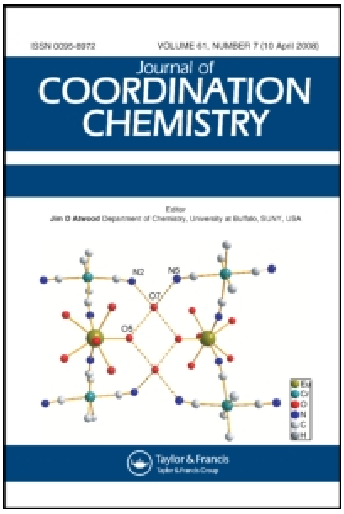

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

THE STEREOCHEMISTRY OF OXOVANADIUM(IV) COMPLEXES DERIVED FROM SUBSTITUTED 2-HYDROXY AROMATIC ALDEHYDES AND AROMATIC DIAMINES

Gabriel A. Kolawole[a]; Kantilal S. Patel[a]; Alan Earnshaw[b]
[a] Department of Chemistry, University of Ibadan, Ibadan, Nigeria [b] School of Chemistry, University of Leeds, Leeds, England

To cite this Article Kolawole, Gabriel A. , Patel, Kantilal S. and Earnshaw, Alan(1985) 'THE STEREOCHEMISTRY OF OXOVANADIUM(IV) COMPLEXES DERIVED FROM SUBSTITUTED 2-HYDROXY AROMATIC ALDEHYDES AND AROMATIC DIAMINES', Journal of Coordination Chemistry, 14: 1, 57 — 63

To link to this Article: DOI: 10.1080/00958978508080678

URL: http://dx.doi.org/10.1080/00958978508080678

J. Coord Chem., 1985, Vol. 14, pp. 57–63
0095-8972/85/1401-0057$18.50/0

THE STEREOCHEMISTRY OF OXOVANADIUM(IV) COMPLEXES DERIVED FROM SUBSTITUTED 2-HYDROXY AROMATIC ALDEHYDES AND AROMATIC DIAMINES

GABRIEL A. KOLAWOLE† and KANTILAL S. PATEL
Department of Chemistry, University of Ibadan, Ibadan, Nigeria

and

ALAN EARNSHAW
School of Chemistry, University of Leeds, Leeds LS2 9JT, England

(Received July 9, 1984)

Twelve Schiff-base complexes of oxovanadium(IV) obtained from 2-hydroxy aromatic aldehydes {salicyladehyde(sal), 3-methoxysalicylaldehyde(Omesal), 5-chlorosalicylaldehyde(Clsal) and nephthaldehyde (naph)} and aromatic diamines {1,2-diaminobenzene[orthophenylenediamine(opd)], 4-chloro-1,2-diaminobenzene(Clopd) and 1,2-diaminotobiene(dat)} have been synthesized and characterised by microanalysis, spectroscopic and magnetic susceptibility measurements. Although most of the complexes exhibit 'unusual' colours, their ν(V=0) frequencies (967–991 cm^{-1}) are normal for five co-ordinate VO^{II}-complexes. Their room-temperature effective magnetic moments fall in the range 1.71–1.84 B.M. and vary little between 320 and 80 K. The relative magnitude of the magnetic moments at 300 K and 80 K is Clsal>sal>Omesal>naph for any amine.

INTRODUCTION

Our previous studies on the stereochemistry of aliphatic – bridged quadridentate Schiff-base complexes of oxovanadium(IV)[1–4] showed that electronic changes in ligand structure cause negligible effects on stereochemistry as the alkyl bridge lengthens. In addition to the 'unusual' properties of the trimethylene-bridged derivatives obtained for all the aldehydes studied the tetramethylene-bridged derivative of 5-chlorosalicylaldimine, with some unique characteristics, has been reported.[4] In a further search for the role played by V=0 and the bridging group in the stereochemical disposition of this class of compounds, we have extended the studies to aromatic bridged derivatives, (I). The complexes are new except (1a)[5] and the studies constitute the first systematic work on oxovanadium(IV) Schiff-base complexes involving aromatic diamines.

