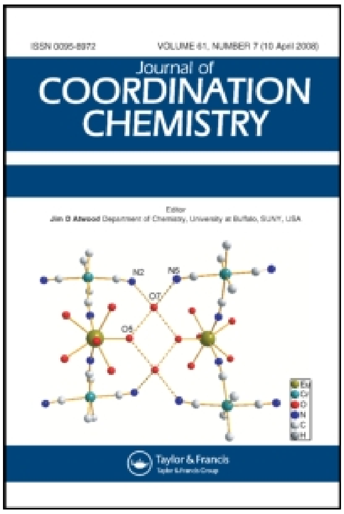

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OXOVANADIUM (IV) COMPLEXES OF SCHIFF-BASES DERIVED FROM 2-AMINOPYRIDINE AND AROMATIC 2-HYDROXYALDEHYDES

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OXOVANADIUM (IV) COMPLEXES OF SCHIFF-BASES DERIVED FROM 2-AMINOPYRIDINE AND AROMATIC 2-HYDROXYALDEHYDES

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Seven new complexes of general formulae $[VO(OC_6H_4X\text{-}CR{=}N\text{-}py)_2]$ and $[VO(OC_{10}H_8CH{=}N\text{-}py)_2]$ have been prepared and characterised by microanalysis, room temperature magnetic moments, conductivity and spectroscopic measurements. Although the complexes are five-coordinate, at least two modes of bonding with the donor atoms are observed, and these depend on electronic effects of the substituents on the phenyl ring.

Keywords: Vanadium, vanadyl, Schiff-base, complexes, properties.

INTRODUCTION

Schiff-base complexes involving heterocyclic compounds have received considerable attention in the literature.[1-3] Our sustained interest in oxovanadium(IV) chemistry with these ligands stems from the mounting evidence[4-6] that vanadium plays a significant role in biological systems. Vanadium has been found to be useful as a probe in some metalloenzymes where it replaces certain other metals without loss of enzyme activity.[7,8] In addition there is growing evidence[9] supporting the essentiality of vanadium. Furthermore, azomethine intermediates are also of biological importance in a large number of enzymatic reactions.[10,11]

Studies[12-14] have shown that bonding occurs preferably through an endocyclic nitrogen atom whenever the ligand possesses more than one type of nitrogen. Gol'dfarb *et al.*,[15] and later Garnovskii *et al.*,[12] showed that in Schiff-bases involving 2-aminopyridine the endocyclic *N* is more basic than the exocyclic azomethine *N*. In the studies carried out by Yamada and Yamonouchi,[1] it was concluded that the ligand **I(a)** was bidentate in all complexes isolated except one where it was found to act as a tridentate. On steric grounds they[1] concluded that it was the azomethine *N* that preferentially bonded to the metal, without adducing any obvious evidence. In any case, this conclusion contradicted earlier[12,14] findings that the pyridine *N* atom is more basic. The focus of our current work is to endeavour to establish those factors that favour bonding *via* either *N* atom. No report could be found in the literature on oxovanadium(IV) complexes of the ligand **I(a)**.†

EXPERIMENTAL

Preparation of the complexes

The ligands were prepared according to literature methods.[16] The complexes were

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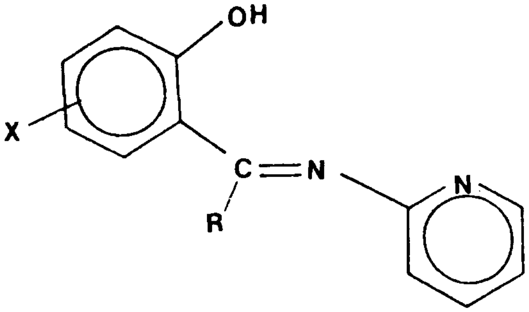
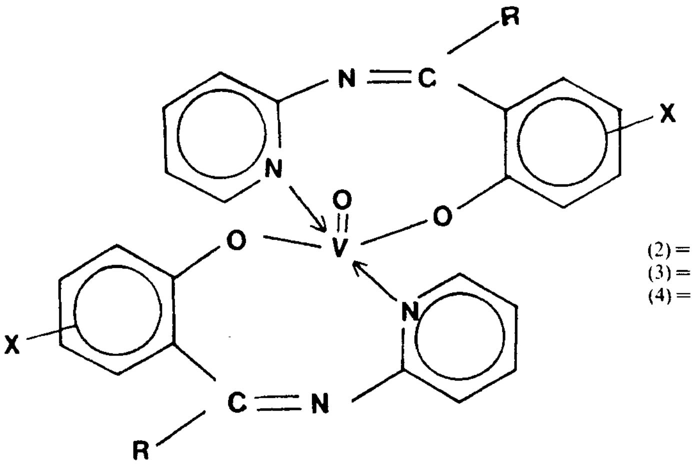
† Sal-anil is the aniline analogue of **I(a)**; for sal-ampy, X=R=H; for the 7-CH_3 ligand, X=H, R=CH_3] for the ligands remaining other than naph-ampy, R=H and the other substituent is in the benzene ring at the indicated position; naph-ampy is the naphthyl analogue of sal-ampy.

