Oxovanadium(IV) Complexes containing Bidentate Schiff-base Ligands: Synthesis and Structural and Spectroscopic Data [1]

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The synthesis and properties of some oxovanadium(IV) complexes, [VOL$_2$], containing *N*-substituted salicylaldimines (L) are reported. An unusually low V=O stretching frequency (<900 cm^{-1}) has been observed when R = C$_6$H$_4$Cl-4 and C$_6$H$_4$NO$_2$-4. This reduction in frequency has previously been attributed to polymerisation of the V=O unit, however the present crystal-structure analysis shows that bis[N-(4-chlorophenyl)salicylideneiminato]-oxovanadium(IV) is monomeric in the solid state. The co-ordination polyhedron, which in the crystal has C_2 symmetry, is based on a distorted trigonal bipyramid. The three oxygen and vanadium atoms are in the equatorial plane and the two nitrogen donors occupy axial positions. The vanadium–oxygen bond length (1.615 Å) is among the largest found in oxovanadium complexes.

IN recent years the complexes of oxovanadium(IV) have received considerable attention.[2] The [VO]$^{2+}$ unit is well known for its ability to co-ordinate four (VOL$_4$) and more rarely five (VOL$_5$) donor atoms. The electronic configuration [Ar]d^1 of V^{IV} makes the oxovanadium(IV) complexes ideal models for magnetic investigations, in different co-ordination environments.[3] A square-pyramidal geometry has been established, or more frequently assumed, for five-co-ordinate oxovanadium(IV) chelate complexes,[2,4] even when at least one example has appeared which serves to shake the confidence in the usual assumptions concerning the structure of vanadyl complexes.[5] Six-co-ordination of V^{IV} may be sometimes achieved in the solid state in oxovanadium(IV) complexes *via* interaction with an oxygen of an other VO unit.[6] The reduction of the V=O bond wavenumber from 950—1 000 to 800—850 cm^{-1} is generally regarded as being diagnostic for this solid-state ' polymerisation '.[7] The utilisation of vanadyl complexes in chemical-reactivity studies either as models for V–O bond reactivity [1] or as potential free-radical-like activators of organic and inorganic molecules [8] makes the knowledge of their structure and relation with the spectroscopic data a fundamental starting point. This paper describes the synthesis of some oxovanadium(IV) complexes containing *N*-substituted salicylaldimines as ligands, for some of which an unusual low V=O stretching vibration frequency has been found. The *X*-ray crystal-structure analysis for bis[*N*-(4-chlorophenyl)salicylideneiminato]oxovanadium(IV) is reported.

EXPERIMENTAL

Solvents were purified by standard methods. All the Schiff bases were prepared by mixing an ethanol solution of the salicylaldehyde and the corresponding amine. I.r. spectra were recorded on a Perkin-Elmer 337 spectrometer and magnetic-susceptibility measurements were made with a Gouy balance. A typical synthesis is described in detail, the preparation of the other complexes being carried out under very similar conditions.

Bis[N(4-*chlorophenyl*)*salicylideneiminato*]*oxovanadium*-(IV), (1; R = C$_6$H$_4$Cl-4).—The salt [VO][SO$_4$]·5H$_2$O (3.30 g, 13 mmol) was dissolved in water (100 cm^3) and the solution was added to a warm stirred solution of *N*-(4-chlorophenyl)-salicylaldimine (6.00 g, 26 mmol) in ethanol (95%, 100 cm^3) yielding a yellow-green solid. An aqueous solution (50 cm^3) of Na[O$_2$CMe] (4.6 g, 56 mmol) was added and the suspension was boiled with stirring for 20 min. The suspension was allowed to stand for 2 h, then the golden-yellow solid was filtered off and washed with water, ethanol, and diethyl ether (yield *ca.* 80%). The solid (1 g) is fairly soluble in hot CS$_2$ (30 cm^3) giving a brown solution, from which yellow-brown monoclinic crystals, used for the crystallographic work, can be obtained.

