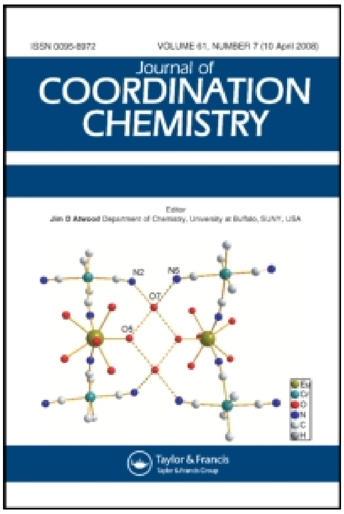


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SPECTROSCOPIC AND MAGNETOCHEMICAL INVESTIGATION OF OXOVANADIUM(IV) 5-CHLOROSALICYLALDIIMINES

Gabriel A. Kolawole[a]; Kantilal S. Patel[a]
[a] Department of Chemistry, University of Ibadan, Ibadan, Nigeria

To cite this Article Kolawole, Gabriel A. and Patel, Kantilal S.(1983) 'SPECTROSCOPIC AND MAGNETOCHEMICAL INVESTIGATION OF OXOVANADIUM(IV) 5-CHLOROSALICYLALDIIMINES', Journal of Coordination Chemistry, 12: 2, 121 — 127

To link to this Article: DOI: 10.1080/00958978308073839

URL: http://dx.doi.org/10.1080/00958978308073839

J. Coord. Chem., Vol. 12, pp. 121–127
0095-8972/82/1202-0121 $6.50/0

SPECTROSCOPIC AND MAGNETOCHEMICAL INVESTIGATION OF OXOVANADIUM(IV) 5-CHLOROSALICYLALDIIMINES

GABRIEL A. KOLAWOLE† and KANTILAL S. PATEL

Department of Chemistry, University of Ibadan, Ibadan, Nigeria.

(*Received March 19, 1982*)

The oxovanadium (IV) complexes of 5-chlorosalicylaldehyde, VO(5-Clsal)$_2$, and its aliphatic diamine derivatives with a general formula, $VO[OC_6ClH_3CH{=}N{-}CR^1R^2(CH_2)_{n-1}-N{=}CHC_6ClH_3O]$ where $n = 2$ ($R^1 = R^2 =$ H or CH_3) and $n = 3$–5 ($R^1 = R^2 =$ H), have been prepared.

Their spectroscopic and magnetic properties suggest that the complexes (1–3; $n = 2$, $R^1 = R^2 =$ H or CH_3) and (6; $n = 5$, $R^1 = R^2 =$ H) are five-coordinate, while VO(5-Clsal)$_2$ and complexes (4 and 5; $n = 3$ and 4, $R^1 = R^2 =$ H) are likely to be six-coordinate and, presumably polymeric.

INTRODUCTION

In our recent studies on the oxovanadium(IV) complexes of quadridentate salicylaldiimine[1] and 3-methoxysalicylaldiimine[2] Schiff-bases containing the N_2O_3 chromophore and long-chain alkyl equatorial bridges it was found that apart from the trimethylene derivatives (having a six-membered equatorial ring-size about V) which were orange-yellow and polymeric, substitution in the aromatic rings did not effect significantly the trend in the stereochemistry of the complexes. Consequently, it appears that geometric factors play a somewhat more major role than electronic factors.

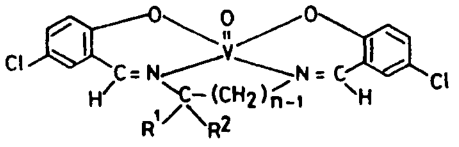
In the present studies we have focused our attention on the effect of the electron-withdrawing chlorine atom on the stereochemistry of the quadridentate Schiff-base oxovanadium(IV) complexes, I, in anticipation that any differences in the spectroscopic and magnetic properties should be due to the substituent effect since the local geometry around the vanadium atom remains N_2O_3.

