N-Salicylideneamino Acidate Complexes of Oxovanadium(IV). Part 1. Crystal and Molecular Structures and Spectroscopic Properties†

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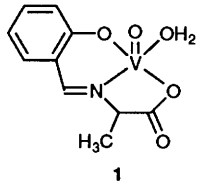
The complex [VO(salgly)(H_2O)] 1 dissolved in pyridine (py) to form brown [VO(salgly)($py)_2$] **2** (salgly = *N*-salicylideneglycinate). A brown complex [VO(sal-L-ala)(bipy)] **3** precipitated on adding 2,2'-bipyridine (bipy) to [VO(sal-L-ala)(H_2O)] **4** (sal-L-ala = *N*-salicylidene-L-alaninate) in methanol. The structures of **2** and **3** have been determined by X-ray diffraction analysis. In both the tridentate Schiff-base ligands occupy equatorial positions and the two heterocyclic nitrogen atoms of py or bipy co-ordinate in equatorial and axial positions, completing an octahedral geometry around the vanadium. The circular dichroism spectra of **3** dispersed in Nujol and in methanolic solutions are very similar. This finding together with EPR and thin-layer chromatographic experiments suggests that **3** is relatively stable to hydrolysis and that its structures in the solid state and solution are similar. Complex **2** and [VO(sal-L-ala)($py)_n$] are not as stable to hydrolysis as **3** and a solid formulated as [VO(salgly)(py)(H_2O)] was also isolated.

The change in ligand reactivity caused by the co-ordination of amino acids to a wide variety of metal ions is well known. The activating effect of the metal ion may be extended[1] by co-ordinating the amino acid as a Schiff base using a suitable carbonyl fragment such as pyridoxal (3-hydroxy-5-hydroxymethyl-2-methylpyridine-4-carbaldehyde), salicylaldehyde or pyruvate.

Vanadium complexes of *N*-salicylideneamino acids and derivatives are model systems for pyridoxal-potentiated enzymes.[2,3] Despite this very little has been published concerning the preparation and reactivity of these compounds. Vanadium is one of the most active metal ions in β eliminations,[4,5] and there are reports of the catalytic activity of these and related complexes in the asymmetric oxidation of sulfides to the corresponding sulfoxides with organic hydroperoxides.[6,7]

Oxovanadium(IV) complexes of Schiff bases derived from the reaction of salicylaldehyde (Hsal) and α-amino acids (glycine, L- and D,L-alanine, L-methionine, L-valine, L-leucine, L- and D,L-phenylalanine) were prepared.[8] They are bluish grey and there is no appreciable interaction between the vanadium atoms. X-ray diffraction study of the L-alanine derivative confirmed that the compounds have a co-ordination geometry as in **1**.[9] One water molecule occupies a co-ordination position and 'prevents' dimerization of the compounds, assumed to be possible by comparison with similar salicylamine complexes.[10]

From a solution containing [VO(sal-L-ala)(H_2O)] in wet methanol, [V^{V}O(sal-L-ala)(OCH_3)(CH_3OH)] (sal-L-ala = *N*-salicylidene-L-alaninate) was obtained,[6] and treatment of the former with wet dichloromethane yielded deep blue crystals of [{V^{V}O(sal-L-ala)}$_2$O]·$2CH_2Cl_2$. The structures of the two products were determined by X-ray techniques. The vanadium(V) complex of the Schiff base formed from *o*-hydroxy-naphthalenecarbaldehyde and histidine[11] and a mixed-valence complex of vanadium-(IV) and -(V), Na[V_2O_3(sal-D,L-ser)$_2$]·$5H_2O$ (sal-D,L-ser = *N*-salicylidene-D,L-serinate) have been isolated and also characterized by X-ray diffraction.[12]



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A study of solutions containing VO^{2+}, Hsal and amino acids by spectroscopic techniques showed evidence of the formation of several complex species.[13] The present paper deals with the preparation and characterization of solid complexes from solutions containing [VO(salgly)(H_2O)] **1** (salgly = *N*-salicylideneglycinate) and pyridine (py), namely [VO(salgly)($py)_2$] **2** and of [VO(sal-L-ala)(bipy)] **3** from solutions containing [VO(sal-L-ala)(H_2O)] and 2,2'-bipyridine (bipy). These and other similar starting materials were used to promote reactions involving the amino acid moiety.[13]

Experimental

Preparations.—[VO(salgly)($py)_2$] **2**. The complex [VO(salgly)(H_2O)] **1** (1 g, 3.82 mmol) was dissolved in a small volume of pyridine, and the solution was kept in a refrigerator. After a week dark brown crystals of **2** separated (Found: C, 55.2; H, 4.6; N, 10.3. $C_{19}H_{17}N_3O_4V$ requires C, 56.7; H, 4.3; N, 10.4%); $\tilde{\nu}_{max}$/cm^{-1} (KBr disk) 950vs (VO), 1600vs, 1540s (ring, asym. CO_2), and 1630vs (C=N).

[VO(salgly)(py)(H_2O)] **7**. The complex [VO(salgly)(H_2O)] was dissolved in the minimum volume of ice-cold pyridine. The solution was kept in a refrigerator. After 24 h a brownish-pink powder was filtered off (Found: C, 49.4; H, 4.3; N, 8.1.

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

$C_{14}H_{14}N_2O_5V$ requires C, 49.3; H, 4.1; N, 8.2%); $\tilde{\nu}_{max}$/cm^{-1} (KBr disk) 960vs (VO), 1535m, 1600 (sh) (ring, asym. CO_2) and 1630vs (C=N).

[VO(sal-L-ala)(bipy)] **3**. The complex [VO(sal-L-ala)(H_2O)] **4** (277 mg, 1 mmol) was dissolved in methanol (30 cm^3). A solution of 2,2′-bipyridyne (162 mg, 1 mmol) in methanol (5 cm^3) was slowly added. After slow evaporation of the solvent at room temperature for 2 d brown crystals of **3** were collected {Found: C, 58.5; H, 4.4; N, 9.9. $C_{20}H_{17}N_3O_4V$ requires C, 58.0; H, 4.0; N, 10.1. Calc. for 2[VO(sal-L-ala)(bipy)]·0.125 H_2O·0.5 CH_3OH (see below): C, 58.3; H, 4.7; N, 9.7%}; $\tilde{\nu}_{max}$/cm^{-1} (KBr disk) 955vs (VO), 1600 (sh), 1530m (ring, asym. CO_2), and 1615vs (C=N). One should note that **3** normally precipitates quite quickly: analytical results from four different preparations varied: C, 55.4–58.5; H, 4.4–4.6; N, 9.7–10.1%.

Circular Dichroism and Absorption Spectra.—The CD spectra were run on a JASCO 720 spectropolarimeter with a red-sensitive photomultiplier, visible absorption spectra with a Beckman DK 2A spectrophotometer and a PbS detector.

Solid complexes **3** *and* **4**. For each solid an extremely fine powder was ground in an agate mortar and mixed with dry Nujol till a relatively concentrated homogeneous paste was formed. One or two 'drops' of this paste were placed between two microscope slides in the sample compartment in a fixed position. A first CD spectrum was run, the sample rotated by ≈70–90° and another spectrum recorded; five rotations were performed for each sample and the corresponding spectra recorded. With this type of solid sample one does not know the position of the baseline but the correct pattern may be obtained if the spectrum recorded after each rotation of the sample is always approximately the same.