Crystal Data.—The cell data were determined by means of rotation and Weissenberg spectra, with nickel-filtered Cu-K_α radiation (λ 1.541 8 Å), and by precession spectra with zirconium-filtered Mo-K_α radiation (λ 0.710 7 Å). C$_{26}$H$_{18}$Cl$_2$N$_2$O$_3$V, M 528.3, Space group $P2_1/n$ (from systematic absences), a = 11.08(2), b = 21.14(3), c = 10.06(2) Å, β = 99.0(2)°, U = 2 326.6 Å^3, D_c = 1.508 g cm^{-3}, Z = 4, F(000) = 1 076. After Cu-K_α irradiation the intensity data were collected by means of Weissenberg photographs using the multiple-film technique and integrating process. A crystal of nearly prismatic shape elongated in the c direction (0.6 mm) with cross dimensions 0.3 × 0.28 mm (mean μR 0.99) was rotated about the c axis and ten layers (l = 0—9) were collected. A total of 1 778 independent reflections was observed. Intensities measured by a Nonius microdensitometer were corrected for Lorentz and polarisation factors; no correction was made for the transmission factor owing to the relatively small dimensions of the crystal. The attribution of phases to the structure factors was accomplished with direct methods, by application of the ' MULTAN ' programme.[9] This located nearly all the heavy atoms. The structure was completed by means of successive Fourier syntheses. All the calculations were made by use of programs in the ' *X*-ray '70 ' system.[10]

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[9] MULTAN, program written by P. Main, M. M. Woolfson, and G. Germain, *Acta Cryst.*, 1971, **A27**, 368.

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TABLE 1

Final atomic positional and anisotropic temperature parameters ($\times 10^4$). * Estimated standard deviations are in parentheses

	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
V	0.581 3(2)	0.351 0(1)	0.121 4(2)	40(1)	12(1)	39(2)	−1(1)	14(1)	3(1)
Cl(1)	1.188 0(3)	0.408 6(2)	0.514 0(4)	46(2)	28(1)	107(5)	−2(1)	−16(3)	−1(2)
Cl(2)	−0.029 6(3)	0.349 1(2)	−0.257 8(4)	77(3)	31(1)	127(5)	−9(2)	−31(3)	13(2)
O(1)	0.488 9(6)	0.405 6(4)	−0.006 5(8)	49(7)	15(2)	61(10)	2(3)	18(6)	12(4)
O(2)	0.637 2(6)	0.357 8(4)	0.309 2(8)	43(6)	22(2)	58(10)	−6(3)	16(6)	0(4)
O(3)	0.621 3(7)	0.286 5(4)	0.054 4(8)	71(8)	13(2)	70(11)	4(3)	27(7)	−4(4)
N(1)	0.738 2(7)	0.408 1(4)	0.100 1(9)	37(7)	14(3)	50(12)	1(4)	17(7)	−5(4)
N(2)	0.407 4(8)	0.325 7(4)	0.174 3(9)	46(8)	16(3)	47(12)	−5(4)	15(7)	0(4)
C(1)	0.519 0(10)	0.439 0(5)	−0.104 3(12)	63(10)	12(3)	52(16)	4(5)	22(10)	−4(5)
C(2)	0.422 6(10)	0.461 0(6)	−0.210 3(10)	77(12)	15(3)	16(14)	−2(5)	2(9)	1(5)
C(3)	0.448 7(12)	0.497 6(6)	−0.313 7(13)	87(13)	14(3)	57(16)	−5(5)	−5(11)	−2(6)
C(4)	0.572 1(14)	0.514 9(7)	−0.320 5(14)	124(16)	25(4)	55(17)	−7(7)	30(13)	0(7)
C(5)	0.665 3(11)	0.495 9(6)	−0.222 1(12)	72(12)	18(4)	45(16)	−6(5)	5(10(	−3(6)
C(6)	0.641 5(10)	0.456 0(5)	−0.112 6(12)	61(10)	10(3)	65(16)	−1(5)	27(10)	5(5)
C(7)	0.739 0(9)	0.443 5(5)	−0.008 7(12)	37(9)	13(3)	63(15)	1(4)	18(9)	5(5)
C(8)	0.845 5(9)	0.408 9(6)	0.197 3(11)	34(8)	17(3)	55(14)	1(4)	6(8)	4(6)
C(9)	0.904 6(10)	0.466 4(6)	0.242 3(12)	49(10)	15(3)	76(16)	−8(5)	5(10)	−10(6)
C(10)	1.010 6(11)	0.467 4(6)	0.336 1(13)	55(11)	18(4)	78(17)	−16(5)	20(10)	0(6)
C(11)	1.054 6(10)	0.409 5(6)	0.397 5(12)	52(10)	19(4)	67(16)	2(5)	15(10)	−5(6)
C(12)	0.996 4(10)	0.352 6(6)	0.355 3(13)	52(10)	15(3)	113(18)	1(5)	25(10)	4(7)
C(13)	0.890 0(10)	0.352 9(6)	0.259 1(12)	46(9)	18(3)	76(16)	−1(5)	1(9)	7(6)
C(14)	9.593 1(10)	0.337 4(5)	0.418 6(12)	65(11)	12(3)	52(15)	9(5)	28(10)	7(5)
C(15)	0.670 0(11)	0.343 6(7)	0.543 8(12)	66(11)	25(4)	50(15)	0(6)	−1(10)	−3(6)
C(16)	0.632 4(11)	0.325 5(6)	0.663 1(13)	80(12)	14(3)	81(17)	13(5)	16(11)	8(6)
C(17)	0.513 6(14)	0.299 9(7)	0.658 3(13)	138(17)	21(4)	43(16)	6(7)	40(13)	4(6)
C(18)	0.436 2(12)	0.293 9(6)	0.536 4(13)	91(13)	19(4)	58(17)	1(6)	33(12)	18(6)
C(19)	0.473 1(10)	0.312 5(6)	0.415 3(12)	56(10)	13(3)	48(15)	1(4)	19(9)	2(5)
C(20)	0.389 2(10)	0.310 2(5)	0.293 4(11)	61(10)	14(3)	57(15)	−4(5)	40(10)	−1(5)
C(21)	0.301 4(10)	0.329 9(5)	0.070 4(11)	67(10)	10(3)	36(14)	−10(4)	10(9)	−1(5)
C(22)	0.302 0(10)	0.302 7(6)	−0.055 9(12)	45(10)	20(4)	69(17)	−3(5)	−11(10)	5(6)
C(23)	0.200 8(11)	0.309 2(6)	−0.155 8(14)	66(12)	21(4)	94(19)	−5(6)	13(11)	5(7)
C(24)	0.097 5(10)	0.340 6(6)	−0.130 2(13)	47(10)	19(4)	114(19)	−13(5)	−3(10)	5(6)
C(25)	0.096 6(11)	0.367 3(6)	−0.005 2(13)	62(11)	24(4)	82(18)	9(5)	16(11)	−3(7)
C(26)	0.195 6(12)	0.360 7(7)	0.095 3(13)	86(13)	23(4)	83(18)	−2(6)	40(12)	−9(7)