EXPERIMENTAL

The complexes were prepared from bis(5-chlorosalicylaldehyde) oxovanadium(IV) using the method described previously.[2,3] The period of refluxing ranged from 1h in *N,N′*-bis(5-chlorosalicylidene) ethylenediiminatooxovanadium(IV), (1, $n = 2$, $R^1 = R^2 =$ H) to 42h in the pentamethylene derivative (6, $n = 5$, $R^1 = R^2 =$ H). Attempts to isolate pure samples of the hexamethylene derivatives were unsuccessful. No suitable solvent was found to recrystallise the complexes; consequently they were purified by digestion with ethanol a number of times and, where necessary, by Soxhlet extraction using either ethanol or methanol. The

---

†To whom correspondence should be addressed.



Compound	R^1	R^2	n	Abbreviation
(1)	H	H	2	VO(5-Clsal$_2$-en)
(2)	H	CH_3	2	VO(5-Clsal$_2$-pn)
(3)	CH_3	CH_3	2	VO(5-Clsal$_2$-Mepn)
(4)	H	H	3	VO(5-Clsal$_2$-tn)
(5)	H	H	4	VO(5-Clsal$_2$-tm)
(6)	H	H	5	VO(5-Clsal$_2$-ptn)

The bis-aldehyde complex, VO(5-Clsal)$_2$,
is given number 0

I

resulting products were analytically pure (Table I) and were further characterised by melting-point determinations, i.r. and electronic spectral measurements, and variable temperature magnetic susceptibility measurements as previously described.[1-3] VO(5-Clsal)$_2$ was found to be electrostatic and stuck to the side of the inner dewar of the Gouy cryostat below 140K irrespective of the inner diameter and thickness of the silica tube used for packing.

RESULTS AND DISCUSSION

Unlike the earlier series reported[1,2] VO(5-Clsal)$_2$ is mustard coloured, while VO(5-Clsal$_2$ – tm), (5, $n = 4$, $R^1 = R^2 = H$) is yellow, the first in this class of compounds having —N—C—C—C—C—N— bridge-length to be reported. The decomposition temperatures of the complexes are high (>200°C) and they were found to be sparingly soluble in non-coordinating solvents, and insoluble in nitromethane, acetonitrile, DMSO and THF. However, they dissolved in pyridine except (4; $n = 3$, $R^1 = R^2 = H$) and (5; $n = 4$, $R^1 = R^2 = H$).

The i.r. data are presented in Table II. Unlike in the earlier series[2,3] the ν(C═O) frequency in VO(5-Clsal)$_2$ is higher than the ν(C═N) frequencies in the Schiff-base complexes, except in (4; $n = 3$, $R^1 = R^2 = H$) where the two frequencies are alike. However, the ν(C═N) frequency in (4) is higher than the ν(C═N) frequency in the other members of the homologous series which suggests that VO(5-Clsal)$_2$ is more planar. This observation is further strengthened by a reduction of about 100–150 cm^{-1} in the ν(V═O) frequencies of VO(5-Clsal)$_2$, VO(5-Clsal$_2$—tn) and VO(5-Clsal$_2$—tm). The similarity in colour and magnitude of the ν(V═O) frequencies in these three complexes indicate that they are six-coordinate and polymeric.[1-5] The ν(V═O) frequencies in (1), (2), (3) and (6) are normal[6] for five-coordinate oxovanadium(IV) complexes and falling within the same range reported for the unsubstituted salicyladiimine complexes[1] showing that the electron-withdrawing effect of chlorine is not transmitted to the V═O bond.