EXPERIMENTAL

Complexes (1)–(3) were prepared by refluxing a suspension of 5 mmoles of oxovanadium(IV) acetate in 60 cm^3 absolute ethanol with 10–11 mmoles of salicylaldehyde and 5–6 mmoles of the respective diamines with constant stirring. The reaction was complete in 28, 24 and 25 h for the above complexes, respectively. On recrystallizing complex (1) from chloroform a product was obtained whose composition is best accounted for by assuming that it has dimerised and incorporated a molecule of chloroform(1b).[2] This complex lost only 1.93% of its weight after drying *in vacuo*

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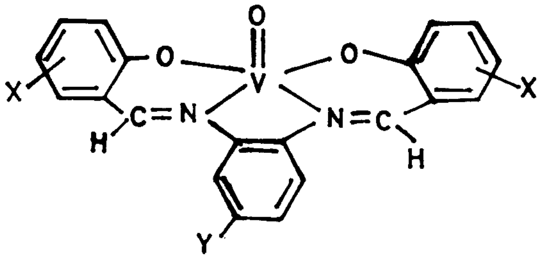
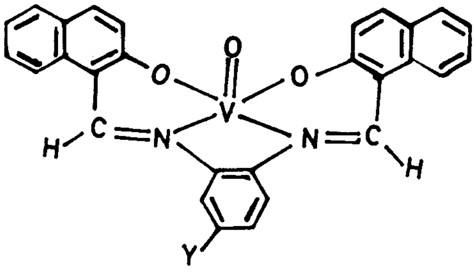
† To whom correspondence should be addressed.

(I)



Type A

Compound	X	Y	Formula
(1a)	H	H	VO(sal$_2$-opd)
(2)	H	4-Cl	VO(sal$_2$-Clopd)
(3)	H	4-CH$_3$	VO(sal$_2$-dat)
(4)	3-OCH$_3$	H	VO(3-omesal$_2$-opd)
(5)	3-OCH$_3$	4-Cl	VO(3-omesal$_2$-4-Clopd)
(6)	3-OCH$_3$	4-CH$_3$	VO(3-omesal$_2$-dat)
(7)	5-Cl	H	VO(5-Clsal$_2$-opd)
(8)	5-Cl	4-Cl	VO(5-Clsal$_2$-4-Clopd)
(9)	5-Cl	4-CH$_3$	VO(5-Clsal$_2$-dat)



Type B

	Y	
(10)	H	VO(naph$_2$-opd)
(11)	4-Cl	VO(naph$_2$-4-Clopd)
(12)	4-CH$_3$	VO(naph$_2$-dat)

in a drying pistol at 95° for 18 h; however, all the chloroform was lost in 12 h at 120° giving complex (1a).

Complexes (4)-(12) were prepared by refluxing a suspension of the bis(aldehyde) oxovanadium(IV) complexes in absolute ethanol with a slight excess of the various aromatic diamines as described elsewhere.[2,3]

The complexes were characterised by microanalysis, melting point determination, i.r. and electronic spectral and variable-temperature (320-80 K) magnetic susceptibility measurements as previously described.[1-3] Owing to the slimy nature of complexes (2) and (4) they could not be packed well and consequently their magnetic measurements were abandoned.

The microanalytical data, along with other physical parameters, are presented in Table I. Except for complexes (1a) and (3), which are green, all the other complexes exhibited diverse colours. The decomposition temperature of most of the complexes are found to be higher than those of their corresponding alkyl-bridged analogues.[1-4]