Solution CD spectra. Before preparing the solutions oxygen was removed from the solvents by bubbling N_2. The spectra were recorded immediately after the preparation of the solutions: the cells had their stoppers reinforced with Parafilm strips but no special care was taken to remove oxygen from the cells.

(1) The complex [VO(sal-L-ala)(H_2O)] (0.02823 g, 0.102 mmol) was dissolved in methanol (total volume = 10 cm^3) and the CD spectrum recorded. To 9.0 cm^3 of this solution several successive additions of pyridine (1, +1, +3 and +3 cm^3) were made and the CD spectrum was run after each addition.

(2) The complex [VO(sal-L-ala)(H_2O)] (0.00699 g, 0.0252 mmol) was dissolved in pyridine (total volume = 5 cm^3) and the CD spectrum of the brownish orange solution recorded. Several successive additions of water (0.2, +2.0, +3.5, +6.5 cm^3) were made and the CD spectrum recorded after each addition.

(3) Several solutions of [VO(sal-L-ala)(H_2O)] in pyridine were prepared in 10.0 cm^3 volumetric flasks (total vanadium concentrations in the range 0.002–0.001 l mol dm^{-3}) and the CD spectrum recorded for each solution.

(4) The complex [VO(sal-L-ala)(bipy)] (0.02096 g, 0.0506 mmol) was dissolved in methanol (10 cm^3) and the CD spectrum recorded.

(5) Solutions of 0.01 mol dm^{-3} [VO(sal-L-ala)(H_2O)] **4** and bipy were prepared in 10 cm^3 volumetric flasks with concentration at several bipy: **4** mole ratios (0.96, 4.0, 9.9, 19.8:1). The CD spectrum for each of these reddish orange solutions was recorded.

Visible absorption spectra. The complex [VO(sal-L-ala)-(H_2O)] (0.0764 g, 0.292 mmol) was dissolved in methanol (50 cm^3) and (0.0771 g, 0.294 cm^3) in absolute ethanol (50 cm^3) and the absorption spectra recorded with 1 and 5 cm optical path cells.

For all sets of spectra except (2) the sample compartment was kept at 25 °C.

EPR Spectra—X-Band EPR spectra were recorded at 77 K (on glasses made by freezing solutions with liquid nitrogen) with a Bruker ESR-ER 200tt connected to a B-MN C5 spectrometer and to a Bruker EPR data system (linked to an IBM XT computer).

TLC Experiments.—These were performed on Merck TLC plates (Art. 5626, 10 × 20 cm). Solutions of [VO(sal-L-ala)-(H_2O)] in methanol and pyridine, of [VO(sal-L-ala)(bipy)] in methanol and of [VO(salgly)(H_2O)] in pyridine were prepared, and 1 and 3 μl samples of each were applied to the plates 20 mm from the bottom. Elutions were carried out in Camag twin chambers with walls covered with filter-paper impregnated with the eluent. Eluents used were: A, ethanol–water (7:3); B, butanol–ethanol–propionic acid–water (10:10:2:5). When the eluents reached ≈120 mm from the bottom the plates were removed and dried. The chromatogram was developed with a ninhydrin–collidine(2,4,6-trimethylpyridine)–copper solution prepared according to Moffat and Lytle.[14]

Distinct and clear spots corresponding to the complexes were detected for samples of **4** dissolved in methanol (R_f ≈ 0.75 and 0.64, for eluents A and B, respectively), of **3** dissolved in methanol (R_f ≈ 0.63 and 0.58, for eluents A and B, respectively) and of **4** dissolved in pyridine (R_f = 0.75 and 0.64, for eluents A and B, respectively). In all cases distinct spots were also detected at the R_f of the free amino acids and the spots corresponding to the Schiff-base complexes had tailing which extended to the spot of the free L-ala. No spot could be detected for **1** dissolved in pyridine; only the spot with R_f corresponding to free glycine, with extensive fronting (more pronounced for eluent A) appeared, indicating that the Schiff-base complex had hydrolysed completely during elution.

Crystal Structure Determination of Complexes **2** *and* **3**.—*Crystal data.* $C_{19}H_{17}N_3O_4V$ **2**, M = 402.30, monoclinic space group $P2_1/n$($P2_1/c$), a = 11.666(4), b = 10.901(3), c = 14.987(4) Å, β = 104.54(2)°, U = 1845(1) Å^3, λ(Mo-Kα) 0.710 69 Å, Z = 4, D_c = 1.45, F(000) = 828, μ(Mo-Kα) = 5.29 cm^{-1}.

$C_{20}H_{17}N_3O_4V$ **3**, M = 414.32, monoclinic, space group $C2$, a = 19.008(6), b = 20.508(3), c = 12.343(4) Å, β = 126.33(1)°, U = 3876(2) Å^3, λ(Mo-Kα) 0.71069 Å, Z = 8, D_c = 1.42, F(000) = 1696, μ(Mo-Kα) = 5.05 cm^{-1}.

Data collection. For complex **2** an Enraf-Nonius CAD-4 diffractometer, ω–2θ scan mode, and graphite-monochromatized Mo-Kα radiation were employed. 4412 Observations of which 3992 were independent (2.0 ≤ θ ≤ 27.0°). Cell dimensions were determined from the measured θ values for 25 intense reflections with 14 ≤ θ ≤ 16°. Data were corrected empirically for absorption.[15] No decay was observed.

Similarly for **3**, except that 5988 observations were made of which 5489 were independent (1.5 ≤ θ ≤ 30.0°) and cell dimensions were determined from the measured θ values for 25 intense reflections with 16 ≤ θ ≤ 17°.

Structure analysis and refinement. For complex **2** the 2171 reflections with $F \geq 3\sigma(F)$ were used. The non-hydrogen atomic positions were determined by a direct method with SHELXS 86[16a] and refined to convergence by full-matrix least squares with anisotropic thermal parameters using SHELX 76[16b]. At this stage the positions of the hydrogen atoms were obtained from a Fourier difference map and included in the refinement process with isotropic thermal parameters. The final refinement was carried out with a weighting scheme of w = 2.2299/[$\sigma^2(F_o)$ + 0.000 584 F_o^2], and converged to R = 0.078, R' = 0.068 for 2355 reflections with $F_o > 2.5\sigma(F_o)$ and 312 refined parameters.