* The temperature factors are of the form: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Atomic co-ordinates, scale factors, and thermal parameters were refined by full-matrix least squares assuming isotropic thermal motion for all the atoms and assigning unit weight to all the observations. At this stage $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.11$ for the observed reflections. Anisotropic temperature factors were then introduced using the weighting scheme $w^{\frac{1}{2}} = 1/(a + |F_o| + b|F_o|^2)$ where $a = 40.0$ and $b = 0.01$. Two further refinement cycles reduced R to 0.09. Hydrogen atoms were introduced in calculated positions with isotropic temperature factors of 6.0 Å^2. One further refinement cycle in which hydrogen parameters were not varied gave R 0.08. Structure amplitudes are available as Supplementary Publication No. SUP 21853 (8 pp.).*

Scattering factors used in the structure-factor calculations were taken from ref. 11 for all the atoms. Computation was carried out on an I.B.M. 370/158 computer at the Centro Nazionale Universitario di Calcolo Elettronico, Pisa. Atomic co-ordinates and molecular dimensions are given in Tables 1—3.

TABLE 2

Bond distances (Å) with estimated standard deviations. The values in the last column were obtained on averaging corresponding bond lengths in the two halves of the molecule

V–O(3)	1.615(8)			
V–O(1)	1.902(7)	V–O(2)	1.900(8)	1.901
V–N(1)	2.153(9)	V–N(2)	2.145(9)	2.149
O(1–C(1)	1.296(14)	O(2)–C(14)	1.342(15)	1.319
C(1)–C(2)	1.463(15)	C(14)–C(15)	1.413(15)	1.438
C(2)–C(3)	1.362(17)	C(15)–C(16)	1.384(19)	1.373
C(3)–C(4)	1.427(20)	C(16)–C(17)	1.416(19)	1.422
C(4)–C(5)	1.375(17)	C(17)–C(18)	1.389(17)	1.382
C(5)–C(6)	1.433(17)	C(18)–C(19)	1.400(18)	1.422
C(6)–C(1)	1.418(16)	C(19)–C(14)	1.425(16)	1.422
C(6)–C(7)	1.406(15)	C(19)–C(20)	1.419(15)	1.413
C(7)–N(1)	1.328(15)	C(20)–N(2)	1.287(15)	1.308
N(1)–C(8)	1.417(12)	N(2)–C(21)	1.448(13)	1.433
C(8)–C(9)	1.421(17)	C(21)–C(26)	1.396(18)	1.409
C(9)–C(10)	1.387(16)	C(26)–C(25)	1.378(17)	1.383
C(10)–C(11)	1.422(18)	C(25)–C(24)	1.380(19)	1.401
C(11)–Cl(1)	1.737(11)	C(24)–Cl(2)	1.760(12)	1.749
C(11)–C(12)	1.400(18)	C(24)–C(23)	1.381(18)	1.391
C(12)–C(13)	1.403(15)	C(23)–C(22)	1.391(16)	1.397
C(13)–C(8)	1.390(17)	C(22)–C(21)	1.396(17)	1.393