The electronic spectral data are tabulated in Table III and presented in Figure 1. The

TABLE I

Colour, melting point, yield and analytical data for the oxovanadium(IV) complexes

					Analysis, Found (calcd.) %				
	Compound	Colour	M.p(°)[a]	Yield (%)	C	H	N	Cl	V
(0)	$VO(5\text{-}Clsal)_2$	mustard	223	68	42.85 (44.48)	1.95 (2.13)	—	19.15 (18.76)	13.62 (13.47)
(1)	$VO(5\text{-}Clsal_2\text{-}en)$	fibrous-green	322	90	47.75 (47.99)	3.10 (3.01)	7.25 (6.97)	17.55 (17.63)	12.58 (12.67)
(2)	$VO(5\text{-}Clsal_2\text{-}pn)$	green	299	88	48.85 (49.07)	3.40 (3.39)	6.55 (6.73)	16.45 (17.04)	12.37 (12.24)
(3)	$VO(5\text{-}Clsal_2\text{-}Mepn)$	slimy-green	312	78	50.26 (50.26)	3.79 (3.75)	6.52 (6.51)	15.55 (16.48)	11.79 (11.84)
(4)	$VO(5\text{-}Clsal_2\text{-}tn)$	orange-yellow	310	92	48.75 (49.07)	3.30 (3.39)	6.30 (6.73)	16.95 (17.04)	12.40 (12.24)
(5)	$VO(5\text{-}Clsal_2\text{-}tm)$	yellow	317	88	50.45 (50.26)	3.75 (3.75)	6.35 (6.51)	16.80 (16.48)	11.68 (11.84)
(6)	$Vo(5\text{-}Clsal_2\text{-}ptn)$	grey-green	228	91	50.05 (51.37)	4.10 (4.08)	5.85 (6.31)	17.30 (15.95)	11.63 (11.47)

[a] With decomposition.

TABLE II
Relevant infrared frequencies of the oxovanadium(IV) complexes

Compound	Frequencies (cm^{-1})			
	ν(C=N)	ν(V=O)	ν(V—N)	ν(V—O)
(0)	1630vs[a]	882vs[b]	—	475m 452w 252m
(1)	1619vs	974vs	540m 487m 375w	466m 433w 242w
(2)	1623vs	990vs	522m 501s 400w	470m 445w 246m
(3)	1615vs	983vs	510s 410w	458s 445m
(4)	1628vs	865vs[b]	516m 380m	472m 447m 299s 251s
(5)	1618vs	960s 880vs[b]	515w 487s 379m	455m
(6)	1619vs	983vs 876m[b] ?	492m 364w	460w

[a] Corresponding ν(C=O) in the bis(5-chlorosalicylaldehyde) complex.
[b] V—O—V vibrational frequencies.
vs = very strong, s = strong, m = medium, w = weak.

diffuse-reflectance spectrum of $VO(5\text{-}Clsal)_2$ is similar to the spectrum of (4) and the spectra reported[1,2,4] for the 6-coordinate polymeric trimethylene derivatives of similar ligands. The chloroform solution spectrum of $VO(5\text{-}Clsal)_2$ is obliquely flat without any obvious band. This behaviour indicates that this compound is six-coordinate in the solid and in chloroform solution.[1] Three bands were observed in pyridine solution corresponding to the d—d transitions[6] $b_2 \rightarrow b_1^*$, $b_2 \rightarrow e_\pi^*$ and $b_2 \rightarrow a_1^*$ expected for a square-pyramidal complex. It is likely that $VO(5\text{-}Clsal)_2$ breaks down to monomers in pyridine but without any strong axial ligation.

Compounds (1), (2) and (3), like their previously reported analogues,[1-3,7,8] have similar spectra in solids, chloroform and pyridine solutions. In addition to a band at 16,000–17,000 cm^{-1} in these complexes the reflectance spectrum of (1) shows two shoulders at 12,120 cm^{-1} and 21,280 cm^{-1}. Using a relatively dilute solution (2×10^{-4} mol dm^{-3}) a charge-transfer band was observed, in addition to the d—d transition for (1), at 26,260 cm^{-1} ($\varepsilon = 744$ m^2 mol^{-1}). A facile interaction[9] of pyridine with vanadium is indicated by the reduction in the molar absorptivity of band II in this solvent. The spectra of these complexes in pyridine also show a long 'tail' at low energy. A low intensity band is therefore most probable at 12,000–14,000 cm^{-1}.