For complex **3** the non-hydrogen atomic positions were determined by a direct method with the program MITHRIL[17] using the 400 reflections with highest normalized structure-factor amplitudes and the configuration of the L-alanine moiety was used to verify the correct hand of the enantiomorph obtained. As the molecule is chiral, refinement was performed in space group $C2$. The model was refined to convergence with

Table 1 Fractional atomic coordinates ($\times 10^5$ for V, $\times 10^4$ for others) for the non-hydrogen atoms of [VO(salgly)(py)$_2$] **2**

Atom	*x*	*y*	*z*
V	70 590(9)	23 813(8)	33 799(7)
O(1)	6 610(4)	2 468(4)	2 285(3)
N(1)	7 683(4)	621(4)	3 577(3)
C(1)	8 748(6)	253(5)	3 710(4)
C(2)	6 725(6)	−272(5)	3 552(5)
C(3)	5 624(6)	376(5)	3 658(4)
O(4)	4 772(4)	−223(4)	3 707(4)
O(5)	5 680(3)	1 567(4)	3 668(3)
C(11)	9 759(5)	1 047(5)	3 761(4)
C(12)	9 688(5)	2 328(5)	3 673(4)
O(12)	8 686(3)	2 955(3)	3 553(3)
C(13)	10 743(7)	2 964(6)	3 742(5)
C(14)	11 805(6)	2 385(8)	3 872(5)
C(15)	11 882(7)	1 129(8)	3 938(5)
C(16)	10 867(7)	465(7)	3 878(5)
N(21)	6 432(4)	4 170(4)	3 620(3)
C(22)	5 328(7)	4 330(7)	3 673(7)
C(23)	4 871(7)	5 468(7)	3 785(7)
C(24)	5 597(7)	6 460(7)	3 889(6)
C(25)	6 712(7)	6 317(6)	3 842(5)
C(26)	7 131(6)	5 157(6)	3 715(5)
N(31)	7 658(4)	2 527(4)	5 096(3)
C(32)	7 047(5)	2 035(5)	5 640(4)
C(33)	7 322(6)	2 183(6)	6 574(5)
C(34)	8 285(6)	2 912(6)	6 979(5)
C(35)	8 929(6)	3 411(6)	6 438(5)
C(36)	8 594(6)	3 218(6)	5 505(5)

anisotropic thermal parameters using SHELX 76.[16b] At this stage it was noted that the highest peaks in the residual electron-density maps corresponded to disordered solvent molecules near the coordinates ($\frac{1}{2}$, $\frac{1}{4}$, 0) and (0, $\frac{1}{4}$, $\frac{1}{2}$). This disordered solvent was modelled by considering four molecules of methanol (two near the first site and two near the second) and one water molecule near the second site. All five solvent molecules were refined isotropically with an occupation factor of $\frac{1}{8}$, arbitrarily chosen to produce reasonable U_{iso} values and the C–O bond lengths in the methanol molecules were loosely constrained to 1.45(4) Å. Then the positions of the hydrogen atoms were obtained from a Fourier difference map and included in the refinement process with isotropic thermal parameters and C–H bond lengths constrained to 1.00(3) Å. Furthermore, the hydrogens in each alanine methyl were refined with group isotropic thermal parameters. However, the hydrogens attached to C(12a) and C(12b) could not be located and were therefore placed in calculated positions and not refined. The final refinement was carried out with a weighting scheme $w = 1.0/[\sigma^2(F_o) + 0.003\,932F_o^2]$ and converged to $R = 0.057$, $R' = 0.065$ for 5115 reflections with $F_o \geqslant 2\sigma(F_o)$ and 661 refined parameters.

Atomic scattering factors were taken from ref. 18. Final atomic coordinates are given in Tables 1 and 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

A molecular diagram of complex **2** presenting the numbering scheme is shown in Fig. 1; bond lengths and angles are listed in Table 3. The complex exhibits essentially octahedral geometry, formed in the equatorial plane by the O, N, O atoms of the Schiff-base ligand and the pyridyl nitrogen; the co-ordination around the metal is completed by the oxo oxygen and by a weak interaction to the nitrogen atom of the second pyridine moiety.

Atoms O(5), N(1), O(12) and N(21) are not coplanar and this can be shown by two different considerations: (*i*) The sum of

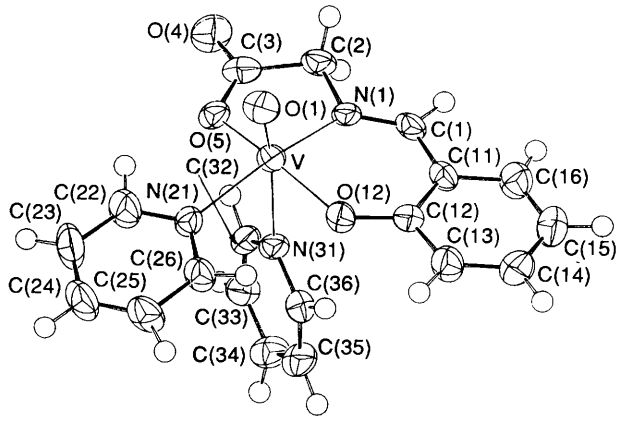


Fig. 1 An ORTEP[19] diagram of [VO(salgly)(py)$_2$] **2** showing the atomic notation. The thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms have been drawn with isotropic thermal parameters arbitrarily set to 0.02 Å^2

squared deviations $[d/\sigma(d)]^2$ for the plane defined by these four atoms is 32.65 while χ^2 for 95% and one degree of freedom should be 3.84; (*ii*) The angle between the planes defined by N(1), O(5), V and N(21), O(12) and O(5) is 25.6(2)°. The vanadium atom is 0.327(1) Å away from the least-squares plane defined by the equatorial atoms and towards the vanadyl oxygen. In other six- and five-co-ordinated complexes the vanadium atom is normally out of the plane by a similar distance.[20,21] The Schiff-base ligand is also not planar; however atoms C(2), C(3), O(4) and O(5) are in a plane and O(12) and all salicylaldehyde carbons are also planar. The angle between these planes is 13.2(2)°. Atom N(1) belongs to neither plane.

Holloway and Melnik[21] surveyed vanadyl complexes, finding a correlation between the V=O distance and the co-ordination geometry. Six-co-ordinated complexes have mean V=O distances of 1.615 Å, while five-co-ordinated complexes normally have shorter distances, mean 1.518 Å. This distance in **2** is close to the six-co-ordinate mean but on the short side. This is not surprising since the six-fold co-ordination is achieved *via* a very weak interaction to the pyridine N(31) atom (see Fig. 1) as indicated by the long V(1)–N(31) distance of 2.495(6) Å.

The V–O and V–N equatorial distances are within the normal range observed in vanadyl complexes[20,21] and the usual geometry is found for the pyridines. The angle between the planes of the two pyridines is 75.9(2)°.

There are two independent molecules, A and B, in the asymmetric unit of the unit cell of complex **3**, with the vanadyl and bipy moieties approximately antiparallel (Fig. 2). The two molecules are related by a pseudo-inversion centre and the lack of true symmetry is due to the chirality of the L-alanine. This pseudo-symmetry is apparent from the crystallographic point of view as the space group *C*2 (non-centrosymmetric) is pseudo-*C*2/*c* (centrosymmetric), because the intensities that should be systematically absent in *C*2/*c*(*h*0*l*, odd) are much weaker than the rest.