RESULTS AND DISCUSSION

There are many reports of the syntheses and characterisation of oxovanadium(IV) complexes containing *N*-substituted salicylaldimines.[2,8] For all the reported complexes, spectroscopic and magnetic data are classified as 'usual' and a square-pyramidal geometry for the N_2O_3 donor set was, generally, assumed.[1,2,4,12] Contrary to an early belief, we must point out that the colour of vanadyl complexes, even within a given class, is neither usually blue-green nor diagnostic of their molecular complexity.[4,6] The colour of complexes (1)

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue (items less than 10 pp. are supplied as full-size copies).

[11] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 3.

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ranges from green to maroon (Table 4). Complexes having colours other than green have often been suggested to contain polymerisation of the V=O unit.[6] In these complexes in the solid state the vanadyl oxygen of one molecule occupies the sixth co-ordination position of a vanadium atom in a neighbouring molecule, the result being a linear chain of V=O units. The lowering in frequency of the V=O stretching vibration, at least in the case of yellow-orange oxo[*NN'*-propylenebis(salicylideneiminato)]vanadium(IV), to 854 cm^{-1} is attributed to this polymerisation.[6] As a consequence, in all the other cases, an unusual colour and a low V=O stretching vibration have been interpreted as evidence for the existence, in the solid state, of a polymeric structure.[4,6,7,13,14]

TABLE 3

Bond angles (°) corresponding to (*a*) and (*b*) the two halves of the molecule

(*a*)			
O(1)–V–O(3)	112.6(4)	C(5)–C(6)–C(7)	118(1)
N(1)–V–O(3)	98.8(4)	C(7)–N(1)–V	120.5(6)
O(1)–V–N(2)	84.8(3)	V–N(1)–C(8)	122.8(7)
O(1)–V–N(1)	87.2(3)	C(7)–N(1)–C(8)	117(1)
V–O(1)–C(1)	131.9(7)	N(1)–C(8)–C(9)	122(1)
O(1)–C(1)–C(6)	123(1)	N(1)–C(8)–C(13)	120(1)
O(1)–C(1)–C(2)	119(1)	C(13)–C(8)–C(9)	118(1)
C(6)–C(1)–C(2)	118(1)	C(8)–C(9)–C(10)	112(1)
C(1)–C(2)–C(3)	121(1)	C(9)–C(10)–C(11)	119(1)
C(2)–C(3)–C(4)	120(1)	C(10)–C(11)–C(12)	120(1)
C(3)–C(4)–C(5)	120(1)	C(10)–C(11)–C(11)	120(1)
C(4)–C(5)–C(6)	121(1)	C(11)–C(11)–C(12)	120(1)
C(5)–C(6)–C(1)	119(1)	C(11)–C(12)–C(13)	120(1)
C(1)–C(6)–C(7)	123(1)	C(12)–C(13)–C(8)	121(1)
(*b*)			
O(2)–V–O(3)	114.3(4)	C(18)–C(19)–C(20)	120(1)
N(2)–V–O(3)	101.8(4)	C(20)–N(2)–V	124.9(7)
O(2)–V–N(1)	85.1(3)	V–N(2)–C(21)	117.7(7)
O(2)–V–N(2)	86.4(3)	C(20)–N(2)–C(21)	117(1)
V–O(2)–C(14)	133.4(7)	N(2)–C(21)–C(26)	121(1)
O(2)–C(14)–C(19)	124(1)	N(2)–C(21)–C(22)	121(1)
O(2)–C(14)–C(15)	117(1)	C(22)–C(21)–C(26)	119(1)
C(19)–C(14)–C(15)	119(1)	C(21)–C(26)–C(25)	121(1)
C(14)–C(15)–C(16)	122(1)	C(26)–C(25)–C(24)	121(1)
C(15)–C(16)–C(17)	119(1)	C(25)–C(24)–C(23)	119(1)
C(16)–C(17)–C(18)	120(1)	C(25)–C(24)–C(12)	120(1)
C(17)–C(18)–C(19)	121(1)	C(12)–C(24)–C(23)	120(1)
C(18)–C(19)–C(14)	119(1)	C(24)–C(23)–C(22)	121(1)
C(14)–C(19)–C(20)	121(1)	C(23)–C(22)–C(21)	120(1)

