Crystal and molecular structure of [V₂O₃(sal-L-val)₂(H₂O)] (sal-L-val = N-salicylidene-L-valinate) and spectroscopic properties of related complexes†

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The dinuclear vanadium(v) complex [V₂O₃(sal-L-val)₂(H₂O)] 1 (sal-L-val = N-salicylidene-L-valinate) has been prepared and characterized and its crystal structure determined. The compound contains a double bridge by O (oxo) and O (carboxylate) and is one of the rare examples where the two VO groups make an angle near 90°. There are two independent molecules, A and B, in the asymmetric unit which are similar and each consists of two VO(sal-L-val) groups at nearly right angles to each other. They exhibit a distorted-octahedral geometry, involving in the equatorial plane the O,N,O atoms of the Schiff-base ligand and the bridging O (oxo) group and in the axial positions a carboxyl oxygen of the second VO(sal-L-val) group and a water molecule. The bridging V–O(oxo) bond lengths range between 1.787 and 1.823 Å, and are significantly shorter than the bridging V–O(carboxylate), ranging between ≈1.93–1.94 Å for equatorial and ≈2.40–2.43 Å for axial. Several known [VO(sal-L-aa)(H₂O)] and new [VO(sal-L-aa)(bipy)] (sal-L-aa = N-salicylidene-L-amino acidate, bipy = 2,2′-bipyridine) complexes were also prepared and their spectroscopic (ESR, UV and CD) properties studied. A correlation observed between the CD intensities and the size of the amino acid side groups is discussed.

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) have been prepared previously.[2,3] They are bluish grey and there is no appreciable interaction between the V atoms. X-Ray diffraction study[4] of the L-alanine derivative confirmed the co-ordination geometry to be as in **I**. One water molecule occupies a co-ordination position and 'prevents' dimerization of the compounds, assumed to be possible by comparison with similar salicylamine complexes.[5] From a solution containing [VO(sal-L-ala)(H₂O)] in wet methanol, [VⱽO(sal-L-ala)(OMe)(MeOH)] (sal-L-ala = N-salicylidene-L-alaninate) was obtained,[6] with a co-ordination geometry as in **II**; treatment of the aqua compound with wet dichloromethane yielded deep blue crystals of [{VⱽO(sal-L-ala)}₂O]·2CH₂Cl₂ (co-ordination geometries as in **IIIa** and **IIIb**). The molecular structures of the products were determined by X-ray techniques.[6] The vanadium(v) complex of the Schiff base formed from 2-hydroxynaphthalenecarbaldehyde and histidine[7] and a mixed-valence complex of vanadium-(iv) and -(v), Na[V₂O₃(sal-D,L-ser)₂]·5H₂O (sal-D,L-ser = N-salicylidene-D,L-serinate), have been isolated and also characterized by X-ray diffraction.[8] The latter has a co-ordination geometry as in **IV**. The preparation and characterization of solid complexes from solutions containing [VO(salgly)(H₂O)] (salgly = N-salicylideneglycinate) and pyridine (py), namely [VO(salgly)(py)₂], and of [VO(sal-L-ala)(bipy)] from solutions containing [VO(sal-L-ala)(H₂O)] and 2,2′-bipyridine (bipy) has also been reported.[9] The preparation and crystal structure of [VⱽO(sal-L-phe)(hquin)] (Hhquin = quinolin-8-ol) was also recently reported.[10] 2-Hydroxy-1-naphthylmethyleneamino-
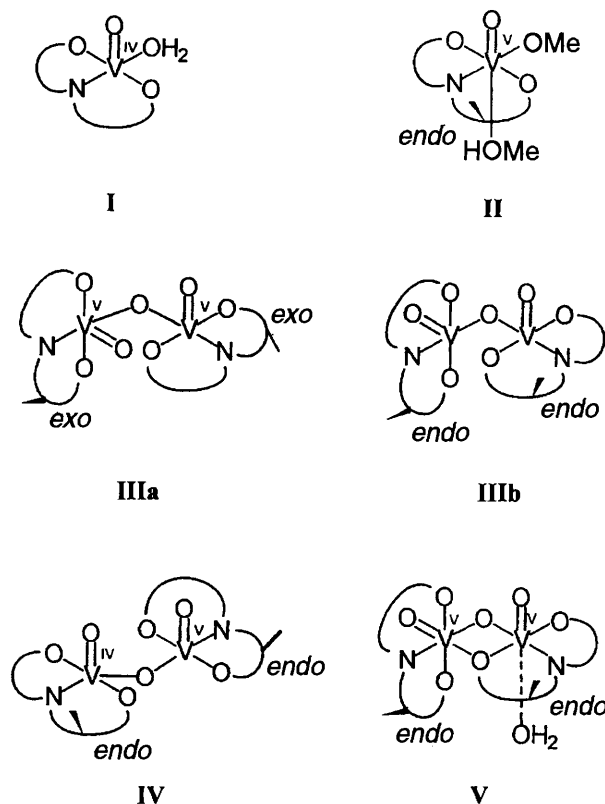
I

endo HOMe

II

IIIa

IIIb

IV

V

acidato complexes of vanadium-(iv) and -(v) have also been prepared[11] (amino acidates = glycinate, D,L-alaninate, D,L-phenylalaninate and L-valinate). Presumably they have co-ordination geometries corresponding to **I** and **II**, respectively. This was recently confirmed[12] for the oxovanadium(v)

compound [VO(naph-L-ala)(OBuˢ)(BuˢOH)] [naph-L-ala =
N-(2-oxido-l-naphthylmethylene)-L-alalinate and BuˢOH =
D,L-sec-butyl alcohol], a complex containing four centres of
chirality.