The two molecules of [VO(sal-L-ala)(bipy)] are similar; their differences are discussed below. A representative molecular diagram of **3** presenting the numbering scheme is shown in Fig. 3 for molecule A, and selected bond lengths and bond angles are listed in Table 4. The molecules exhibit essentially an octahedral geometry, formed in the equatorial plane by O, N, O atoms of the Schiff-base ligand and a nitrogen donor of bipy; again the co-ordination is completed by the oxo oxygen and by a weak interaction to the second bipy nitrogen. In both molecules, the equatorial donor atoms O(3), N(11), O(16) and N(28) are approximately coplanar. The maximum deviation from the least-square planes defined by these atoms is 0.027(5) Å for O(16A) and 0.024(5) Å for N(28B). The vanadium atoms are 0.347(1) Å away from the least-squares plane defined by the

Table 2 Fractional atomic coordinates ($\times 10^5$ for V, $\times 10^4$ for others) for the non-hydrogen atoms of [VO(sal-L-ala)(bipy)] **3**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Molecule A				Molecule B			
V(1A)	32 502(5)	−7 452	45 942(7)	V(1B)	−32 181(4)	8 232(4)	4 291(7)
O(2A)	4 103(2)	−327(3)	5 186(4)	O(2B)	−4 080(2)	372(2)	−263(4)
O(3A)	2 313(2)	−137(2)	3 484(4)	O(3B)	−2 315(2)	160(2)	1 513(3)
C(4A)	1 749(3)	134(3)	3 642(5)	C(4B)	−1 769(3)	−132(2)	1 354(5)
C(5A)	1 099(4)	538(3)	2 644(5)	C(5B)	−1 181(4)	−596(3)	2 329(5)
C(6A)	493(4)	827(3)	2 757(6)	C(6B)	−566(3)	−904(3)	2 234(5)
C(7A)	512(4)	731(3)	3 886(6)	C(7B)	−518(3)	−775(3)	1 168(5)
C(8A)	1 131(3)	339(3)	4 887(6)	C(8B)	−1 113(3)	−353(3)	176(5)
C(9A)	1 770(3)	35(3)	4 805(5)	C(9B)	−1 732(3)	−14(2)	251(4)
C(10A)	2 440(3)	−337(3)	5 972(4)	C(10B)	−2 298(3)	430(3)	−794(5)
N(11A)	3 057(3)	−647(2)	6 054(3)	N(11B)	−2 887(2)	791(2)	−866(3)
C(12A)	3 739(4)	−985(3)	7 294(5)	C(12B)	−3 357(3)	1 279(3)	−1 973(4)
C(13A)	3 515(6)	−1 155(4)	8 268(6)	C(13B)	−4 036(5)	965(5)	−3 296(7)
C(14A)	3 951(4)	−1 618(4)	6 819(6)	C(14B)	−3 758(4)	1 787(3)	−1 578(6)
O(15A)	4 285(4)	−2 081(3)	7 581(5)	O(15B)	−4 032(4)	2 292(3)	−2 198(5)
O(16A)	3 825(2)	−1 571(2)	5 692(3)	O(16B)	−3 756(2)	1 656(2)	−558(4)
N(17A)	2 108(2)	−1 499(2)	3 447(4)	N(17B)	−2 044(3)	1 527(2)	1 763(4)
C(18A)	1 613(3)	−1 721(3)	3 818(5)	C(18B)	−1 516(3)	1 743(3)	1 444(5)
C(19A)	940(4)	−2 149(3)	3 068(6)	C(19B)	−868(3)	2 200(3)	2 199(6)
C(20A)	746(3)	−2 381(3)	1 859(6)	C(20B)	−780(3)	2 439(3)	3 304(6)
C(21A)	1 247(3)	−2 175(3)	1 472(5)	C(21B)	−1 308(4)	2 218(3)	3 677(5)
C(22A)	1 926(3)	−1 729(3)	2 274(5)	C(22B)	−1 946(3)	1 747(2)	2 845(4)
C(23A)	2 529(3)	−1 481(3)	1 969(5)	C(23B)	−2 542(3)	1 497(3)	3 106(4)
C(24A)	2 414(3)	−1 666(3)	765(5)	C(24B)	−2 513(4)	1 623(3)	4 224(5)
C(25A)	2 989(4)	−1 419(3)	525(5)	C(25B)	−3 121(5)	1 382(4)	4 357(6)
C(26A)	3 670(4)	−1 031(3)	1 486(6)	C(26B)	−3 763(5)	987(4)	3 400(7)
C(27A)	3 742(3)	−874(3)	2 650(5)	C(27B)	−3 809(4)	857(3)	2 246(6)
N(28A)	3 164(2)	−1 090(2)	2 876(3)	N(28B)	−3 197(3)	1 104(2)	2 127(4)

Table 3 Selected bond lengths (Å) and angles (°) for [VO(salgly)$(py)_2$] **2**

O(1)–V	1.594(6)	N(1)–V	2.047(7)
O(5)–V	1.977(6)	O(12)–V	1.953(6)
N(21)–V	2.144(7)	N(31)–V	2.495(6)
C(1)–N(1)	1.273(8)	C(2)–N(1)	1.475(8)
C(11)–C(1)	1.449(9)	C(3)–C(2)	1.509(11)
O(4)–C(3)	1.206(8)	O(5)–C(3)	1.300(8)
N(1)–V–O(1)	102.5(3)	O(5)–V–O(1)	100.2(3)
O(5)–V–N(1)	80.0(3)	O(12)–V–O(1)	100.1(3)
O(12)–V–N(1)	89.0(3)	O(12)–V–O(5)	158.6(2)
N(21)–V–O(1)	94.7(3)	N(21)–V–N(1)	162.2(2)
N(21)–V–O(5)	92.3(3)	N(21)–V–O(12)	92.7(3)
N(31)–V–O(1)	172.4(2)	N(31)–V–N(1)	85.0(3)
N(31)–V–O(5)	80.5(3)	N(31)–V–O(12)	80.3(3)
N(31)–V–N(21)	77.8(3)	C(1)–N(1)–V	128.0(5)
C(2)–N(1)–V	112.0(5)	C(2)–N(1)–C(1)	120.0(6)
C(11)–C(1)–N(1)	124.7(6)	C(3)–C(2)–N(1)	110.4(6)
O(4)–C(3)–C(2)	119.3(7)	O(5)–C(3)–C(2)	115.2(7)
O(5)–C(3)–O(4)	125.4(7)	C(3)–O(5)–V	119.2(5)

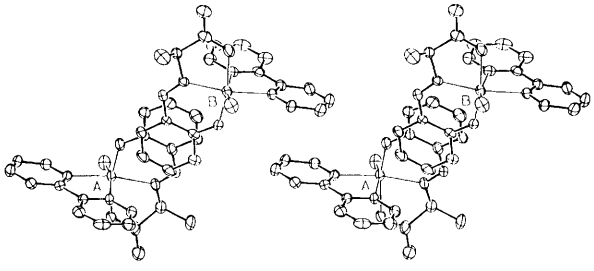


Fig. 2 An ORTEP[19] stereodiagram showing the two independent molecules in the asymmetric unit of [VO(sal-L-ala)(bipy)] **3**