TABLE 4

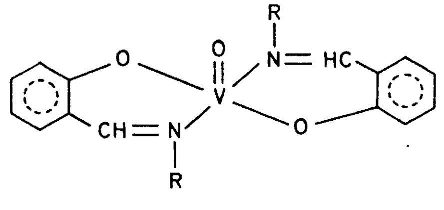
Analytical, magnetic, and i.r. data for complexes (1)

		Analysis (%) [a]					
R	Colour	C	H	N	$\mu_{eff.}$ [b]/B.M. (*T*K)	*M* [a,c]	$\tilde{\nu}$(V=O) [d]/ cm^{-1}
C_6H_4Cl-4 [e]	Golden-yellow	59.2 (59.1)	3.7 (3.4)	5.2 (5.3)	1.81 (292)		885
C_6H_4Cl-3 [f]	Yellow-green	59.6 (59.1)	3.8 (3.4)	5.7 (5.3)	*g*		940
$C_6H_4NO_2$-4	Light green	56.8 (56.8)	3.6 (3.3)	10.6 (10.2)	1.76 (293)		875
$C_6H_4NO_2$-3	Light green	56.8 (56.8)	3.4 (3.3)	10.6 (10.2)	1.66 (293)		980
C_6H_4OMe-4	Yellow-green	63.5 (64.7)	4.5 (4.6)	5.6 (5.4)	*g*		970
CH_2Ph	Green	69.2 (69.0)	5.3 (4.9)	5.9 (5.8)	1.76 (293)		992
C_6H_4OMe-2	Yellow-green	64.1 (64.7)	4.6 (4.6)	5.4 (5.4)	*g*		970
$C_{12}H_{25}$	Beige-maroon	70.4 (60.9)	9.4 (9.3)	4.8 (4.4)	*g*	650 (643)	970, 985 [h]
$C_{16}H_{33}$	Beige-maroon	73.2 (73.1)	10.3 (10.1)	4.1 (3.7)	*g*	720 (755)	975, 985 [h]
Bu^n	Maroon	63.2 (63.0)	7.1 (6.7)	6.7 (6.7)	1.77 (293)	402 (419)	975, 895 [h]

[a] Calculated values are given in parentheses. [b] Results expressed per metal atom; 1 B.M. = 9.27 × 10^{-24} A m^2. [c] By cryoscopy in benzene. [d] In Nujol except where indicated otherwise. [e] Cl 13.7 (13.5%). [f] Cl 13.9 (13.5%). [g] Not determined. [h] In CS_2.

For complexes (1) which are soluble in hydrocarbons, the molecular weight determined by cryoscopy in benzene (Table 4) together with the V=O stretching frequencies (solid state and CS_2 solution) show the monomeric nature. Attempts to convert these complexes into the corresponding six-co-ordinate species, [VOL_2L'], failed. Treatment of (1; R = Bu^n) in CS_2 or benzene solution with pyridine or cyclohexyl isocyanide, gave no evidence, either in the solid state or in solution (i.r. spectrum), of six-co-ordinate V^{IV}.

The most unexpected results were obtained when R is a substituted phenyl group. For the 3-substituted phenyl derivatives, apart from the colour, all the reported properties (Table 4) lay in the usual range, as was also the case for 4-substituted phenyl derivatives containing electron-donor groups (Me or OMe). A reduction of the V=O stretching vibration to 875—885 cm^{-1} was nevertheless observed in the case of electron-attracting substituents (4-Cl or 4-NO_2). The colours and the V=O stretching values are reminiscent, in these cases, of the properties found for oxo[*NN'*-propylenebis(salicylideneiminato)]vanadium(IV).[6,7] The assignment of ν(V=O) was made by comparison with the i.r. spectra of the corresponding [VCl_2L_2] [1] (Table 4). This prompted us to formulate (1; R = C_6H_4Cl-4 or $C_6H_4NO_2$-4) as polymeric complexes.[1] An easy explanation might be the increase of the long-range vanadium acidity in the presence of electron-attracting groups.[14] The very poor solubility, together with the failure to obtain six-co-ordinate species in the solid state, were also considered to be support for the proposed molecular complexity. The final answer to this question was left to an *X*-ray analysis of (1; R = C_6H_4Cl-4) recrystallised from CS_2.