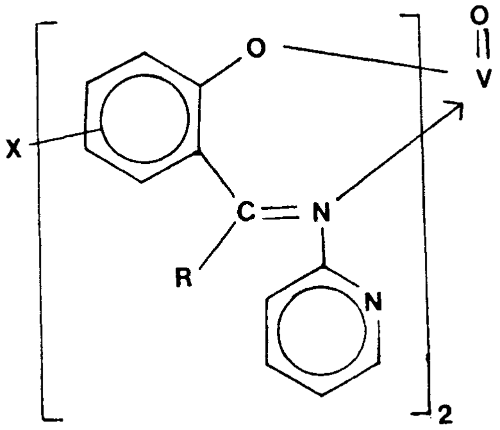


I(a) Ligand



(2) = H R = H
(3) = H R = CH_3
(4) = 3-OCH_3 R = H

I(b)



I(c)

prepared[17] from methanolic solutions of the preformed ligand and either a methanolic solution of $VOSO_4 \cdot 2H_2O$ [for complexes (**1**), (**5**)–(**8**)] or syrupy $VOCl_2$ for complexes (**2**) and (**4**). Complex (**3**) was obtained by templating stoichiometric amounts of $VOCl_2$, 2-hydroxyacetophenone and 2-aminopyridine. Refluxing time for all the preparations was 1-3 h and where products did not form excess triethylamine was added as a buffer. The products were thoroughly washed with methanol and dried *in vacuo* over P_2O_5.

Physical measurements

Microanalysis was carried out by the microanalytical laboratory of the University of Ibadan. V was estimaed by permanganate titration after a known weight of the complex has been digested with 1:1 HNO_3 and 1:1 H_2SO_4. The i.r. spectra were run on Perkin-Elmer 457 grating spectrometer in the range 4000–250 cm^{-1} in KBr discs. The room temperature magnetic moments were determined using the Guoy method with $Hg[Co(CNS)_4]$ as the calibrant. The conductivity measurements were carried out in DMF on an Electrolytic Conductivity measuring set (Model MC-1 Mark V). The diffuse reflectance spectra were run on Pye Unicam SP500 spectrophotometer equipped with a reflectance attachment using A.R. $CaCO_3$ as the reference. The solution electronic spectra (10^{-4}–10^{-5} mol dm^{-3}) were run on a HP8451A rapid-scan diode array spectrophotometer in the 190–900 nm range.

RESULTS AND DISCUSSION

All the complexes are green except (7) which is yellow. Microanalysis confirms the purity of the ligands and the complexes (Table I) and the 1:2 (metal:ligand) stoichiometry of the complexes. The complexes were either insoluble or only slightly soluble in most organic solvents, except for DMF, DMSO and pyridine in which they are fairly soluble.

The very low conductivities (Table I) of solutions of the complexes in DMF show that they are non-electrolytes in this solvent. The residual conductivities observed might be due to impurities. The room temperature mangetic moments are normal[18] for d^1 VO^{2+} complexes.