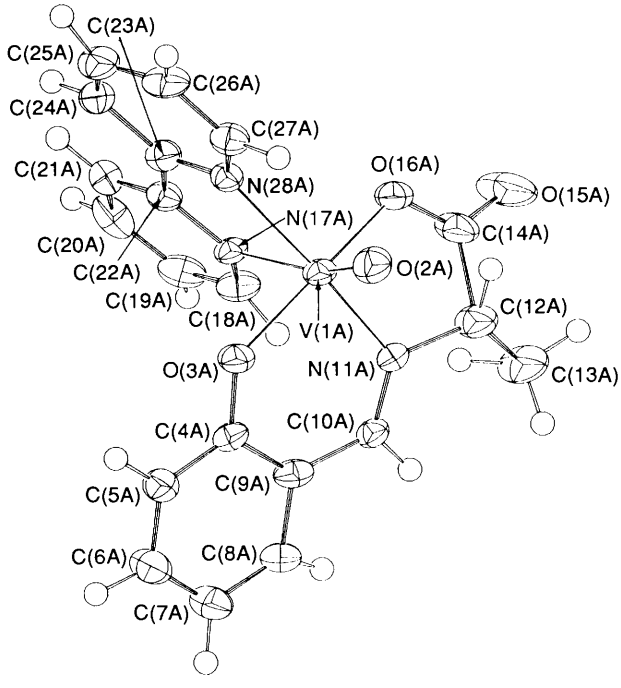


Fig. 3 An ORTEP[19] diagram of [VO(sal-L-ala)(bipy)] **3** (molecule A), showing the atomic notation. The thermal ellipsoids are drawn at the 40% probability level and hydrogen atoms have been drawn with isotropic thermal parameters arbitrarily set to 0.02 $Å^2$

equatorial atoms, within the normal range for vanadyl complexes.[20,21]

As for complex **2**, the Shiff base is not planar but two of its fragments can be regarded as planar: (*i*) C(12), C(14), O(15) and O(16) with maximum deviations of 0.013(7) Å for molecule A and 0.036(8) Å for molecule B; (*ii*) O(3) and all salicylaldehyde carbons, with maximum deviations of 0.035(5) Å for molecule A and 0.030(6) Å for B. The angles between these planes are much greater than the corresponding angle in **2**: 34.8(2) for molecule A and 23.0(2)° for B. As in **2**, atoms N(11) do not belong to any of these planes.

The vanadyl V=O bond distance in molecule B [1.616(6) Å]

Table 4 Selected bond lengths (Å) and angles (°) for [VO(sal-L-ala)(bipy)] **3**. For each entry, the value for molecule A is indicated first

O(2)–V	1.580(6)	O(3)–V	1.927(6)
	1.616(6)		1.966(6)
N(11)–V	2.051(5)	O(16)–V	2.035(6)
	2.037(6)		1.992(6)
N(17)–V	2.338(6)	N(28)–V	2.148(6)
	2.329(6)		2.151(6)
C(4)–O(3)	1.320(7)	C(10)–C(9)	1.450(8)
	1.415(7)		1.416(7)
N(11)–C(10)	1.283(7)	C(12)–N(11)	1.468(7)
	1.300(6)		1.490(7)
C(13)–C(12)	1.534(10)	C(14)–C(12)	1.573(10)
	1.500(10)		1.531(9)
O(15)–C(14)	1.217(8)	O(16)–C(14)	1.268(7)
	1.206(9)		1.285(8)
C(18)–N(17)	1.347(7)	C(22)–N(17)	1.358(7)
	1.350(7)		1.315(7)
N(28)–C(23)	1.323(7)	C(27)–C(26)	1.397(8)
	1.353(12)		1.399(9)
N(28)–C(27)	1.358(7)		
	1.354(7)		
O(3)–V–O(2)	103.9(3)	N(11)–V–O(2)	102.1(3)
	99.6(3)		104.7(3)
N(11)–V–O(3)	89.4(2)	O(16)–V–O(2)	98.3(3)
	87.7(2)		100.1(3)
O(16)–V–O(3)	156.5(2)	O(16)–V–N(11)	78.6(3)
	159.0(2)		80.4(2)
N(17)–V–O(2)	165.9(2)	N(17)–V–O(3)	82.0(3)
	167.3(2)		82.1(2)
N(17)–V–N(11)	90.7(2)	N(17)–V–O(16)	78.1(3)
	87.8(3)		80.2(3)
N(28)–V–O(2)	95.3(3)	N(28)–V–O(3)	90.8(2)
	95.5(3)		91.0(3)
N(28)–V–N(11)	162.1(2)	N(28)–V–O(16)	94.6(2)
	159.6(2)		94.2(3)
N(28)–V–N(17)	71.6(2)	C(4)–O(3)–V	131.1(3)
	71.9(3)		131.6(3)
C(5)–C(4)–O(3)	119.6(5)	C(9)–C(4)–O(3)	123.2(6)
	118.4(6)		123.9(5)
C(9)–C(4)–C(5)	117.2(5)	C(6)–C(5)–C(4)	121.8(6)
	117.7(5)		120.8(6)
C(7)–C(6)–C(5)	121.1(6)	C(8)–C(7)–C(6)	119.5(6)
	121.3(6)		118.7(5)
C(9)–C(8)–C(7)	120.8(6)	C(8)–C(9)–C(4)	119.6(6)
	121.9(6)		119.5(5)
C(10)–C(9)–C(4)	124.0(5)	C(10)–C(9)–C(8)	116.4(5)
	122.6(5)		118.0(5)
N(11)–C(10)–C(9)	124.2(5)	C(10)–N(11)–V	127.6(4)
	126.0(5)		128.2(4)
C(12)–N(11)–V	111.2(4)	C(12)–N(11)–C(10)	121.2(5)
	113.6(4)		118.1(5)
C(13)–C(12)–N(11)	116.2(6)	C(14)–C(12)–N(11)	105.4(5)
	111.8(6)		107.9(5)
C(14)–C(12)–C(13)	110.9(6)	O(15)–C(14)–C(12)	119.1(6)
	111.7(6)		119.4(7)
O(16)–C(14)–C(12)	115.0(6)	O(16)–C(14)–O(15)	125.5(7)
	117.1(6)		123.4(7)
C(14)–O(16)–V	118.2(5)	C(18)–N(17)–V	127.1(4)
	118.8(4)		124.3(4)
C(22)–N(17)–V	115.7(4)	C(22)–N(17)–C(18)	117.2(5)
	115.4(4)		120.2(6)
C(19)–C(18)–N(17)	123.4(6)	N(28)–C(23)–C(22)	116.5(5)
	123.1(6)		115.8(5)
C(23)–N(28)–V	122.1(4)	C(27)–N(28)–V	119.8(4)
	120.0(4)		118.9(5)
C(27)–N(28)–C(23)	117.9(5)		
	121.0(6)		

practically coincides with the mean value found for six-co-ordinated complexes (see above) while the corresponding distance for molecule A [1.580(6) Å] is close to the six-co-ordinate mean but on the short side, reflected in the V(1)–N(17) bond distance which is slightly longer for molecule A.