The present paper deals with the preparation and charac-
terization by X-ray diffraction of [V_2O_3(sal-L-val)$_2$(H_2O)] with
a co-ordination geometry as in V, and with spectroscopic and
magnetic studies of a few related Schiff-base complexes. There
have been many O-bridged dinuclear vanadium(IV and/or V)
complexes the structures of which have been determined by X-
ray diffraction, e.g. refs. 6, 8 and 13–29, although those
involving the OV^VOV^VO unit are relatively rare. This is the first
example of such a complex involving double (mixed) bridging
by O (oxo) and O (carboxylate), and one of the rare examples
where the two VO groups make an angle near 90°.

Experimental

Preparations

[V_2O_3(sal-L-val)$_2$(H_2O)] 1. The complex [VO(sal-L-
val)(H_2O)] 2 was prepared as described in ref. 2. After
precipitation of 2 from the reaction mixture, the solid was
filtered off. The filtrate was kept at room temperature in a
beaker covered with Parafilm®. After several months, black
crystals of 1 were separated and studied by X-ray diffraction.
$\tilde{v}_{max}$/cm⁻¹ (microcrystal Fourier-transform IR, see below):
2967, 2934, 2876 (methyl C–H); 1714, 1689vs (C=N); 1624,
1615vs v(C=N) and v_{asym}(CO$_2$); 1558s (C=N and phenyl
coupling),[31,32] 1310 (sh) (O–Ph)[7] and 955s (VO).

Complexes 3–13.
The complexes [VO(sal-L-phe)(H_2O)] 3,
[VO(sal-L-met)(H_2O)] 4, [VO(sal-L-ile)(H_2O)] 5, [VO(sal-L-
ala)(H_2O)] 6 and [VO(naph-L-val)(H_2O)] 7 were obtained as
described by Theriot et al.[2] (sal-L-phe = N-salicylidene-L-
phenylalaninate, sal-L-met = N-salicyclidene-L-methioninate
and sal-L-ile = N-salicylidene-L-isoleucinate); [VO(sal-L-met)-
(bipy)]·H_2O 8, [VO(sal-L-val)(bipy)]·1.5H_2O 9, [VO(sal-L-
phe)(bipy)]·1.5H_2O 10 and [VO(sal-L-phe)(py)]·2H_2O 11 were
also obtained, similarly to[9] [VO(sal-L-ala)(bipy)] 12 and
[VO(salgly)(py)]·H_2O 13, and are new. The brownish orange
solid 8 was obtained shortly after mixing the reagents (Found:
C, 53.2; H, 4.4; N, 9.2. $C_{22}H_{23}N_3O_5SV$ requires C, 53.65; H,
4.70; N, 8.55%); $\tilde{v}_{max}$/cm⁻¹ (KBr disc) 2920w (C–H), v(C=N)
and v_{asym}(CO$_2$) centred at 1660vs (br). The brownish orange
solid 9 was also obtained shortly after mixing the reagents
(Found: C, 56.1; H, 4.8; N, 8.9. $C_{22}H_{24}N_3O_{5.5}V$ requires C,
56.30, H, 5.15; N, 8.95%); $\tilde{v}_{max}$/cm⁻¹ (KBr disc) 2960, 2930w
(C–H), v(C=N) and v_{asym}(CO$_2$) centred at 1660vs (br). For the
brownish orange solid 10 (Found: C, 59.7; H, 4.2; N, 7.9.
$C_{26}H_{24}N_3O_{5.5}V$ requires C, 60.35; H, 4.65; N, 8.10%);
$\tilde{v}_{max}$/cm⁻¹ (KBr disc) v(C=N) and v_{asym}(CO$_2$) centred at 1630vs
(br) and 1605s (br), respectively. Small brown crystals of 11
were collected 5 d after mixing the reagents (Found: C,
56.5; H, 5.3; N, 6.6. $C_{21}H_{22}N_2O_6V$ requires C, 56.15; H, 4.95; N,
6.25%); $\tilde{v}_{max}$/cm⁻¹ (KBr disc) 1640vs (br) (C=N) and 1600s (sh)
v_{asym}(CO$_2$). Complexes 8–11 also exhibit IR bands at 1535–
1540m (C=N and phenyl coupling),[30,31] 1340–1350m/s
v_{sym}(CO$_2$), 1308–1312s (O–Ph)[7] and 955–960vs (VO).

The preparation of [VO(sal-aa)(bipy)] (aa = gly, val or phe)
has recently been reported by Chakravorty and co-workers,[32]
complexes included here were recently presented at international
meetings.[33,34]

Magnetic moments

The magnetic susceptibilities were measured for [VO(naph-L-
val)(H_2O)] 7 (13.37 mg), in the range 4.9–292 K using a 7 T
Oxford Instruments Faraday system coupled to a Sartorius
S3D-V microbalance, operating at 1 T, with forward and
reverse gradients of 5 T m⁻¹.

Circular dichroism and ESR spectra

The CD spectra were run on a JASCO 720 spectropolarimeter
either with 175–700 nm or with red-sensitive (400–1000 nm)
photomultipliers, ESR spectra on a Bruker ER 200d (connected
to a Brucker B-MN C5) spectrometer. Samples were prepared
as described in ref. 9 and placed between two microscopic slides.
One to three such slides were placed in the sample compart-
ment. Each final spectrum is the average of six to eight spectra,
recorded as described in ref. 9. For solution CD spectra, oxygen
was removed from the solvents by bubbling N_2. The spectra
were recorded immediately after the preparation of the solu-
tions: the cells had their stoppers reinforced with Parafilm strips
but no special care was taken to remove oxygen from the cells.

Crystallography

Crystal data. $C_{24}H_{26}N_2O_{10}V_2$ 1, M_r = 604.35, hexagonal,
space group $P6_5$, a = 14.470(5), c = 46.601(10) Å, U = 8450(5)
Å³, Z = 12, $F(000)$ = 3720, D_c = 1.425 Mg m⁻³, μ(Mo-Kα) =
0.718 mm⁻¹, crystal dimensions 0.4 × 0.4 × 0.5 mm, $F(000)$ =
3720.