The spectra of (4) in the solid and in chloroform are similar to those of corresponding complexes reported[1,2] earlier and it is therefore six-coordinate and polymeric. The reflectance spectrum of (5) is unique, having two bands at ~9,900 cm^{-1} and 12,990 cm^{-1}. Considering the intensities of these bands, they could be assigned as:

$$d_{xy} \rightarrow d_{x^2-y^2} \text{ and } d_{xy} \rightarrow d_{xz}, d_{yz} \quad \text{or} \quad d_{xy} \rightarrow d_{xz} \text{ and } d_{xy} \rightarrow d_{yz} \text{ respectively.}$$

TABLE III
Electronic spectral data on the oxovanadium(IV) complexes

		Band maxima/1000 cm^{-1} (ε/m^2 mol^{-1})			
Compound	Medium[a]	Band I $b_2 \rightarrow b_1^*$	Band II $b_2 \rightarrow e_\pi^*$	Band III $b_2 \rightarrow a_1^*$	C.T.[b]
(0)	R	11.76			26.67
	P	13.18(13)	17.04(20)	19.44(28)	—
(1)	R	12.12	17.09	21.28	23.81 27.62
	C		16.74(108)		26.62(744)
	P		16.76(20)		
(2)	R	15.87	16.67	20.96	25.00 28.17
	C		16.35(55)		
	P		16.75(20)		
(3)	R		16.67		25.97 27.03
	C		16.46(56)		
	P		16.71(20)		
(4)	R		10.99	19.80	26.18
	C		~15.75br		
(5)	R	~9.90[d]	12.99		28.99
(6)	R	~10.00[d] 11.98	16.95	18.80	28.17
	P	13.71(6)		19.36(10)	

[a] R = Diffuse – reflectance, C = chloroform, P = pyridine.
[b] Charge – transfer bands. [d] By extrapolation. br = Broad.

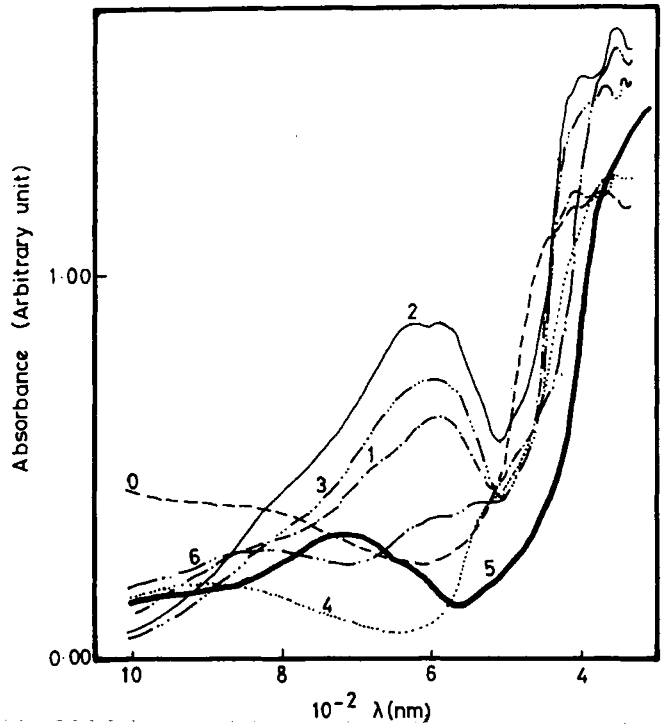


FIGURE 1 Reflectance spectra of the 5-chlorosalicylaldiimine complexes.