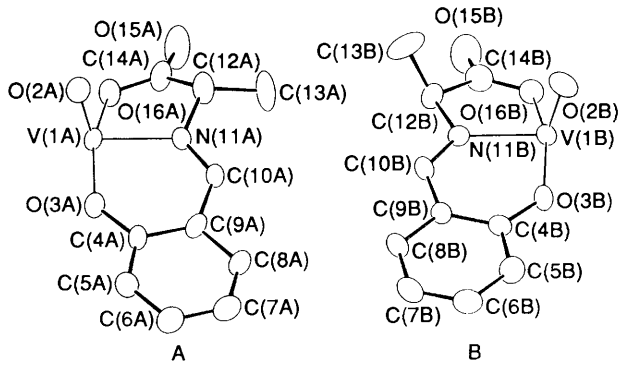
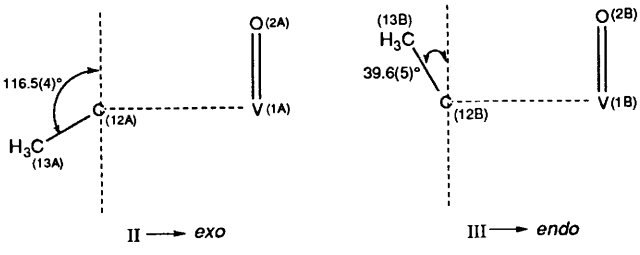
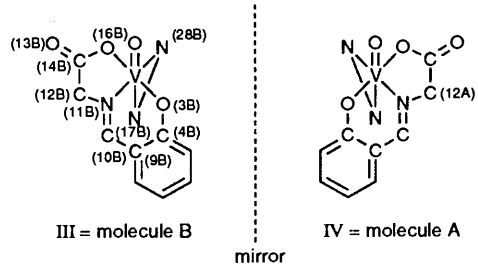


Fig. 4 The ORTEP[19] diagrams of the VO(sal-L-ala) fragments of molecules A and B of [VO(sal-L-ala)(bipy)] **3** emphasizing the relative positions of the V=O and CH_3 groups (*endo* for molecule B and *exo* for A). The position of the atoms of molecules A and B correspond to structures **III** and **II** in Scheme 1, respectively



Scheme 1 Antiparallel (**II**) and parallel (**III**) disposition of the V=O and C(12)–C(13) bonds in molecules A and B respectively



Scheme 2 Demonstration that, apart from the chirality of the L-alanine fragment and different conformations of the ligand, molecules A and B are enantiomers, *i.e.* vanadium(IV) is a chiral centre. Considering the chirality of the L-ala moiety, A and B are diastereoisomers

The conformation of the CH_3 group of the L-ala moiety is equatorial and antiparallel to the VO group in molecule A (**II** in Scheme 1) while in B the conformation is axial and parallel to the V=O group (**III** in Scheme 1). The dihedral angle between the V(1B)=O(2B) and C(12B)–C(13B) bonds is 9.65°.

Apart from the chirality of the L-alanine moiety and slight differences due to the unequal conformations of this fragment, molecules A and B (which are actually diastereoisomers) may be considered as enantiomers. This is emphasized in Scheme 2. It is a general characteristic of vanadyl complexes of this type, *i.e.* those with at least two non-equal adjacent equatorial donor atoms in a chelate molecule. For the parent glycine Schiff base there would be two enantiomeric octahedral complexes [**III** and **IV** of Scheme 2, with C(12B) and C(12A) both methylene groups, CH_2]. Each such enantiomer, when the methylene group is substituted to form CHR, the asymmetric chiral carbon centre of an α-amino acid, generates two diastereoisomers giving a total of four. Denoting the octahedral combinations as Λ and Δ, and those of the asymmetric amino acids D and L, these would be the racemic pairs ΛD, ΔL and ΛL, ΔD. However, in a case, like the present one, where only one hand of the amino acid is present (here L), only two diastereomers can form, ΛL and ΔL.

The situation is akin to that in 'quasi-racemates', an organic description of stereochemical relations between two closely

Table 5 Bond distances (Å) A and B for Cu^{II} and vanadyl Schiff-base complexes established by X-ray diffraction methods

(amino acid part) C(A)–N=C(B)–(aldehyde part), M^{2+}

Complex[a]	Bond A	Bond B	Ref.
$[Cu(salgly)(H_2O)]\cdot 4H_2O$	1.461	1.302	30
$[Cu(salgly)(H_2O)]\cdot 0.5H_2O$	1.446	1.282	31
$[\{Cu(sal\text{-}L\text{-}val)(H_2O)\}_2]$	1.48(2)	1.29(2)	32
$[Cu(sal\text{-}L\text{-}thr)(H_2O)_2]$	1.47(2)	1.29(2)	33
	1.45(2)	1.26(2)	
[Cu(sal-L-tyr)]	1.446(15)	1.280(14)	34
$[\{Cu(sal\text{-}L\text{-}phe)(H_2O)\}_2]$	1.51(4)	1.30(4)	35
	1.44(4)	1.32(4)	
	1.44(3)	1.36(4)	
$[Cu(HL^1)(H_2O)]\cdot H_2O$	1.480	1.247	36
$[Cu_2(sal\text{-}\beta\text{-}ala)_2(H_2O)]\cdot H_2O$	1.482	1.314(20)	37
$[VO(sal\text{-}L\text{-}ala)(H_2O)]$	1.469(5)	1.292(5)	9
$[V^VO_2(HL^2)]$	1.475(3)	1.292(3)	11
$Na[V_2O_3(D,L\text{-}salser)_2]\cdot 5H_2O$ V^{IV}	1.474(7)	1.292(6)	12
V^V	1.462(6)	1.299(7)	
$[VO(sal\text{-}L\text{-}ala)(bipy)]$ A:	1.468(7)	1.283(7)	*b*
B:	1.490(7)	1.300(6)	*b*
$[VO(salgly)(py)_2]$	1.475(8)	1.273(8)	*b*

[a] sal-L-val = *N*-salicylidene-L-valinate; sal-L-thr = *N*-salcylidene-L-threoninate; sal-L-phe = *N*-salicylidene-L-phenylalaninate; HL^1 = *N*-(1-carboxyethylidene)-β-alininate; HL^2 = *N*-(2-hydroxynaphthylmethyleneimino)-L-histidine. [b] This work.

similar but not isomeric compounds, based on m.p. diagrams.[22] A few examples are known among co-ordination compounds (*e.g.* refs. 23–27), including the quasi-racemate formed by Δ-*mer*-[Co(L-val)$_3$] with its diastereomer, Λ-mer-[Co(L-val)$_3$] (val = valine).[23]

The individual *N*-heterocyclic rings of bipyridyl are planar and the twist angles are 3.8(2) and 7.1(2)° for molecules A and B, respectively. The N–V–N angles are 71.6(2) and 71.9(3)° for molecules A and B compared with 77.4(2)° for [VO(mida)(bipy)] **5** (mida = *N*-methoxyiminodiacetate)[28] and 76.81(8)° for [VO(ida)(bipy)] **6**[29] (ida = iminodiacetate), where the two bipy nitrogens co-ordinate in equatorial positions. Except for the V–N (axial) (equatorial in **5** and **6**) and V(1)–N(28)–C(23) angles [122.1(4), 120.0(4) and 116.1(3)° for molecules A, B and **5**, respectively], the bond lengths and angles of the five-membered chelate ring of bipy in molecules A, B, **5** and **6** do not differ significantly.