Data collection. X-Ray measurements were made with an
Enraf-Nonius CAD-4 diffractometer and graphite-monochro-
mated Mo-Kα radiation (λ 0.710 69 Å). Cell dimensions were
determined from the measured θ values for 25 intense
reflections having 10 < θ < 13°. The intensities of 6455
observations of 5252 independent reflections [R_{int} = 0.0930,
$R_\sigma(I)$ = 0.1214] in the range 2.0 ⩽ θ ⩽ 26.0° were measured
by the ω-scan mode. The data were corrected for Lorentz-
polarization and absorption effects.

Structure determination and refinement. The positions of the
four vanadium atoms were determined by a direct method with
the program SHELXS 86.[35] The positions of the remaining
non-hydrogen atoms in each of the two independent molecules
in the asymmetric unit were found from subsequent refinements
followed by Fourier-difference syntheses. Following conver-
gence of the anisotropic refinement, no hydrogen atoms could
be located from the difference electron-density map, therefore
all but the hydrogen atoms attached to the water molecules
were placed in calculated positions and included in the
refinement using the riding model. Group isotropic thermal
motion parameters were refined for the aromatic and the
methyl hydrogens in each molecule. The Flack x
parameter[36] converged to a value near zero, which indicates
that the space group of the crystal structure and the absolute
configuration of the molecule were correctly determined. The
final refinement statistics are presented in Table 1 and
fractional atomic coordinates in Table 2. The structure-
refinement calculations were carried out using the program
SHELXL 93.[37] Atomic scattering factors were taken from
International Tables.[38]

Complete atomic coordinates, thermal parameters, and bond
lengths and angles have been deposited at the Cambridge
Crystallographic Data Centre. See Instructions for Authors,
J. Chem. Soc., Dalton Trans., 1996. Issue 1.

Results and Discussion

A molecular diagram presenting the atomic numbering scheme
is shown in Fig. 1 Selected bond distances for both molecules
in the asymmetric unit are listed side-by-side in Table 3 and
the agreement is very good. Each molecule consists of two
VO(sal-L-val) groups nearly at right angles to each other, the
dihedral angles between the vanadyl groups being O(1)–V(1)···
V(2)–O(2) 87.8(6)° in molecule A and O(3)–V(3)···
V(4)–O(4) 87.6(7)° in B. This is uncommon in oxo-bridged
dinuclear vanadium complexes where these bonds are normally
either parallel or antiparallel. The two V atoms are six-co-

ordinated and equatorially bridged by an oxygen atom. The remaining three equatorial co-ordination positions involve bond distances similar to those reported for other vanadium(IV) complexes with sal-aa ligands.[9] Finally, the *trans* axial position with respect to the vanadyl oxygen is co-ordinated to a carboxyl oxygen of the second VO(sal-L-val) group in the case of V(1) and V(3), and to a water molecule in the case of V(2) and V(4). The V ᐧᐧᐧ V distances in each molecule are very similar.

The vanadium atoms are significantly displaced from the least-squares plane of the equatorially ligated atoms in the direction of the vanadyl oxygen. The distances are 0.379(3), 0.314(3), 0.372(4) and 0.334(4) Å for V(1), V(2), V(3) and V(4),

respectively. In other six-co-ordinated complexes the vanadium atom is normally out of the plane by similar distances.[40] Since V(1) and V(2) in molecule A are equivalent to V(3) and V(4) in B, there appears to be a systematic effect in these distances, possibly arising from the different strengths of the interaction with the axial ligand. In fact, for V(1) and V(3), these donor atoms are carboxylate O at $\approx 2.433(9)$ and 2.474(10) Å, respectively. For V(2) and V(4) these donor atoms are oxygens from water molecules at significantly shorter distances, 2.398(9) and 2.398(11) Å, respectively. Shorter distances to the axial ligands correspond to smaller displacements of the V atoms from the least-squares plane of the equatorially ligated atoms.

The bridging oxo bond angles are 117.4(5) and 117.8(5)°, for molecules A and B, respectively. Such angles near 120° for oxo-bridged dinuclear vanadium complexes are rare; the one other known case was reported[18] only recently. The angles between the bonds V(1)–O(1) ᐧᐧᐧ C(18)–C(19) 7.7(6), V(3)–O(3) ᐧᐧᐧ C(38)–C(39) 7.3(9), V(2)–O(2) ᐧᐧᐧ C(28)–C(29) 0.7(1.0) and V(4)–O(4) ᐧᐧᐧ C(48)–C(49) 1.8(1.1)° show that these are roughly parallel, and that the two halves of each dinuclear unit have the same geometric configuration in respect of the disposition of the CH(CH₃) and V=O groups, both being *endo* isomers. The structure of complex 1 may therefore be schematically represented as V. The amino acid chelate rings bonded to V(1) and V(3) correspond to asymmetric envelope conformations. Those bonded to V(2) and V(4) correspond to a δ conformation.

Although the hydrogen atoms attached to the co-ordinated water molecules could not be located from difference-density maps, geometrical considerations allow the inference of two hydrogen bonds (Fig. 2) between molecules A and B [O(22) ᐧᐧᐧ O(372) 2.84(1), O(44) ᐧᐧᐧ O(172) 2.86(2) Å].