TABLE I
Analytical data for the complexes

Compound	% Yield	Colour	D.t.[†] (°)	%C Found (Calc.)	%H Found (Calc.)	%N Found (Calc.)	%Cl Found (Calc.)	%V Found (Calc.)
(1a)	75	green	313	62.90 (63.00)	3.70 (3.70)	6.85 (7.35)		13.11 (13.36)
(1b)[‡]		bright-green		55.85 (55.84)	3.35 (3.31)	6.35 (6.35)	12.03 (12.06)	11.50 (11.55)
(2)	76	orange-green	320	56.70 (57.78)	3.15 (3.15)	6.55 (6.74)	8.60 (8.53)	12.41 (12.25)
(3)	72	green	299	63.95 (63.81)	4.15 (4.08)	6.95 (7.09)		13.15 (12.89)
(4)	93	dirty-yellow	298	58.60 (59.87)	4.50 (4.11)	6.60 (6.35)		11.72 (11.54)
(5)	88	orange-green	294	55.40 (55.54)	3.68 (3.60)	5.75 (5.89)	7.60 (7.45)	10.62 (10.71)
(6)	80	mustard-brown	271	61.20 (60.67)	4.50 (4.43)	6.15 (6.15)		10.99 (11.19)
(7)	96	bright-mustard	340	53.40 (53.36)	3.10 (2.69)	6.00 (6.22)	15.75 (15.75)	11.00 (11.22)
(8)	95	mustard	>340	49.25 (49.57)	2.35 (2.29)	5.65 (5.78)	22.20 (21.95)	10.83 (10.51)
(9)	87	bright mustard	>340	54.40 (54.33)	3.05 (3.04)	6.25 (6.03)	15.25 (15.28)	10.84 (10.97)
(10)	94	maroon	>340	70.00 (69.86)	3.90 (3.77)	5.75 (5.82)		10.37 (10.58)
(11)	95	dirty-yellow	340	64.90 (65.19)	3.45 (3.32)	5.50 (5.43)	7.15 (6.87)	9.33 (9.87)
(12)	97	maroon	310	69.80 (70.31)	4.15 (4.07)	5.50 (5.65)		10.06 (10.28)

[†] Decomposition temperatures. [‡] Compound obtained on crystallising (1a) from chloroform analysed as $\{VO(sal_2\text{-}opd)\}_2.CHCl_3$.

RESULTS AND DISCUSSION

The relevant i.r. data are given in Table II. In type A complexes, (I), the ν(C=N) frequencies are at 1600–1608 cm^{-1}, a reduction of about 15 cm^{-1} with respect to the corresponding alkyl-bridged series.[1–4] The trend reveals that the polymeric six-coordinate trimethylene derivatives[1,4,6,7] are more planar and tend to have higher ν(C=N) frequencies. The reduction in ν(C=N) may therefore suggest that these complexes are somewhat slightly distorted, like their Cu(II) analogues.[8] In type B complexes, the ν(C=N) frequencies fall within the same range as in the alkyl-bridged derivatives.

The split of the band into a doublet suggests that the two azomethine groups are more distorted below and above the horizontal plane[3] than in Type A complexes. The distortion of the C=N groups implies that the overlap of π-orbitals is out of alignment and consequently that conjugation may not be so effective. The two ν(C=C) bands observed for all the complexes suggest non-equivalence of the aldehydic- and diamino-aromatic rings. The bands at 1570–1580 cm^{-1} are most probably due to ν(C=C) in the diamine aromatic ring since they are invariant for a particular amine irrespective of the aldehyde. The bands at 1550–1515 cm^{-1} which vary with changes in aldehyde and reflects the electronic disposition of the substituents on the aldehyde is assigned to the aldehydic ν(C=C) stretch.

The ν(V=0) frequencies in all the complexes are normal[9,10] for isolated V=0 in five coordinate complexes. The small shift to lower frequencies in complexes (2), (5), (7)–(9)

TABLE II
Relevant i.r. bands (cm^{-1}) for the complexes†.

Compound	ν(C=N)	ν(C=C)	ν(C-N)	ν(C-O)	ν(V=O)	ν(V-N)	ν(V-O)
(1)	1605vs	1578 m 1531vs	1378 s	1316vs	983vs	566 m	390 s
(2)	1603vs	1578 m 1530vs	1378vs	1320vs	992sh 967vs	556 s 488 m	399 m 334 w
(3)	1605vs	1580 m 1530vs	1375 s	1315 s	991vs 968sh	560 s 486 m	400 w
(4)	1605vs	1583 s 1549 s	1389 s	1320 s	981vs 971vs	577 s	377 m
(5)	1600vs	1578 m 1545 s	1381 s	1315 s	983sh 976vs	579 s	375 m
(6)	1610vs	1589 m 1549 s	1383 s	1318 s	980vs	580 m 504 m	373 m
(7)	1603vs	1578 s 1520vs	1376vs	1310 s	990sh 973vs	553 s 523 s 495 m	380 m 355 m 235 m
(8)	1600vs	1572 w 1518vs	1369vs	1302 s	985sh 970vs	581 m 560 m 523 s 493 m	441 m 362 m 338 w
(9)	1608vs	1581 w 1520 s	1370 s	1309 s	988sh 971 s	585 w 567 w 520 m 508 m	465 w 440 w 361 w 355 w
(10)	1616) 1600) vs	1575 s 1533vs	1380 m	1303 m	983sh 980vs	561 s 507 s 479 m	418 w 379 w 368 s 327 w 300 w
(11)	1616) 1599) vs	1572 m 1533vs	1378sh 1360vs	1304 m	983sh 980vs	567 s 510 s 480 m	465 w 431 m 324 w 314 w
(12)	1615) 1598) vs	1575 m 1536vs	1383 w 1360vs	1305 m	985vs	568 s 510 m 494 m	460 w 418 w 315 w 265 w