As stated in the Introduction, *N*-salicylideneamino acidato complexes may be considered as model systems for pyridoxal-potentiated enzymes, namely in transaminations. In these reactions one important step involves migration of the double bond around the nitrogen atom. Therefore, the bond distances concerning the N atom may give a clue to the reaction mechanism. The bond lengths established by X-ray diffraction are summarized in Table 5 for several Schiff-base complexes of Cu^{II} and vanadyl. Normal single- and double-bond carbon–nitrogen distances are 1.47–1.49 and 1.29–1.30 Å, respectively. For complexes of Cu^{II} there are examples both of rather short bonds {*e.g.* C–N in $[Cu(salgly)(H_2O)]\cdot 0.5H_2O$,[31] C=N in $[Cu(pyr\text{-}\beta\text{-}ala)(H_2O)]$[36]} and normal bond distances {*e.g.* in $[\{Cu(sal\text{-}L\text{-}val)(H_2O)\}_2]$[32]}. However, for vanadium *N*-salicylideneamino acidato complexes of known structure, both C–N and C=N bond distances are within the normal range. Therefore, the presence of bipy or pyridine ligands induces no appreciable changes in these internuclear distances. The scarce structural data do not yet help in elucidating the mechanism of vanadium-activated β eliminations.

EPR Spectra.—The EPR spectra may help to elucidate which groups co-ordinate in equatorial position in solution. The spin-Hamiltonian parameters were calculated following the method described in ref. 38 by an iterative calculation procedure using the corrected equations given in ref. 39. For [VO(sal-L-ala)(bipy)] in methanol two species were present and we have analysed these spectra as a superposition of two axial spectra. Coincident perpendicular lines had to be assumed for the two species because these lines were not resolved. Even the parallel lines are close to each other, and only the high-field lines corresponding to $M_I = \frac{5}{2}$ and $\frac{7}{2}$ indicate the presence of two species.

The $g_{\|}$ and $A_{\|}$ values obtained (Table 6) are in the range expected for complexes with the present ligand donor atoms[38,39] ($g_{\|}$ somewhat lower than predicted). The presence of py or bipy gives rise to a slight decrease in $A_{\|}$ and $A_{\perp}$. Chasteen[38] does not include values for vanadium-51 hyperfine coupling constants for additivity calculations for a group such as Ph-CH=N-CHR: they are certainly different from those for =N(bipy). Assuming that, in methanolic solutions of complex **4**, H_2O is co-ordinated in equatorial position or, if MeOH is in fact the fourth equatorial ligand, that its hyperfine coupling constants for additivity calculations are equal to those of H_2O, a back calculation of $A_{\|}$ (=N-, Schiff base) gave a value of 171×10^{-4} cm^{-1}. Similar back calculations for components 1 and 2 in the spectra of [VO(sal-L-ala)(bipy)] gave estimates of this coupling constant in the range $(166–174) \times 10^{-4}$ cm^{-1}. Hyperfine coupling constants calculated for the EPR spectra of methanolic solutions of **4** with additions of several amounts of pyridine and of **4** dissolved in pyridine with addition of water suggests that, although apparently only one species is detected, two actually exist in solution. This is in accord with the CD spectra (see below).

CD and UV/VIS Spectra.—Fig. 5 shows the CD spectra of complexes **3** and **4** in methanol and dispersed in Nujol mulls, and Fig. 6 the visible absorption spectra of **4** in methanol and ethanol. Circular dichroism generally gives more useful structural information on vanadyl complexes than do visible absorption spectra,[40] and Figs. 5 and 6 demonstrate this. In the visible absorption spectra band I ($d_{xy} \longrightarrow d_{xz}$, d_{yz}) appears broad, between ≈650 and ≈900 nm (at least): in contrast, the CD spectra show two clear bands (Ia, $\Delta A < 0$; Ib, $\Delta A > 0$), emphasizing the non-symmetrical nature of the ligand field.

Table 6 The EPR spectral parameters for vanadium(IV) complexes in frozen solutions (77 K)

Compound	$g_\perp$	$g_\parallel$	$10^4A_\perp/cm^{-1}$	$10^4A_\parallel/cm^{-1}$
4 [VO(sal-L-ala)(H_2O)]	1.982	1.938	62.6	170.0
4 + pyridine*	1.975	1.941	57.9	167.3
3 [VO(sal-L-ala)(bipy)]				
Component 1	1.978	1.940	59.0	165.9
Component 2	1.988	1.952	62.1	163.8

* Two types of spectra were run: (*i*) of complex **4** dissolved in pyridine, followed by addition of water (mole ratio of **4**: py : H_2O = 1 : 1181 : 265); (*ii*) of **4** dissolved in methanol, followed by additions of pyridine (mole ratios of **4**: py = 1 : 690 and 1 : 135). Very slight differences in the spectra exist but the estimated EPR parameters for (*i*) and (*ii*) practically coincide.

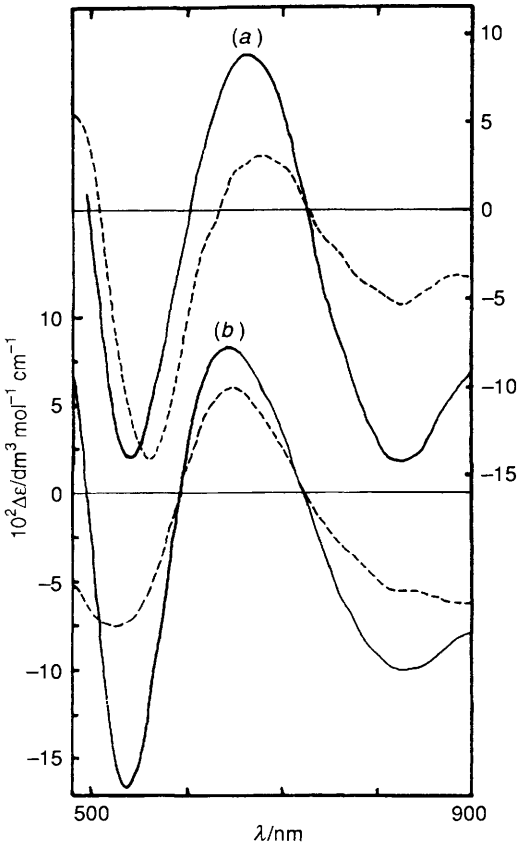


Fig. 5 The CD spectra of solid samples of complexes **3**(*a*) and **4**(*b*) dispersed in Nujol (- - - - -) and of their methanolic solutions (——)

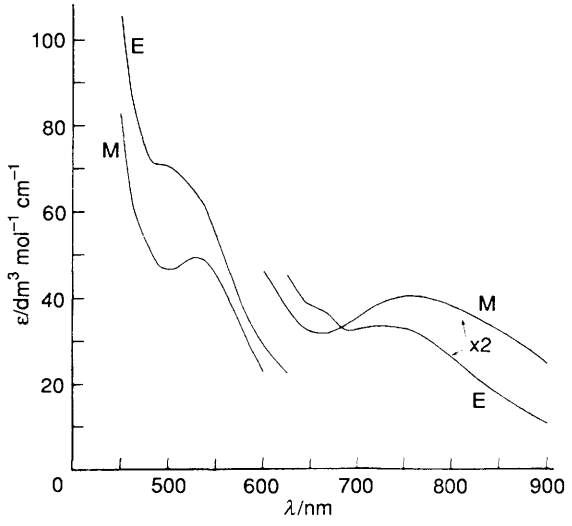


Fig. 6 Visible absorption spectra of complex **4** dissolved in methanol (M) and in ethanol (E)

Band II ($d_{xy} \longrightarrow d_{x^2-y^2}$) has λ_{max} around 520–550 nm and a negative Cotton effect in all spectra recorded. Also λ_{max} for **3** (bands Ib and II) is slightly shifted to the red as compared to **4**; λ_{max} for bands Ia is approximately the same for **3** and **4** ($\approx$820 nm).