Table 1 Final refinement statistics for $[V_2O_3(sal-L-val)_2] \cdot H_2O$. Refinement method: full-matrix least squares on F^2; calculated weights: $w = 1/[\sigma^2(F_o^2) + (0.0571P)^2 + 0.1768P]$ $\{P = [\max(F_o^2, 0) + 2F_c^2]/3\}$

No. refined parameters	697
No. unique reflections	5252
No. used reflections ($F > 0$)	4308
No. observed reflections $[F^2 > 2\sigma(F^2)]$	2616
R (observed data)	0.0708
(used data)	0.1122
(F, all data)	0.1734
wR (observed data)	0.1344
(used data)	0.1604
(F^2, all data)	0.2010
Goodness of fit, S (used data)	1.083
(all data)	1.211
$\Delta\rho_{max}$, $\Delta\rho_{min}/e$ Å^{-3}	0.29(6), $-0.28(6)$
Flack parameter x	$-0.02(5)$

Table 2 Atomic coordinates ($\times 10^4$) for $[V_2O_3(sal-L-val)_2] \cdot H_2O$

Atom	x	y	z	Atom	x	y	z
V(1)	28(2)	3959(2)	866(1)	V(3)	694(2)	5843(2)	$-958(1)$
O(1)	953(7)	4689(7)	1082(2)	O(3)	1727(8)	6400(8)	$-1158(2)$
N(1)	$-1186(10)$	4321(9)	956(2)	N(3)	116(13)	4219(11)	$-1010(2)$
C(10)	$-2137(14)$	3665(15)	1028(3)	C(30)	$-804(17)$	3534(15)	$-1095(4)$
C(11)	$-2536(14)$	2547(12)	1122(3)	C(31)	$-1584(16)$	3795(15)	$-1216(3)$
C(12)	$-3598(14)$	1930(16)	1176(4)	C(32)	$-2626(19)$	2958(15)	$-1279(4)$
C(13)	$-3941(18)$	888(18)	1262(4)	C(33)	$-3331(22)$	3164(18)	$-1390(5)$
C(14)	$-3226(22)$	538(18)	1301(5)	C(34)	$-3069(18)$	4210(19)	$-1450(4)$
C(15)	$-2159(15)$	1172(13)	1245(4)	C(35)	$-2034(20)$	5062(18)	$-1394(4)$
C(16)	$-1779(14)$	2218(12)	1150(3)	C(36)	$-1299(17)$	4824(13)	$-1278(4)$
C(17)	$-199(14)$	5582(12)	583(3)	C(37)	1280(13)	4546(14)	$-619(4)$
C(18)	$-902(12)$	5395(11)	853(3)	C(38)	823(15)	3842(15)	$-891(4)$
C(19)	$-304(15)$	6248(15)	1087(4)	C(39)	1743(17)	4079(17)	$-1115(4)$
C(191)	19(28)	7273(17)	992(6)	C(391)	2510(17)	3767(17)	$-965(5)$
C(192)	$-984(17)$	5992(16)	1368(4)	C(392)	1292(21)	3410(22)	$-1384(5)$
O(16)	$-760(8)$	2823(8)	1104(2)	O(36)	$-322(10)$	5632(8)	$-1234(2)$
O(171)	275(8)	5047(7)	580(2)	O(371)	1303(8)	5462(8)	$-631(2)$
O(172)	$-142(10)$	6199(9)	385(2)	O(372)	1585(10)	4281(10)	$-403(2)$
O(12)	627(6)	3403(7)	631(2)	O(34)	739(7)	6929(7)	$-764(2)$
V(2)	$-232(2)$	2435(2)	363(1)	V(4)	$-401(2)$	6653(2)	$-538(1)$
O(2)	$-619(7)$	1351(7)	533(2)	O(4)	$-1149(9)$	6810(10)	$-760(3)$
N(2)	$-1440(8)$	1787(9)	49(2)	N(4)	$-1564(9)$	5816(9)	$-223(3)$
C(20)	$-1363(11)$	1433(10)	$-209(3)$	C(40)	$-1797(11)$	6234(13)	1(3)
C(21)	$-468(12)$	1403(12)	$-315(3)$	C(41)	$-1296(12)$	7347(12)	53(3)
C(22)	$-628(15)$	863(13)	$-588(4)$	C(42)	$-1665(13)$	$-2261(15)$	287(3)
C(23)	214(16)	841(15)	$-701(3)$	C(43)	$-1230(15)$	$-1227(15)$	347(4)
C(24)	1182(15)	1310(13)	$-573(4)$	C(44)	$-360(15)$	$-548(12)$	200(3)
C(25)	1350(14)	1844(13)	$-300(3)$	C(45)	42(16)	$-823(12)$	$-20(4)$
C(26)	489(13)	1858(12)	$-175(3)$	C(46)	$-402(13)$	8106(12)	$-95(3)$
C(27)	$-2092(12)$	2691(12)	353(2)	C(47)	4369(14)	5860(14)	1215(4)
C(28)	$-2397(10)$	1845(12)	117(3)	C(48)	$-2116(12)$	4655(11)	$-237(3)$
C(29)	$-3342(14)$	713(14)	210(5)	C(49)	$-3298(15)$	4187(15)	$-330(4)$
C(291)	$-3167(18)$	274(17)	464(5)	C(491)	$-3390(16)$	4474(17)	$-653(4)$
C(292)	$-4368(14)$	777(17)	222(5)	C(492)	$-3974(18)$	3108(21)	$-259(6)$
O(26)	601(7)	2325(8)	87(2)	O(46)	8(10)	7781(8)	$-303(3)$
O(271)	$-1248(7)$	2835(7)	503(2)	O(471)	$-831(8)$	5186(7)	$-623(2)$
O(272)	$-2592(10)$	3107(9)	404(2)	O(472)	3471(8)	5077(10)	1191(2)
O(22)	247(8)	3987(8)	76(2)	O(44)	631(9)	6358(8)	$-185(2)$

Table 3 Selected bond distances (Å) and angles (°) in $[V_2O_3(sal\text{-}L\text{-}val)_2]\cdot H_2O$