TABLE IV

Variable temperature magnetic moments (μ_e/B.M.)[a] for the oxovanadium(IV) complexes

Compound Temp. (K)	(0)	(1)	(2)	(3)	(4)	(5)	(6)
320.0	1.78	1.79	1.79	1.76	1.83	1.85	1.79
300.0	1.77	1.81	1.785	1.76	1.83	1.86	1.80
280.0	1.76	1.795	1.78	1.75	1.82	1.87	1.78
260.0	1.76	1.80	1.78	1.74	1.81	1.87	1.77
240.0	1.76	1.78	1.78	1.74	1.79	1.865	1.77
220.0	1.74	1.78	1.77	1.74	1.80	1.85	1.76
200.0	1.74	1.78	1.77	1.74	1.79	1.85	1.75
180.0	1.73	1.77	1.76	1.73	1.78	1.85	1.74
160.0	1.73	1.755	1.75	1.73	1.775	1.85	1.74
140.0	1.72	1.76	1.74	1.72	1.77	1.84	1.74
120.0	—	1.75	1.73	1.71	1.77	1.84	1.73
100.0	—	1.75	1.72	1.705	1.76	1.84	1.725
83.0	—	1.75	1.72	1.70	1.76	1.84	1.72
θ(K)	[b]	[c]	13	9	[c]	4	5[d]
$-\chi_L \times 10^6$(cm^3 mol^{-1})	193	221	233	245	233	245	257

[a] The moments are calculated from the expression $\mu_e = 2.828(\chi_A \cdot T)^{1/2}$ and the Curie–Weiss law χ_A^{-1} $(C + \theta)$. χ_A = Molar magnetic susceptibility; C = Curie constant; 1 B.M. = 0.927×10^{-23} Am^2.

[b] See text (Experimental).

[c] Curved.

[d] θ-value for low temperatures because of deviation at high temperatures.

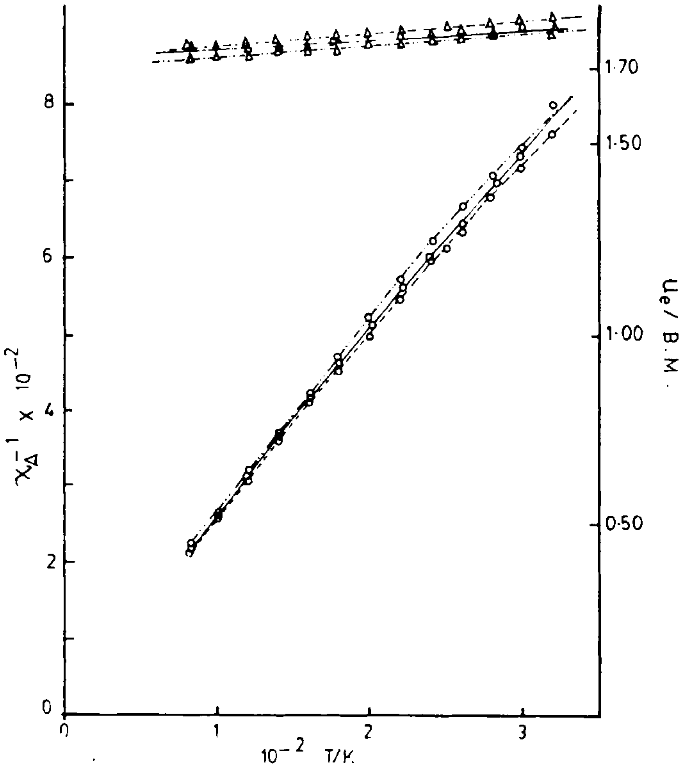


FIGURE 2 Variation of magnetic susceptibility (O), and magnetic moment (Δ) with temperature for complexes (1) —, (4) - - -, and (6) - · · - · · -