†vs = very strong; s = strong; m = medium; w = weak; sh = shoulder.

is due to the deactivating effect of the chloro substituent in either the aldehyde or the amine and is in agreement with previous reports.[11,12] It is therefore obvious that the 'unusual' colours of these complexes do not arise from polymerisation involving V=0 . . . V=0 . . . linkages but could be due to the extended conjugated double bonds in the complexes. It does not seem from the ν(V=0) values that the metal-centre is involved in π-delocalisation over the Schiff base plane as is the case in Co(sal$_2$-opd).[13]

It is suggested that the orange-yellow colour consistently observed[1–4, 6–7] in the trimethylene alkyl-bridged derivatives along with the attendant drastic reduction in ν(V=0) may be due to the planar geometry[6] imposed on the complex by the ligand which favours the delocalisation of the V=0 and C=N π-electrons into the six-membered ring resulting in a 'pseudo-conjugated (aromatic)' system.

The electronic spectral data are presented in Table III. Although the energy ordering proposed by Ballhausen and Gray[14] has been employed in assigning the bands we have incorporated our recent proposal[2] that in this class of complexes the e_π* and b_1* levels are inverted.

TABLE III
Electronic spectral data for the complexes.

Compound	Medium	Band maxima in kK ($\varepsilon/m^2\ mol^{-1}$)				
		$b_2 \rightarrow b_1^*$	$b_2 \rightarrow e_\pi^*$	$b_2 \rightarrow a_1^*$	C.T.	
(1)	R	12.35^b	15.38	21.28		25.64
	C		15.15(113)	$18.77^b(109)$		
	P	c				
(2)	R	12.50	17.24	22.22^b		25.32
	C	c				
	P	c				
(3)	R	12.05^b	15.27	21.05		26.67
			16.67^b			
	C	12.94(20)	$15.9^d(26)$	$19.30^b(31)$		
(4)	R	12.5^d	16.4^d	22.73		28.98
	C	13.52(120)	$16.75^b(107)$			
	P	c				
(5)	R	12.58	16.67^b	21.74	23.81	28.57^b
	C	c				
	P	c				
(6)	R	12.5^d	17.0^d	23.53	25.32	28.82
	C	c				
	P	c				
(7)	R	10.53	16.26	21.50	23.42	25.84
	C		$14.00^d(175)$	$18.77^b(236)$		
(8)	R	12.35^d	16.67	21.74	25.00	27.40
	C	$13.38^d(262)$	$16.46^d(291)$			$24.69^b(726)$
(9)	R	12.5^d	16.67^d		24.94	26.53
	C	e				
	P	c				
(10)	R	12.50^b	15.63	19.80	22.22	25.00
	C		16.80			
	P	c	14.57(128)			
(11)	R	12.99	13.79	21.05^b	22.37	28.57
	C	c				
	P	c				
(12)	R		15.38	21.51		26.67
	C		16.67			
	P	c	13.36(80)			

[a] R = Diffuse-reflectance, C = chloroform, P = pyridine. C.T. = Charge-transfer. [b] Shoulder. [c] A flat unresolved spectrum covering 10–20 kK. [d] Broad. [e] Insoluble in chloroform.

The spectra of complexes (1), (3), (10) and (12) in the solid and chloroform solutions are similar to those reported for five-coordinate square-pyramidal VO^{II} complexes.[1–4,15] However, in pyridine the spectra of these complexes were rather flat without any obvious band. This observation indicates that complexes (1), (3), (10) and (12) are five-coordinate in the solid and in chloroform but are six-coordinate[1,2] in pyridine. It therefore seems likely that these complexes offer less steric hindrance to axial ligation than their ethylenediamine analogues. The reflectance spectra of complexes (2), (4)-(9) and (11) are intermediate between those expected for five-coordinate square-pyramidal and six-coordinate distorted octahedral complexes. Except for minor shifts in band positions, the solution spectra of complexes (4), (7) and (8) in chloroform are similar to their reflectance spectra, but in pyridine they gave flat, unresolved spectra.