V(1)–O(1)	1.583(8)	V(3)–O(3)	1.596(10)	V(2)–O(12)	1.826(8)	V(4)–O(34)	1.825(9)
V(1)–O(12)	1.816(9)	V(3)–O(34)	1.787(9)	V(2)–O(26)	1.823(10)	V(4)–O(46)	1.801(11)
V(1)–O(16)	1.831(10)	V(3)–O(36)	1.858(11)	V(2)–O(271)	1.943(9)	V(4)–O(471)	1.931(9)
V(1)–O(171)	1.953(9)	V(3)–O(371)	1.974(10)	V(2)–N(2)	2.105(11)	V(4)–N(4)	2.100(13)
V(1)–N(1)	2.109(11)	V(3)–N(3)	2.078(14)	V(2)–O(22)	2.398(9)	V(4)–O(44)	2.398(11)
V(1)–O(271)	2.433(9)	V(3)–O(471)	2.474(10)	V(1) ··· V(2)	3.112(3)	V(3) ··· V(4)	3.095(4)
V(2)–O(2)	1.589(9)	V(4)–O(4)	1.593(11)				
O(1)–V(1)–O(12)	104.3(5)	O(3)–V(3)–O(34)	103.9(5)	O(2)–V(2)–O(26)	100.9(5)	O(4)–V(4)–O(46)	101.7(7)
O(1)–V(1)–O(16)	98.8(5)	O(3)–V(3)–O(36)	98.3(6)	O(2)–V(2)–O(12)	100.6(5)	O(4)–V(4)–O(34)	101.4(5)
O(12)–V(1)–O(16)	100.8(4)	O(34)–V(3)–O(36)	99.9(5)	O(26)–V(2)–O(12)	108.9(4)	O(46)–V(4)–O(34)	107.5(5)
O(1)–V(1)–O(171)	98.2(4)	O(3)–V(3)–O(371)	99.0(5)	O(2)–V(2)–O(271)	100.4(4)	O(4)–V(4)–O(471)	98.9(6)
O(12)–V(1)–O(171)	90.6(4)	O(34)–V(3)–O(371)	91.6(4)	O(26)–V(2)–O(271)	153.4(4)	O(46)–V(4)–O(471)	154.2(5)
O(16)–V(1)–O(171)	156.4(4)	O(36)–V(3)–O(371)	156.2(5)	O(12)–V(2)–O(271)	82.4(4)	O(34)–V(4)–O(471)	83.2(4)
O(1)–V(1)–N(1)	103.9(5)	O(3)–V(3)–N(3)	104.4(5)	O(2)–V(2)–N(2)	96.0(4)	O(4)–V(4)–N(4)	97.4(5)
O(12)–V(1)–N(1)	150.5(4)	O(34)–V(3)–N(3)	150.5(4)	O(26)–V(2)–N(2)	84.8(4)	O(46)–V(4)–N(4)	84.5(5)
O(16)–V(1)–N(1)	83.2(4)	O(36)–V(3)–N(3)	84.1(5)	O(12)–V(2)–N(2)	155.8(4)	O(34)–V(4)–N(4)	154.9(4)
O(171)–V(1)–N(1)	77.0(4)	O(371)–V(3)–N(3)	75.9(5)	O(271)–V(2)–N(2)	77.4(4)	O(471)–V(4)–N(4)	77.6(5)
O(1)–V(1)–O(271)	173.9(4)	O(3)–V(3)–O(471)	173.4(4)	O(2)–V(2)–O(22)	175.4(4)	O(4)–V(4)–O(44)	176.5(5)
O(12)–V(1)–O(271)	69.8(3)	O(34)–V(3)–O(471)	69.6(4)	O(26)–V(2)–O(22)	78.2(4)	O(46)–V(4)–O(44)	78.1(5)
O(16)–V(1)–O(271)	84.1(4)	O(36)–V(3)–O(471)	83.8(4)	O(12)–V(2)–O(22)	84.0(4)	O(34)–V(4)–O(44)	82.0(4)
O(171)–V(1)–O(271)	80.6(3)	O(371)–O(3)–O(471)	80.8(4)	O(271)–V(2)–O(22)	79.3(4)	O(471)–V(4)–O(44)	80.4(4)
N(1)–V(1)–O(271)	81.7(4)	N(3)–V(3)–O(471)	82.0(4)	N(2)–V(2)–O(22)	79.5(4)	N(4)–V(4)–O(44)	79.0(4)
V(1)–O(12)–V(2)	117.4(4)	V(3)–O(34)–V(4)	117.9(5)	V(1)–O(271)–V(2)	89.9(3)	V(3)–O(471)–V(4)	88.4(4)
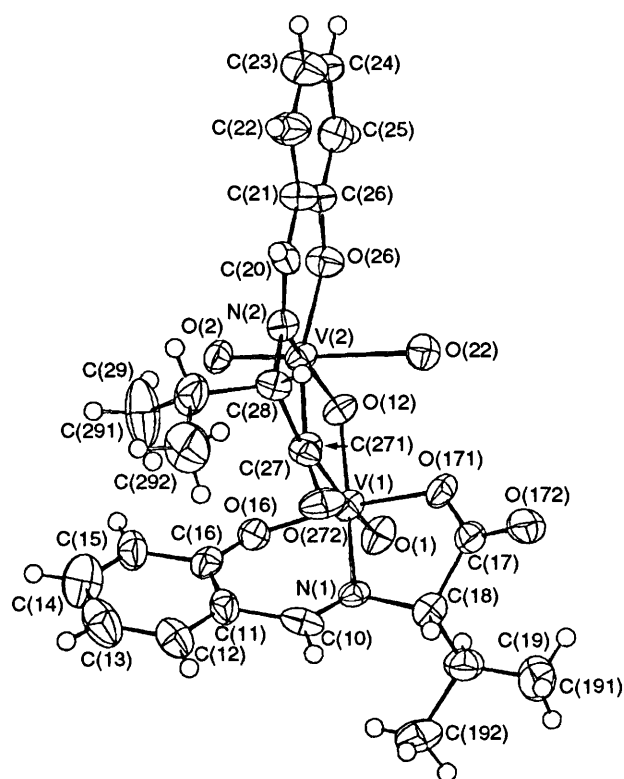
Fig. 1 An ORTEP[39] diagram of $[V_2O_3(sal\text{-}L\text{-}val)_2]\cdot H_2O$ **1** showing the atomic notation of molecule A. The notation used for molecule B (not shown) is similar, the first digit being 3 or 4 instead of 1 or 2 for in A. The thermal ellipsoids of the hydrogen atoms have been drawn with an arbitrary isotropic thermal parameter of 0.02 Å².