[VOL_2] (1)

The unit cell of (1; R = C_6H_4Cl-*p*) comprises monomers

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of approximate C_2 symmetry. Selected interatomic bond distances and angles together with their standard deviations are given in Tables 2 and 3. A view of the structure projected along the V=O bond direction is shown in Figure 1, which also includes the atom numbering. As the molecule shows approximate C_2 (2) symmetry, a half-normal probability plot [15] was constructed in order to examine the agreement between corresponding bond distances in the two halves of the molecule. The plot was approximately linear, of gradient 1.3, indicating some underestimation of the standard deviations of the bond distances. The mean values for corresponding bond lengths are given in the third column of Table 2 and Figure 1. The geometry of the central vanadium atom is basically trigonal bipyramidal formed by three oxygens in the equatorial plane and two nitrogen atoms in the axial positions (Figure 2). The bond lengths and angles compare very well with those reported for bis(2-methylquinolin-8-olato)oxovanadium(IV), [VO(mqo)$_2$].[5] The V=O distance, 1.615 Å, is among the largest found in oxovanadium(IV) complexes.[16] Table 5 gives geometrical parameters of the two idealised polyhedra,[17] namely trigonal bipyramid (tbp) and square pyramid (spy), with those found for some representative oxovanadium complexes. The terms 'square pyramid' and 'trigonal bipyramid' are not intended to imply C_{4v} or D_{3h} symmetry, but refer only to the approximate

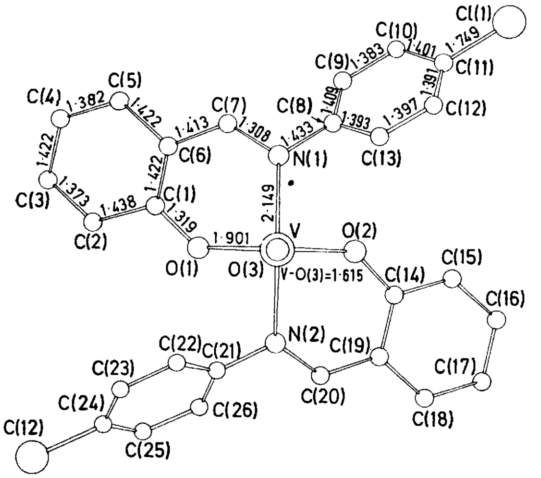


FIGURE 1 Molecular structure of (1; R = C_6H_4Cl-4) viewed along the vanadyl bond direction, with relevant bond distances

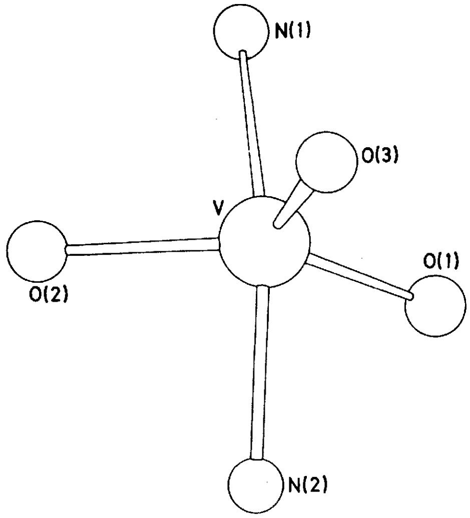
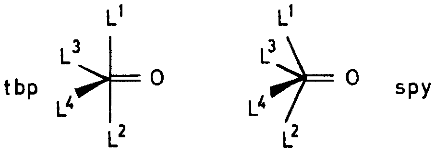


FIGURE 2 Vanadium co-ordination polyhedron. The V,N(1),O(3),N(2), and V,O(1),O(2),(3) planes are perpendicular

TABLE 5

Comparison between the vanadium co-ordination polyhedra in some five-co-ordinate oxovanadium(IV) complexes, and the two idealised tbp and spy geometries