The tentative i.r. assignments are presented in Table II. Complex (**1**) has been reported but we have included it in this work for comparison. The $\nu(C{=}N)$ modes of the ligands are observed at 1600–1620 cm^{-1} and shift to lower frequencies in (**1**), (**5**), (**7**) and (**8**) indicating bonding through the azomethine *N* atom.[19] However, in (**2**), (**3**), (**4**) and (**6**) the $\nu(C{=}N)$ frequencies shift to higher wavenumbers indicating non-involvement of the imine *N* atom in bonding. The $\nu(C\text{–}O)$ frequencies shifts to higher wavenumbers in the corresponding complexes indicating that the phenolic *O* atom participates in bonding.[20] According to the nomenclature of Kline and Turkevitch,[21] four of the pyridine modes sensitive to pyridine *N* atom-metal bonding are *8a*, 8b, 19a, and *19b* corresponding to 1589–1608, 1565–1573, 1471–1495 and 1431–1443 cm^{-1}, respectively. It is expected that these vibrational modes would overlap with some of the phenyl ring vibrations. However, we observe that on complexation *8a* shifts to higher frequencies in (**2**), (**3**) and (**4**) indicating that the endocyclic *N* atom is involved in complexation[22] while in (**5**), (**6**), (**7**) and (**8**) where *8a* and *19a* remain either unchanged or decreased, the pyridine *N* atom is not involved in bonding. It thus seems that electron-density in the phenyl ring plays a decisive role concerning the relative electron density on the two types of *N* atom. Electron releasing groups tend to favour bonding *via* the pyridine *N* atom while electron withdrawing groups favour bonding *via* the azomethine *N* atom.

TABLE I

Analytical data[a], room temperature magnetic moments and molar conductivities of the complexes.

Compound	Colour	M.P./°C	%C	%H	%N	%V	μ_{eff}/B.M.	Am/ohm^{-1} cm^2 mol^{-1}
1. VO(sal-anil)$_2$	green	228	68.05 (67.98)	4.35 (4.39)	6.05 (6.10)	11.05 (11.09)	1.69	0
2. VO(sal-ampy)$_2$	dark-green	220[b]	62.00 (62.19)	3.90 (3.93)	11.90 (12.14)	10.88 (11.04)	1.68	12.80
3. VO(7-CH$_3$sal-ampy)$_2$	green	185	63.62 (63.81)	4.27 (4.53)	11.68 (11.45)	9.30 (9.56)	1.64	18.55
4. VO(3-OCH$_3$sal-ampy)$_2$	green	150	59.62 (59.39)	4.00 (4.25)	10.92 (10.75)	9.83 (9.77)	1.73	12.93
5. VO(5-Clsal-ampy)$_2$	green	>250	54.14 (54.36)	3.28 (3.04)	10.36 (10.57)	9.26 (9.24)	1.83	3.20
6. VO(5-Brsal-ampy)$_2$	green	220[b]	46.72 (46.52)	2.48 (2.60)	8.93 (9.05)	8.22 (8.23)	1.81	4.13
7. VO(5-NO$_2$sal-ampy)$_2$	yellow	>250	52.00 (52.28)	2.98 (2.93)	14.98 (15.24)	9.26 (9.26)	1.90	8.20
8. VO(naph-ampy)$_2$	green	202[b]	68.28 (68.45)	3.67 (3.95)	9.79 (9.98)	9.40 (9.07)	1.79	12.80

[a]Calculated values are given in parentheses. [b]Decomposition temperatures.

TABLE II
Relevant i.r. frequencies for the complexes.[a]

Compound	ν(C=N)	Pyridine ring vibrations				ν(C-O)	ν(V=O)
		8a	8b	19a	19b		
2-NH_2py		1600	1565	1486	1444		
VO(sal-anil)$_2$	1605vs					1306vs	979vs
	(1620vs)					(1285vs)	
VO(sal-ampy)$_2$	1660s	1620	1541	1474	1460	1323m	982vs
	(1621s)	(1591)	(1558)	(1471)	(1435)	(1283vs)	
VO(7-CH_3sal-ampy)$_2$	1664vs	1625	1544	1468	1418	1324m	987vs
VO(3-OCH_3sal-ampy)$_2$	1664m	1610	1551	1450	1438	1332vs	970vs
	(1611s)	(1592)	(1565)	(1474)	(1440)	(1258vs)	
VO(5-Clsal-ampy)$_2$	1604m	1590	1558	1463	1435	1305m	977vs
	(1612s)	(1592)	(1559)	(1469)	(1439)	(1284vs)	
VO(5-Brsal-ampy)$_2$	1657s	1590	1564	1460	1434	1303vs	978sh) } vs
	(1612s)	(1590)	(1556)	(1467)	(1437)	(1284vs)	959)
VO(5-NO_2sal-ampy)$_2$	1605vs	1593	1550	1464	1493	1322vs	955) } s
	(1616vs)	(1594)	(1567)	(1470)	(1434)	(1301s)	900)
VO(naph-ampy)$_2$	1601) } vs						
	1614)	1578	1536	1457	1426	1307m	984vs
	(1618) } vs	(1593)	(1566)	(1477)	(1443)	(1290vs)	
	(1623)						

[a]Corresponding frequencies for the ligands are given in parentheses; vs = very strong, m = medium.