The two independent molecules in the asymmetric unit (Fig. 2) are related by a quasi-two-fold rotation axis approximately perpendicular to the crystallographic c axis. This corresponds to a rotation of 170.5° about an axis nearly perpendicular (89.6°) to the crystallographic c axis and at an angle of 43.6° from the crystallographic a axis, which superimposes molecule A onto B.
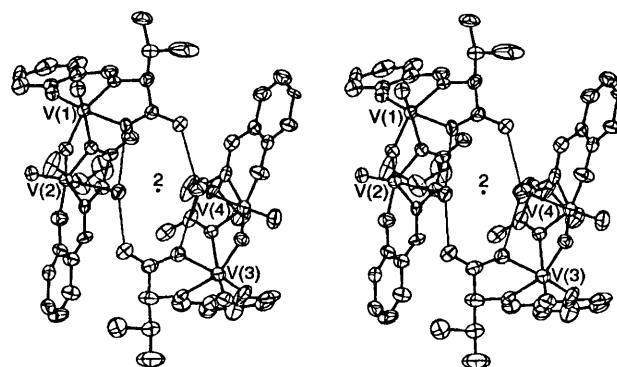
Fig. 2 An ORTEP[39] diagram of the two independent molecules in the asymmetric unit. This view is approximately parallel to the quasi-two-fold rotation axis (circle labelled 2) which is perpendicular to the crystallographic c axis. Calculations with the program LSQKAB[41] of the CCP4 program suite[42] yield a rotation matrix which can be expressed in terms of the spherical polar angles (ω,φ,χ), with values (89.6, 43.6, 170.5°). The root mean square (r.m.s.) deviation between the atoms of molecule A superimposed onto those of B after the rotation is 0.21 Å, the maximum deviation being 0.5 Å between C(292) and C(492). The hydrogen-bonding scheme between the carboxyl oxygens and the water molecules which co-ordinate to the vanadium atoms are represented by thin lines

N-Salicylideneamino acidato complexes may be considered as model systems for pyridoxal potentiated enzymes,[3,43] namely in transaminations. The bond distances concerning the N atom may give clues to the reaction mechanisms involved. The bond lengths established by X-ray diffraction were summarized[9] for several Schiff-base complexes of Cu and vanadyl. Normal single- and double-bond carbon–nitrogen distances are 1.47–1.49 and 1.29–1.30 Å, respectively. In the present compound, these are 1.47(2), 1.27(2) and 1.46(2), 1.34(2) for molecules A and 1.49(2), 1.26(2) and 1.46(2), 1.33(2) Å for B. These bonds are roughly within the normal range except for N(3)–C(30) 1.26(2) Å which is significantly shorter than the average, and N(2)–C(20) and N(4)–C(40) 1.34(2) and 1.33(2) Å, respectively, longer than the average. The fact that the compound separated out of the solution after several months shows that no decomposition reaction is catalysed in the present system.

Magnetic moments

The magnetic susceptibilities (measured by the Faraday method at 1 T) for complex **7** are shown in Fig. 3. The plot of the reciprocal paramagnetic susceptibility as a function of temperature exhibits deviations from linearity. Such deviations can be eliminated by subtracting a constant A, in the full temperature range of measurements. Therefore the results can be fitted by $\chi = [C/(T - \theta)] + A$, a Curie–Weiss law. The constant A represents a term due to temperature-independent paramagnetism but may also include errors in the estimation of the diamagnetic contribution, calculated from tabulated Pascal constants as $\chi_d = -1.63 \times 10^{-4}$ emu. With such a procedure, $A = 4.56 \times 10^{-4}$ emu, the Weiss constant is close to zero ($\theta = -0.8$ K) and $\mu_{eff} = 1.65$ μ_B, denoting that interactions (antiferro- or ferro-magnetic) are very weak. For the same compound, Syamal and Theriot[11] using the Gouy method in the temperature range 120–297 K, found $\theta = +2$ and $\mu_{eff} = 1.69$–1.73 μ_B, assuming $A = 50 \times 10^{-6}$ emu. The differences found may result from the wider range of temperature covered by our experiment.

Infrared spectra

All the complexes exhibit a broad water band centred at ≈ 3400 cm^{-1}. Those derived from salicylaldehyde possess a medium/strong band at 1530–1560 cm^{-1} which may originate from coupling between the C=N bond and the phenyl ring.[30,31] The corresponding band for **7** appears at 1535 cm^{-1} and at 1558 cm^{-1} in the microcrystal Fourier-transform IR spectrum of **1**. The [VO(sal-L-aa)X] (X = H$_2$O or bipy) complexes also have very strong and broad bands corresponding to v(C=N) and v_{asym}(CO$_2$) centred around 1630–1660 cm^{-1}. Probably the bands are broadened due to overlap with aromatic ring-carbon stretching. In some cases peaks at ≈ 1630–1650 and ≈ 1600 cm^{-1} emerge from the broad band corresponding to v(C=N) and v_{asym}(CO$_2$), respectively. The symmetric carboxylate stretch, v_{sym}(CO$_2$), probably corresponds to the medium/strong bands in the range 1340–1370 cm^{-1}, depending on the complex. In some cases this band may be confused with other absorptions. Medium-to-strong bands in the range 1290–1320 cm^{-1} probably correspond to v(O–Ph). The v(V=O) band appears in the range 950–960 cm^{-1} except in the Fourier-transform IR spectrum of [V$_2$O$_3$(sal-L-val)$_2$(H$_2$O)] **1**, where two distinct bands at 995 and 972 cm^{-1} probably correspond to the two different types of V^V=O groups present.