Bond lengths (Å) or angles (°)	tbp	spy	Complex			
			(1; R = C_6H_4Cl-4)	[VO(mgo)$_2$][5]	[VO(pd)$_2$][18]	[VO(dpep)][1]
V=O			1.615	1.600	1.571	1.62
V–L^1			2.149	2.136	1.968	2.06
V–L^3			1.901	1.921		
L^1–V=O	90	104.1	100.4	99.5	106.2	103
L^3–V=O	120		113.4	116.4		
L^1–V–L^2	180	151.9	159.1	161.0	147.5	153
L^3–V–L^4	120		133.2	129.2		
L^1–V–L^3	90	86.6	86.8	80.6	85.5	87
L^3–V–L^2	90		84.9	91.0		

For the first two complexes L^1 = L^2 = N and L^3 = L^4 = O; for [VO(pd)$_2$], L^1 = L^2 = L^3 = L^4 = O; for [VO(dpep)], L^1 = L^2 = L^3 = L^4 = N. For all the cases, C_2 symmetry was assumed with the binary axis coincident with the V–O direction.

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angular geometry of the co-ordination polyhedron about the vanadium atom. Oxobis(pentane-2,4-dionato)vanadium(IV),[18] [VO(pd)$_2$], and (deoxophylloerythroetioporphyrin)oxovanadium(IV), [VO(dpep)],[19] have been chosen as examples of the usual square-pyramidal geometry for oxovanadium(IV) complexes; these two complexes are best described as square pyramids with deviations of the vanadium atom from the basal plane (0.55 and 0.48 Å respectively). In (1; R = C_6H_4Cl-4) the distance of the vanadium atom from the N–N and O–O planes is 0.39 and 0.76 Å respectively. Complete delocalisation of electrons in the Schiff base is prevented by the high torsional angles around N(1)–C(8) and N(2)–C(21) (46.9 and 46.0° respectively). The bond lengths N(1)–C(8) and N(2)–C(21) (average 1.433 Å) are normal for the C(sp^2)–N(sp^2) single bond. Planarity of the ligands is probably prevented by non-bonding interactions between H(7)–H(9) and H(20)–H(26). The salicylideneiminate moiety is approximately planar and the bond distances compare well with mean values obtained from a large number of structural determinations,[20] indicating predominance of an orthoquinoid resonance structure. The chlorophenyl groups are planar; the C(11)–Cl(1) and C(24)–Cl(2) distances (mean 1.749 Å) correspond to the sum of the covalent radii of chlorine and carbon in sp^2 hybridisation.

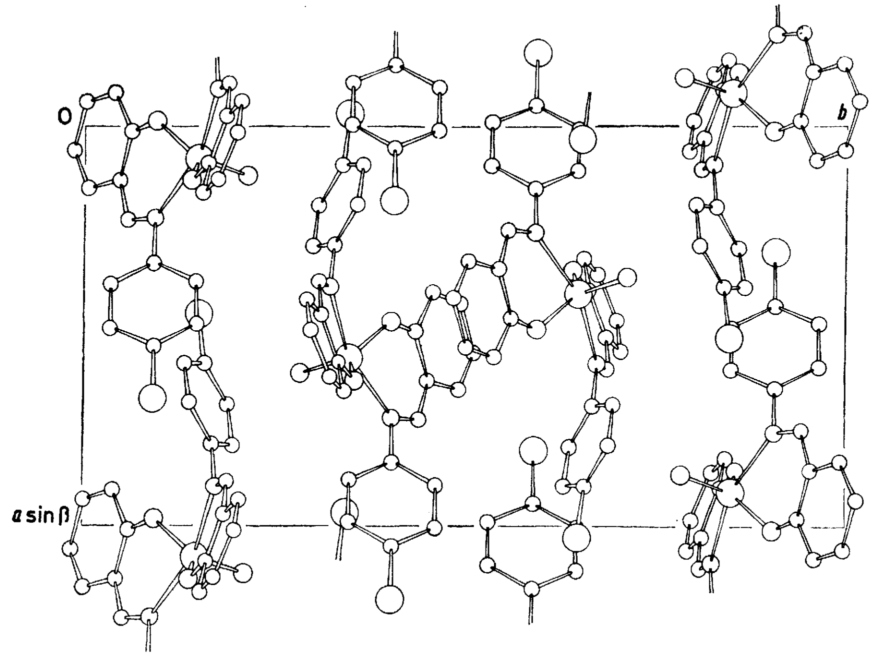

FIGURE 3 Molecular packing for (1; R = C_6H_4Cl-4) as viewed along *c*

TABLE 6

Shortest intermolecular distances (Å)