Complexes (2), (5), (6), (8) and (11) gave flat unresolved spectra in chloroform and pyridine solutions, indicating that they are six-coordinate in both solvents. Complex (9) was insoluble in chloroform but its spectrum in pyridine is flat.

TABLE IV
Variation of magnetic moments (μ_e/B.M.)[a] with temperature for the complexes.[b]

Compound / T(K)	(1)	(3)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
320	1.77	1.84	1.80	1.73	1.77	1.80	1.84	1.73	1.78	1.71
300	1.77	1.82	1.79	1.74	1.76	1.79	1.82	1.71	1.755	1.71
280	1.76	1.83	1.795	1.72	1.78	1.79	1.83	1.72	1.76	1.70
260	1.76	1.82	1.79	1.74	1.77	1.78	1.815	1.72	1.75	1.72
240	1.76	1.81	1.79	1.73	1.77	1.78	1.81	1.72	1.735	1.70
220	1.76	1.80	1.785	1.725	1.77	1.78	1.80	1.73	1.75	1.69
200	1.75	1.80	1.77	1.73	1.76	1.76	1.80	1.72	1.74	1.68
180	1.75	1.78	1.78	1.735	1.77	1.77	1.78	1.72	1.73	1.68
160	1.75	1.79	1.76	1.72	1.76	1.77	1.79	1.72	1.73	1.69
140	1.74	1.78	1.76	1.72	1.75	1.77	1.78	1.71	1.72	1.695
120	1.74	1.78	1.745	1.72	1.77	1.74	1.78	1.72	1.71	1.71
100	1.74	1.76	1.76	1.72	1.76	1.74	1.76	1.71	1.72	1.69
85	1.74	1.76	1.75	1.72	1.77	1.75	1.76	1.72	1.72	1.68
θ/K	8	4	11	1	1	8	c	0	3	6
$-\chi_L \times 10^6$ (cm^3 mol^{-1})	164	209	199	209	199	216	209	222	240	234

[a] The moments are calculated from the expression $\mu_e = 2.828\,(\chi_A \cdot T)^{1/2}$ and the Curie-Weiss law $\chi_A^{-1} \alpha (C + \theta)$. χ_A = Molar magnetic susceptibility. χ_L = Diamagnetic corrections for the ligands. C = Curie constant; 1 B.M. = 0.927 x 10^{-23} A m^2. [b] Complexes (2) and (4) are unsuitable for packing. [c] Curved.

The interpretation and the band assignment of the spectra of these complexes is made complex by the extended conjugation involving three aromatic rings containing bathochromic auxochrome substituents.[16] These have the effect that absorptions due to the ligands can occur in the visible region. While we do not rule out overlap between d-d and ligand transitions, it seems unlikely because of the low intensities of these transitions.

The magnetic data for ten of the complexes are tabulated in Table IV. With the exception of complexes (6), (10) and (12), which have 'normal' moments for a d^1-VO^{II} system, the room-temperature moments are higher than those reported for the five-membered ring alkyl-bridged analogues,[1-3] but fall within the range of values reported for the trimethylene-bridged derivatives.[1-4,7,17,18] and some five-coordinate trigonal bipyramidal complexes.[11] The magnetic data obey the Curie-Weiss law except for (9) whose χ_A^{-1} *vs* T plots gave a curve. The variation of effective magnetic momenet and θ-value is very small, indicating the absence of any appreciable interaction. The relative magnitude of the magnetic moments at 300 K and 80 K is Clasal>sal>Omesal>naph for any amine in agreement with observations made previously.[1-4]

These complexes are obviously more planar than the corresponding alkyl-bridged analogues but less planar than the trimethylene bridged polymeric complexes. Although the planarity is such that it favours axial solvent interaction, it is not enough to favour polymerisation involving . . . V=0 . . . V=0 linkages. We are, however, not ruling out some form of molecular aggregation in these complexes.

ACKNOWLEDGEMENT

The authors are grateful to Professor N.N. Greenwood for allowing the use of the facilities of the School of Chemistry, University of Leeds.

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