The spectrum of complex **1** shows very strong bands at 1714, 1689, 1624, 1615 (sh) and 1603 (sh) cm^{-1}. For N-salicylideneamino acidate complexes, bands at 1620–1660 and at 1590–1620 cm^{-1} are normally attributed to v(C=N) and v_{asym}(CO$_2$), respectively. There are four distinct C=N and CO$_2^-$ groups in the present case. Two of the CO$_2^-$ groups are involved in hydrogen bonds [O(172) and O(372)] and O atoms of the other two CO$_2^-$ groups, O(271) and O(471), are involved in the binding of the two units of compounds A and B. Therefore there is no reason to ascribe the bands at 1714 and 1689 cm^{-1} to v_{asym}(CO$_2$). The four C=N bands correspond to different internuclear distances (see above). In order to estimate the spectral region for each stretching vibration one can use[44] the equation for a simple harmonic oscillator $v = 1307 (k/\mu)^{\frac{1}{2}}$ where v is the frequency in cm^{-1}, μ the reduced mass of the atom pair and k the force constant $\times 10^{-5}$ in dyn cm^{-1}. Using Gordy's rule to estimate the force constants,[45] assuming the bond order is two, one can estimate v(C=N) 1726, 1716, 1660 and 1651 cm^{-1} for the internuclear distances of 1.26, 1.27, 1.33 and 1.34 Å, respectively. The estimated stretching frequencies of 1726 and 1716 cm^{-1} agree relatively well with the observed values, 1714 and 1689 cm^{-1}, which can therefore be ascribed to v[C(30)=N(3)] and v[C(10)=N(1)].

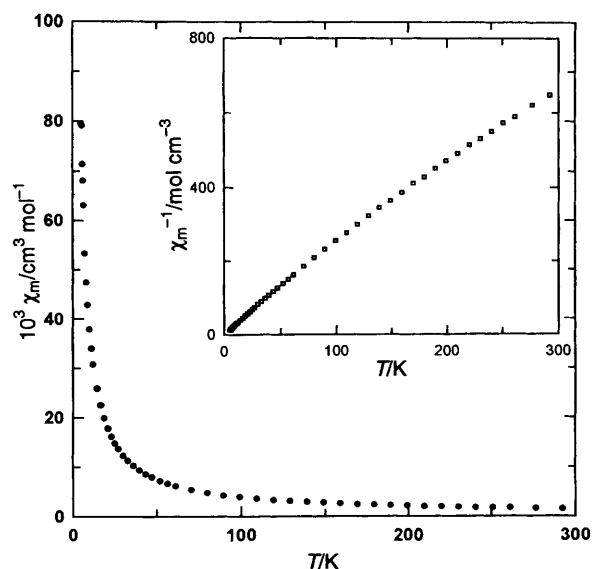The spectrum of complex **1** contains two weak bands at

Fig. 3 Temperature dependence of the magnetic susceptibility (χ_m) and $1/\chi_m$ of complex **7** at 1 T, between 4.9 and 292 K. The data were corrected for the diamagnetic contribution ($\chi_d^M = -1.63 \times 10^{-4}$ emu)

3069 and 3032 cm^{-1}, probably due to aromatic C–H stretches, and medium-intensity bands at 2967, 2934 and 2876 cm^{-1} probably due to the methyl C–H stretch. There are also strong bands at 824, 785, 775 (sh), 762, 717 (sh), 691, 665, 631 and 571 cm^{-1}. The v_{asym}(V–O–V) band is tentatively ascribed at 785 cm^{-1}.

ESR spectra

The ESR spectra may help to elucidate which groups co-ordinate in equatorial positions in solution. The spin-Hamiltonian parameters were calculated following the method described in ref. 46 by an iterative procedure using the corrected equations given in ref. 47.

The $g_{\parallel}$ and $A_{\parallel}$ values obtained (Table 4) are in the range expected for complexes with the present ligand donor atoms,[48] and with the structures found for [VO(sal-L-ala)(H$_2$O)][4] and [VO(sal-L-ala)(bipy)].[9] The presence of bipy gives rise to a slight decrease of $A_{\parallel}$ and $A_{\perp}$. Chasteen[46] does not include values for vanadium-51 hyperfine coupling constants for additivity calculations for a group such as Ph-CH=NCHR; they are certainly different from those for =N (bipy). Assuming that, in methanolic solutions of **6**, H$_2$O 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$_2$O, back calculations of the $A_{\parallel}$ (=N–, Schiff base) gave estimates of this coupling constant in the range (166–174) $\times 10^{-4}$ cm^{-1}. Similar back calculations with the present set of [VO(sal-L-aa)(H$_2$O)] and [VO(sal-L-aa)(bipy)] complexes suggest a narrowing of this range to (166–168) $\times 10^{-4}$ cm^{-1}.
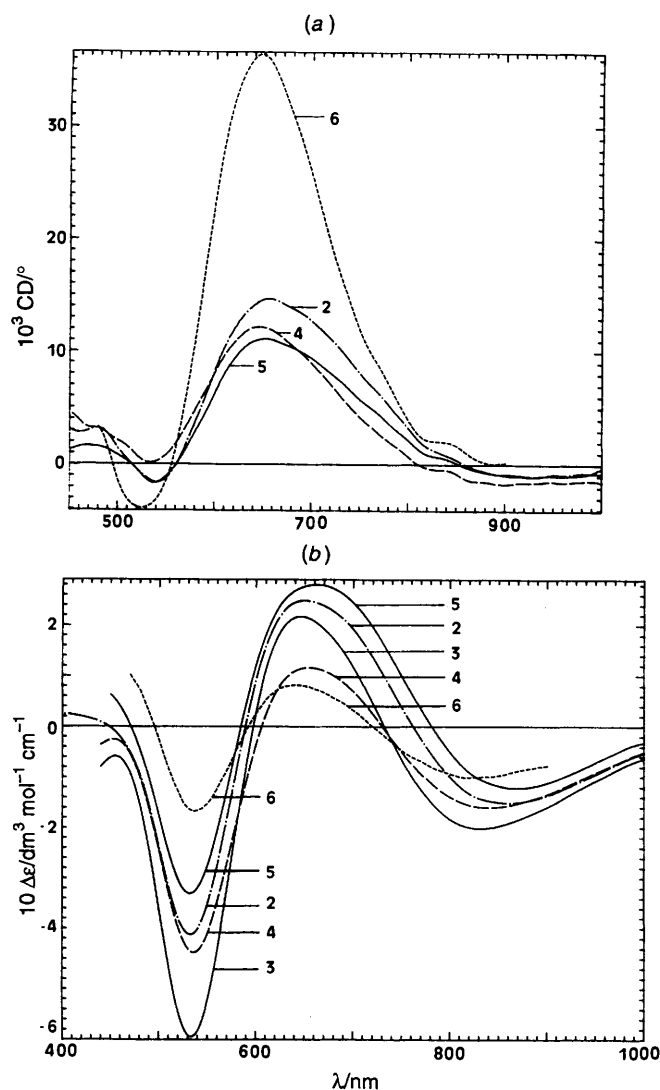
CD spectra: visible range