C(6) $\cdots$ C(16$^{\mathrm{I}}$)	3.56	O(1) $\cdots$ C(1$^{\mathrm{II}}$)	3.48
C(6) $\cdots$ O(1$^{\mathrm{II}}$)	3.55	N(1) $\cdots$ C(2$^{\mathrm{II}}$)	3.56
C(4) $\cdots$ O(2$^{\mathrm{II}}$)	3.57	C(26) $\cdots$ C(5$^{\mathrm{II}}$)	3.55
C(2) $\cdots$ N(1$^{\mathrm{II}}$)	3.56	O(3) $\cdots$ C(23$^{\mathrm{III}}$)	3.55
C(1) $\cdots$ C(1$^{\mathrm{II}}$)	3.40	C(19) $\cdots$ C(24$^{\mathrm{III}}$)	3.58
O(2) $\cdots$ C(3$^{\mathrm{II}}$)	3.20	C(14) $\cdots$ C(23$^{\mathrm{III}}$)	3.45
C(1) $\cdots$ O(1$^{\mathrm{II}}$)	3.48	C(20) $\cdots$ Cl(2$^{\mathrm{III}}$)	3.55
C(3) $\cdots$ O(2$^{\mathrm{II}}$)	3.20		

Roman numeral superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z: I $x, y, -1 + z$; II $1 - x, 1 - y, -z$; III $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

The crystal packing is shown in Figure 3. It appears from this Figure and from Table 6, which lists intermolecular distances shorter than 3.6 Å, that the packing of the molecules in the crystal is assured only by van der Waals interactions. A V–O $\cdots$ V interaction cannot be invoked to explain the reduction of the V=O stretching vibration. Least-squares planes are reported in Table 7; planes containing V, N(1), O(3), N(2) and V, O(1), O(2), O(3) respectively are mutually perpendicular.

Conclusions.—This is the first structural study of an oxovanadium(IV) complex containing ' classical ' ligands such as bidentate Schiff bases. The results suggest that any conclusions based on the V=O stretching frequency and on the colour of vanadyl complexes are unwarranted. The previously proposed square-pyramidal geometry must be regarded as more rare than the norm. In addition, we consider that, even for co-ordination environments which are chemically very similar, the V=O bond lengths may be very different, the geometries of the vanadyl oxygens being much exposed to the influence of the neighbouring molecules in the crystal. There is probably no relation between the V=O bond length or V=O stretching frequency and polymerisation and/or

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TABLE 7

Least-squares planes

Plane	Atom defining the plane and distance (Å) from the least-squares plane									Angles (°) between this plane and the plane:					
										1	2	3	4	5	6
(1)	O(1)	O(2)	N(1)	N(2)											
	0.183	0.184	−0.182	−0.184											
(2)	O(1)	O(2)	O(3)	V						88.7					
	0.002	0.002	0.002	−0.006											
(3)	N(1)	N(2)	O(3)	V						89.2	89.0				
	0.0	0.0	0.0	0.0											
(4)	O(1)	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	N(1)	9.2	85.6	82.3			
	−0.007	−0.026	0.016	0.033	0.004	−0.019	−0.065	0.046	0.018						
(5)	O(2)	C(14)	C(15)	C(16)	C(17)	C(18)	C(19)	C(20)	N(2)	15.7	86.6	73.5	24.2		
	−0.014	−0.031	0.014	0.037	0.006	−0.028	−0.039	0.024	0.031						
(6)	C(8)	C(9)	C(10)	C(11)	C(12)	C(13)	Cl(1)			53.5	46.6	66.6	52.6	63.8	
	−0.033	0.019	−0.009	0.033	−0.002	0.012	−0.020								
(7)	C(21)	C(22)	C(23)	C(24)	C(25)	C(26)	Cl(2)			61.3	36.7	66.5	62.5	53.6	65.4
	0.019	−0.006	−0.001	−0.015	0.006	−0.014	0.009								

the co-ordination geometry at the vanadium. Nevertheless, in the present case, the reduction of the the V=O stretching frequency seems to be in agreement with the rather long V=O bond distance (1.615 Å). This work has clearly shown that any conclusions on the co-ordination geometry of the vanadyl cation, in the absence of strucural data, must be suspect.

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