The first assignment implies the inversion of the e_{π}^{*} and b_1 levels[2,10] whereas the latter assumes the possibility of a split of the e_{π}^{*} degenerate level[11-13]. It is difficult on the strength of our results to deduce the absolute stereochemistry of this complex but it seems that although the complex is polymeric, the polymerisation leaves some VO-entity in C_{2v} and some in distorted O_h or even trigonal bipyramidal[14] environments. The reflectance spectrum of (6) gives four bands indicating a square-pyramidal geometry but in pyridine the complex is six-coordinate.[1]

The variable temperature magnetic susceptibility data are tabulated in Table IV and presented in Figure 2. All the room temperature magnetic moments are high (1.76–1.86 B.M.), falling within the range reported for six-coordinate VO^{2+}-complexes[5,15,16] or five-coordinate trigonal bipyramidal complexes.[14] However, there are larger variation of moment with temperature when compared with similar compounds reported previously.[1-3] The χ_A^{-1}vs. T plots for (1), (4) and (6) are curved at high temperatures (Figure 2) but at low temperatures tend to obey the Curie–Weiss law. This suggests a strong TIP effect or possibly some form of structural rearrangement at low temperatures.

A small but significant increase in moments is found to accompany increases in the length of the methylene bridge. A corresponding increase in similar copper complexes[18,19] was interpreted as being indicative of an increasing distortion from planarity towards a tetrahedral geometry. It is difficult to make a parallel deduction in these complexes but it seems this trend reflects the stereochemical changes that are observed to accompany lengthening the methylene bridge.

ACKNOWLEDGEMENT

We are grateful to Dr. Earnshaw for making available the facilities of his laboratory.

REFERENCES

1. G. A. Kolawole and K. S. Patel, *J. Chem. Soc. (Dalton)*, 1241 (1981).
2. K. S. Patel, G. A. Kolawole and A. Earnshaw, *J. Inorg. Nucl. Chem.*, **43**, 3107 (1981).
3. K. S. Patel and G. A. Kolawole, *J. Coord. Chem.*, **11**, 231 (1982).
4. M. Mathew, A. J. Carty, and G. J. Palenik, *J. Am. Chem. Soc.*, **92**, 3197 (1970).
5. R. L. Farmer and F. L. Urbach, *Inorg. Chem.*, **13**, 587 (1974).
6. C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).
7. L. J. Boucher and T. F. Yen, *Inorg. Chem.*, **8**, 689 (1969).
8. K. S. Patel and J. C. Bailar, Jr., *J. Coord. Chem.*, **3**, 113 (1973).
9. A. Pasini and M. Gullotti, *J. Coord. Chem.*, **3**, 319 (1974).
10. J. Selbin, L. H. Holmes, Jr., and S. P. McGlynn, *J. Inorg. Nucl. Chem.*, **25**, 1359 (1963).
11. J. Selbin, T. R. Ortolano and F. J. Smith, *Inorg. Chem.*, **2**, 1315 (1963).
12. G. Baus, W. Yeranos and R. L. Belford, *Inorg. Chem.*, **3**, 929 (1964).
13. H. A. Kuska and P. Yang, *Inorg. Chem.*, **13**, 1090 (1974).
14. M. Pasquali, F. Marchetti and C. Floriani, *J. Chem. Soc. (Dalton)*, 139 (1977).
15. J. J. R. Frausto da Silva, R. Wootton and R. D. Gillard, *J. Chem. Soc.*, 3369 (1970).
16. G. D. Simpson and G. O. Carlisle, *Inorg. Nucl. Chem. Lett.*, **9**, 815 (1973).
17. F. E. Mabbs and D. J. Machin, *Magnetism and Transition Metal Complexes*, London, Chapman and Hall, p. 22 (1973).
18. S. J. Gruber, C. M. Harris and E. Sinn, *Inorg. Nucl. Chem. Lett.*, **4**, 107 (1968).
19. S. J. Gruber, C. M. Harris and E. Sinn, *J. Inorg. Nucl. Chem.*, **30**, 1805 (1968).