The fact that the CD spectra of complexes **3** or **4** have similar patterns and λ_{max} in the solid state and solution suggests that the co-ordination geometry does not change upon dissolution in methanol. As distinct and clear spots are detected in the TLC experiments with **3** and **4** both with acid and neutral eluents, the complexes are relatively stable to hydrolysis. Apparently this is not the case of **1** dissolved in pyridine where the only spot detected corresponded to 'free' glycine. As the R_f values of the two spots observed for samples of **4** dissolved in pyridine coincide with those of **4** dissolved in methanol, the two bands detected for each of these two samples correspond to **4** and 'free' L-alanine.

Fig. 7(*a*) shows CD spectra of complex **4** dissolved in pyridine and of this solution after several additions of water, and 7(*b*) the CD spectra of **4** dissolved in methanol and of this solution after several additions of pyridine. These CD spectra and the EPR spectra recorded clearly indicate that although no solid was isolated from solutions containing **4** and pyridine, as was the case of **1**, *N*-salicylidene-L-alaninate co-ordinates to vanadium forming complexes with geometry equivalent to those of **2** and **7**.

In Fig. 7(*a*) the spectrum in pyridine (1) shows the pattern (−,+,+) with λ_{max} and $\Delta\varepsilon$: band II (520 nm, −0.30 dm^3 mol^{-1} cm^{-1}), Ib(630 nm, +0.197 dm^3 mol^{-1} cm^{-1}) and Ia($\approx$950 nm, +0.05 dm^3 mol^{-1} cm^{-1}). As water is added the pattern progressively changes to (−,+,−). In Fig. 7(*b*) addition of the first amounts of pyridine to methanolic solutions of **4** gives rise to a UV shift of bands Ia, Ib and II, an increase in $|\Delta\varepsilon|$ for band Ia and a decrease for band II. Further additions of pyridine do not change λ_{max} [for pyridine concentrations used in spectra of Fig. 7(*b*)], but do result in a decrease in $|\Delta\varepsilon|$ of band II and especially of Ia, and a slight increase in $\Delta\varepsilon$ of band Ib. These observations and the EPR spectra recorded for solutions of **4** in methanol with several additions of pyridine may be explained assuming the reactions in Scheme 3.

The formation of species **VI** was confirmed by the X-ray characterization of [VO(salgly)($py)_2$] **2** and the elemental analysis of **7** is in accord with structure **V**. Several other solids obtained from similar reaction mixtures in this work are probably mixtures of complexes with structures such as **I**, **V** and **VI**. Previous reports have only mentioned the formation of orange compounds formulated as [VO(sal-gly)(py)(H_2O)][2] and [VO(OH)L(py)][11] (L is the Schiff-base anion derived from *o*-hydroxynaphthalenecarbaldehyde and phenylalanine).

Addition of bipy to methanolic solutions of [VO(sal-L-ala)(H_2O)] **4** changes the CD spectra of the solution. However, the CD spectra of solutions with bipy: **4** mole ratios of 1, 5, 10 and 20 : 1 coincide within experimental error but differ slightly from those of methanolic solutions of [VO(sal-L-ala)(bipy)] **3**. These small differences probably arise from the presence of

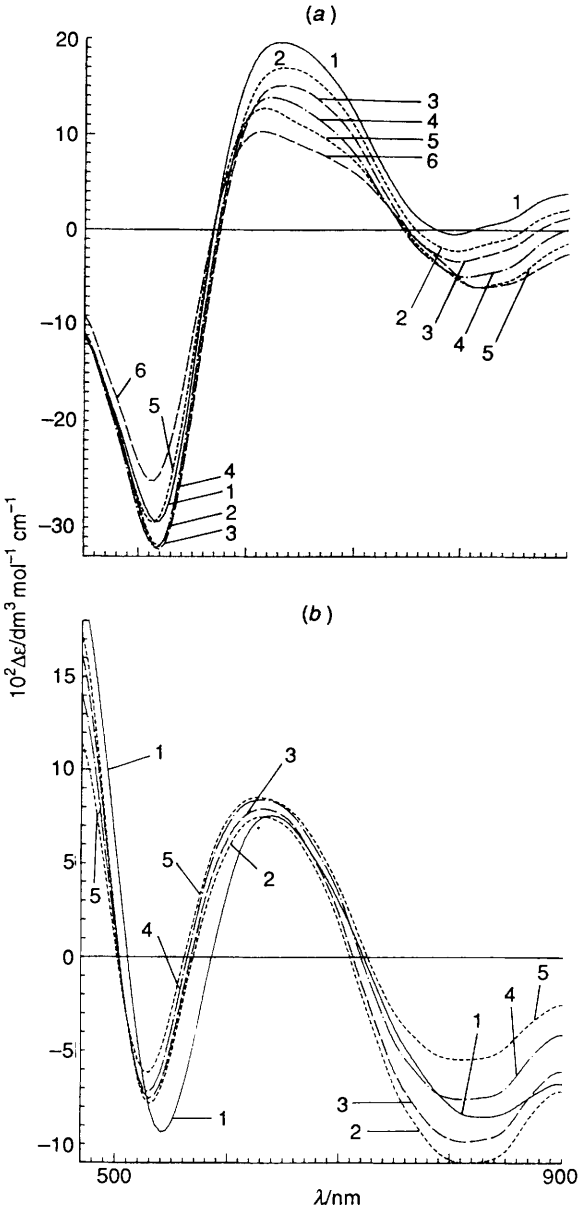
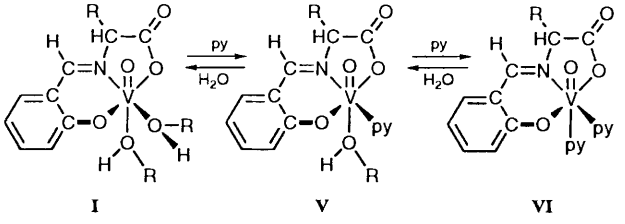


Fig. 7(*a*) The CD spectra of [VO(sal-L-ala)(H_2O)] **4** in pyridine (1) (total volume 5.0 cm^3) and after several additions of water: 0.2 (2), 1.5 (3), 3.5 (4), 5.5 (5) and 6.5 cm^3 (6). As the CD spectra in pyridine for concentrations of **4** in the range 0.0022–0.011 mol dm^{-3} coincide within experimental error, this rules out the existence of dimers under these experimental conditions. (*b*) The CD spectra of **4** in methanol (1) (total volume 9.0 cm^3) and after several additions of pyridine: 1.0 (2), 2.0 (3), 5.0 (4) and 8.0 cm^3 (5)



Scheme 3 Species present in solutions of complexes **1** or **4** in methanol (**I**) or pyridine (**VI**) and after addition of water to the pyridine solutions of **1** or **4**. The CD spectrum of **4** in pyridine, where a slightly negative band may be seen between ≈780 and 810 nm, probably corresponds to **VI** with a small fraction of **V**. The presence of **V** occasions this slightly negative band. R = H or CH_3

water in methanolic solutions of complex **4**; the amount of water present in methanolic solutions of **3** is much lower.

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