The behaviour of the bromo derivative (**6**) is unique and cannot be rationalised on the basis of our present data. The two proposed modes of bonding are represented in **I(b)** and **I(c)**.

The ν(V=O) frequencies are normal[23] for five-coordinate VO^{2+} complexes and are not effected by ring substituents except in (**7**) where a substantial reduction is observed (due to the $-I$ effect of the NO_2 group) for which one could not rule out some V=O...V interaction.[24]

The electronic spectral data are given in Table III. The complexes display a diversity of spectral shapes but most of them gave four bands in the visible region in the solid and in solution suggesting a basic C_{2v} symmetry,[25] but probably subjected to varying degrees of distortions and/or re-ordering of the energy level sequence.[26] The energy level sequence[18] $b_2(d_{xy}) < e_\pi^*(d_{xz}, d_{yz}) < b_1^*(d_{x^2-y^2}) < a_1^*(d_{z^2})$ is adopted with the e_π^* level splitting.[26] Five bands are observed between 24–50 kK (24–28, 26–33, 32–36, 35–40 and 40–50 kK) in the UV region. The bands at 24–28 kK are assigned to d–π or π–d metal-ligand or ligand-metal charge-transfers while the bands at 26–33 kK and 40–50 kK are assigned[27] to the intraligand spin-allowed transitions π_3–π_4^* and π_3–π_5^*, respectively. The bands at 32–40 kK arise from the aromatic (phenyl and pyridyl) π–system.[28]

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TABLE III
Electronic spectral data for the complexes[a].

Compound	Medium	Band I $b_2 \rightarrow e_\pi^*$	Band II $b_2 \rightarrow b_1^*$	Band III $b_2 \rightarrow a_1^*$	Band IV C.T.	Band V C.T.	Band VI $\pi_3 \rightarrow \pi_4^*$	Band VII $\pi \rightarrow \pi^*$	Band VIII $\pi_3 \rightarrow \pi_5^*$
VO(sal-anil)$_2$	solid	12.99 13.33	17.09	18.69					
	CHCl$_3$				26.95(3.83)	27.70(3.85)	33.33(3.85)	39.37(3.39)	48.54(3.20)
	DMSO				26.46(3.81)	28.25(3.84)	33.56(3.83)	35.21(3.78)	49.50(3.10)
VO(sal-ampy)$_2$	solid	10.36–11.90	17.09sh	23.53sh					
	CHCl$_3$[b]								
	DMSO	13.19(2.90) 13.66(2.85)	17.79(2.66)				33.11(3.86)	35.71(3.79)	47.17(3.14)
VO(7-CH$_3$sal-ampy)$_2$	solid	10.26–11.76 13.89sh	17.39sh						
	CHCl$_3$[b]			22.94			33.78	39.06	
	DMSO						33.56(4.08)	37.88(4.11)	49.02(3.47)
VO(3-OCH$_3$sal-ampy)$_2$	solid	11.43 12.58	16.39	22.22					
	CHCl$_3$	13.30(2.52)	15.20(2.54)	20.41(3.09)		27.32(2.62)	32.57sh(3.56)	36.36(3.76)	47.62(3.33) 40.98(3.08)
	DMSO	12.59(2.65) 13.19(2.63)	15.38(2.70)	19.84(3.18)			33.55(3.88)	36.50(4.22)	47.17(3.22)
VO(5-Clsal-ampy)$_2$	solid	12.20	16.67	18.69	24.10				
	CHCL$_3$	12.56(1.61) 13.09(1.67)	14.25(1.69)	22.03(2.42)		30.30(3.76)	33.11(3.84)	38.17(3.74)	47.62(3.27)
	DMSO				25.90(3.87)	32.05(3.89)	33.78(3.90)		
VO(5-Brsal-ampy)$_2$	solid	10.15–11.83 12.82	16.39	22.22sh	24.69				
	CHCl$_3$	12.59(2.21) 13.19(2.24)	14.84(2.30) 17.12(2.38)	21.60sh(2.78)		27.78(3.84)	33.56(3.89)	38.76(3.83)	47.62(2.08)
	DMSO		14.84(2.28)			28.57(3.85)	33.11(3.88)		47.17(2.21)
VO(5-NO$_2$sal-ampy)$_2$	solid	11.11 12.90	14.08	19.23sh					
	CHCl$_3$					27.47(3.86)	33.78(3.89)	38.46(3.86)	46.30(3.42)
	DMSO			20.00sh(2.88)	24.75(3.90)	26.74(3.90)	33.33(3.90)		46.73(3.46)
VO(naph-ampy)$_2$	solid	10.25sh 14.81	17.01	23.81sh					
	CHCl$_3$	12.50(1.62) 13.09(1.76)			28.74(3.79)	29.94(3.78)	32.89sh(3.66)	38.46(3.79)	48.54(3.25)
	DMSO			22.22sh(3.00)	24.88(3.83)	28.01(3.86)	33.11(3.86)		48.54(3.46)

