(20)			
(2)	R	12.66 [c]	15.87	21.28 [c]	24.27	
			17.24			
	C	11.37(12)	16.34(132)	21.18 [c] (106)		
	P	13.13(6)	16.84(22)	20.93(10)		
(3)	R	12.50 [c]	15.87	21.88	25.00	28.98
			17.04			
	C	*d*	16.87(52)			
	P	13.10(9)	16.69(17)	20.85(11)		
(4)	R	11.11		20.41	25.00	27.78
	C		15.49(214)			
	P	13.22(12)		19.47(16)		
(5)	R	11.76	16.67	18.18	27.78 [c]	28.41
		13.79				
	P	13.57(5)		19.51(8)		
(6)	R	11.98	16.67	18.69	27.78 [c]	28.99
	P			19.23(12)		
(7)	R	11.43	15.87	18.02	27.62 [c]	28.99
(8)	R	12.20	16.95	18.52		28.17
	C		16.51(88)			
	P	13.38(6)		19.15(8)		
(9)	R	12.12	16.95	18.52		28.41
	C		16.17(39)	19.63(77)		
	P	14.00(5)		19.31(8)		
(10)	R	12.20	16.67	18.69	25.00	28.99
	C [e]		16.00(39)	19.07 [c] (73)		
	P	13.59(b)		19.35(8)		
(11)	R	11.98	16.81	18.80	27.03	28.01
	C		16.21(56)	20.00(89)		
	P	13.66(7)		19.35(9)		

[a] Band positions in 1 000 cm^{-1}; molar absorption coefficients ($\text{m}^2\ \text{mol}^{-1}$) are in parentheses. C.T. = Charge-transfer band. [b] C = Chloroform, P = pyridine, R = reflectance spectrum. Where a solvent is omitted, the compound is insoluble in the solvent. [c] Shoulder. [d] A broad 'tail.' [e] Using 10^{-4} mol dm^{-3} solution: band II = 15 230 cm^{-1} (250 $\text{m}^2\ \text{mol}^{-1}$).

members are also six-co-ordinated in pyridine. The evidence of six-co-ordination in pyridine in these complexes show that the alkyl bridge is equatorial in solution, and the increase in readiness to attain this co-ordination in the solvent indicates a decrease in strain as the length of the alkyl bridge increases. The lowering of the energy of band III to 18 000—22 000 cm^{-1} in all the complexes is significant and offers a further support to an earlier speculation[1] that in low-symmetry complexes this band might be observed at energies below 20 000 cm^{-1}.

The magnetic data for the compounds studied are presented in Table 1 and Figure 4. They obey the Curie–Weiss law, except for (7; $R^1 = R^2 = H$, $n = 6$), and the results agree with reported values for compounds (1)—(4).[3,16] Complex (7) has a 'normal' magnetic moment at room temperature but obeys the Curie–Weiss law at low temperatures. It may be that the low-temperature behaviour indicates antiferromagnetic interaction arising because the compound is not a simple monomer, while at high temperature the moment is raised back to a more 'normal' value by some temperature independent paramagnetism, although the origin of this is not clear.[17]

The stereochemistry of the complexes varies from distorted square-pyramidal to octahedral geometry and the spectral behaviours of (5; $R^1 = R^2 = H$, $n = 4$) and

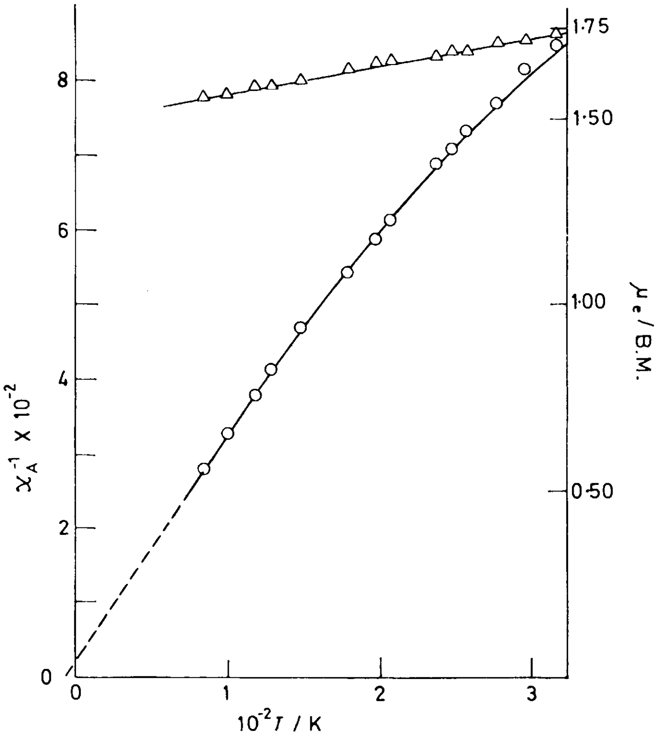


FIGURE 4 Variation of magnetic susceptibility, (○), and magnetic moment, (△), with temperature for complex (7)

(10) do not rule out the possibility of some molecular aggregation in the solid state.

The authors are very grateful to Professor N. N. Greenwood for allowing the use of the facilities at the University of Leeds, and to Dr. A. Earnshaw for useful suggestions.

[0/1201 *Received*, *29th July*, 1980]

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