[a] Band maximum in kK (log ε); ε in molar^{-1}cm^{-1}. [b] Sparingly soluble or insoluble hence the molar absorptivity is not reported.

REFERENCES

1. S. Yamada and K. Yamanouchi, *Bull. Chem. Soc. Japan*, **42,** 2562 (1969).
2. D.K. Rastogi and P.C. Pachauri, *J. Inorg. Nucl. Chem.*, **39,** 151 (1977).
3. U. Casellato, S. Sitran, S. Tamburini, P.A. Vigato and R. Graziani, *Inorg. Chim. Acta*, **114,** 111 (1986).
4. E. Sabbioni and E. Marafante, *Bioinorg. Chem.*, **9,** 389 (1978).
5. R.L. Robson, R.R. Eady, T.H. Richardson, R.W. Miller, M. Hawkins and J.R. Postgate, *Nature*, **322,** 288 (1986).
6. R. Cammack, *Nature*, **322,** 312 (1986).
7. N.D. Chasten, R.J. DeKoch, B.L. Rogers and M.W. Hanna, *J. Am. Chem. Soc.*, **95,** 1301 (1973).
8. I. Bertini, G. Canti, C. Luchinat and A. Scozzafara, *Inorg. Chim. Acta*, **36,** 9 (1979).
9. E. Frieden, *J. Chem. Educ.*, **62,** 917 (1985).
10. G.A. Hamilton and F.H. Westheimer, *J. Am. Chem. Soc.*, **81,** 6332 (1959).
11. R. Morton, *Prog. Chem. Org. Nat. Prod.*, **14,** 244 (1957).
12. A.D. Garnovskii, V.I. Minkin, O.A. Osipov, V.T. Panyushkin, L.K. Isaeva and M.I. Kuyazhanskii, *Russ. J. Inorg. Chem.*, **12,** 1288 (1967).
13. P.S. Relan, S.L. Chopra and I.S. Bhatia, *Proc. Chem. Symp.*, **2,** 31 (1969).
14. M.K. Misra, R.C. Das and S.K. Mahanty, *Indian J. Chem.*, **14A,** 679 (1976)
15. Y.L. Gol'dfarb, M.A. Pyranishnikova and K.A. Zhukova, *Bull. Acad. Sci. USSR*, **129,** 135 (1953).
16. A.C. Dash, B. Dash and P.K. Mahapata, *J. Chem. Soc., Dalton*, 1503 (1983).
17. G.A. Kolawole and K.S. Patel, *J. Chem. Soc., Dalton*, 1241, (1981).
18. C.J. Ballhansen and H.B. Gray, *Inorg. Chem.*, **1,** 111 (1962).
19. S. Kher, S.K. Sahni, V. Kumari and R.N. Kapoor, *Inorg. Chim. Acta*, **37,** 121 (1979).
20. P. Gluvchinsky, G.M. Mockler and E. Sinn, *Spectochim. Acata*, **33A,** 1073 (1977).
21. C.H. Kline, Jr. and J. Turkevich, *J. Chem. Phys.*, **12,** 300 (1944).
22. D.P. Madden, M.M. daMota and S.M. Nelson, *J. Chem. Soc. (A)*, 890 (1970).
23. J. Selbin, L.H. Holmes, Jr. and S.P. McGlynn, *J. Inorg. Nucl. Chem.*, **25,** 1359 (1963).
24. M. Mathew, A.J. Carty and G.J. Palenik, *J. Am. Chem. Soc.*, **92,** 3197 (1970).
25. H.A. Kuska and P. Yang, *Inorg. Chem.*, **13,** 1090 (1974).
26. K.S. Patel, G.A. Kolawole and A. Earnshaw, *J. Inorg. Nucl. Chem.*, **43,** 3107 (1982).
27. D. Ogden and J. Selbin, *J. Inorg. Nucl. Chem.*, **30,** 1227 (1968).
28. K.S. Patel and G.A. Kolawole, *J. Coord. Chem.*, in press.