Fig. 4(a) shows the CD spectra of several [VO(sal-L-aa)(H$_2$O)] complexes **2–6** dispersed in Nujol mulls and Fig. 4(b) the solution CD spectra. Circular dichroism (visible range) generally gives more useful structural information on vanadyl complexes than do visible absorption spectra.[9,48] 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. Band II ($d_{xy} \longrightarrow d_{x^2 - y^2}$) has λ_{max} around 520–550 nm and a negative Cotton effect in all CD spectra recorded for

| Complex*		$10^4 A_{\parallel}/cm^{-1}$	$g_{\parallel}$	$10^4 A_{\perp}/cm^{-1}$	$g_{\perp}$
6	[VO(sal-L-ala)(H$_2$O)]	170.0	1.938	62.6	1.982
2	[VO(sal-L-val)(H$_2$O)]	168	1.949	63.8	1.984
4	[VO(sal-L-met)(H$_2$O)]	169	1.949	63.5	1.982
3	[VO(sal-L-phe)(H$_2$O)]	167.9	1.944	63.7	1.982
5	[VO(sal-L-ile)(H$_2$O)]	169.3	1.939	63.9	1.980
7	[VO(naph-L-val)(H$_2$O)]	168.9	1.948	63.6	1.982
12	[VO(sal-L-ala)(bipy)]	165.9	1.940	59.0	1.978
		163.8	1.952	62.1	1.988
9	[VO(sal-L-val)(bipy)]	163.2	1.952	59.5	1.983
8	[VO(sal-L-met)(bipy)]	161.6	1.950	59.7	1.984
10	[VO(sal-L-phe)(bipy)]	162.5	1.952	59.6	1.984
	[VO(naph-L-val)(bipy)]	163.3	1.952	59.5	1.983

* The [VO(sal-aa)(bipy)] solutions were prepared by adding an excess of 2,2'-bipyridine (mol ratio VO:bipy $\approx$ 1:5) to methanolic solutions of the corresponding complexes [VO(sal-aa)(H$_2$O)].

Fig. 4 Circular dichroism spectra in the visible range: (a) solid samples of complexes 2 (–·–·–), 4 (-----), 5 (—) and 6 (·····) dispersed in Nujol mulls; (b) methanolic solutions of 2 (–·–·–), 3 (—), 4 (-----), 5 (—) and 6 (·····)

[V^{IV}O(sal-L-aa)(H$_2$O)] complexes. This indicates that the co-ordination geometry is similar in all cases.

The fact that the CD spectra of complexes **2–6** have similar spectra in the solid state and solution suggests that the co-ordination geometry does not change upon dissolution in methanol. On adding bipy to these solutions (bipy:VO $\approx$ 5:1) the pattern of the spectra remains the same but λ_{max}(band Ia)
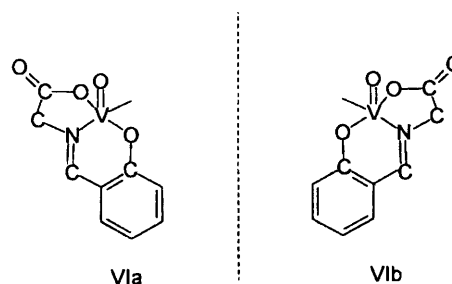
shifts to the UV by ca. 50–60 nm, and λ_{max}(band Ib) and λ_{max}-(band II) shift to the red by ca. 20–40 and ca. 10 nm, respectively.

As emphasized in previous papers,[9,40] apart from the chirality of the amino acid moiety, two enantiomers **VIa, VIb** may be considered for each Schiff-base complex (in both the asymmetric carbons are considered to have the L configuration). This 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. Each such enantiomer, when the methylene group is substituted to form CHR, the asymmetric chiral carbon centre of the α-amino acid, generates two diastereoisomers, giving a total of four. This was confirmed for [V^{V}O(sal-L-ala)(OBu^s)(Bu^{s}OH)], which shows four signals in the ^{51}V NMR spectrum.[12] In **1** all V^V(sal-L-val) units have the same configuration, as in **VIa**.

It has been emphasized[49] that, in transition-metal complexes, asymmetric deviation of ligating atoms from regular polyhedra may have a contribution to the CD spectrum comparable to that of an asymmetric configuration of chelate rings or asymmetric arrangement of ligating atoms. As the V atom in [V^{IV}O(naph-L-ala)(H$_2$O)] complexes is above the plane of ligating atoms, different proportions of *exo* and *endo* isomers or of enantiomers **VIa** and **VIb** may correspond to significantly different contributions from asymmetric deviation of ligating atoms from regular polyhedra and give rise to important differences in the CD spectra. In solution spectra of complexes **2–6**, bands Ia, Ib and II have opposite signs and it is difficult to obtain the true values of λ_{max} and $\Delta\varepsilon$ for each band. As $|\Delta\varepsilon|$ values for band II are apparently greater, the values recorded possibly follow the order of the true $|\Delta\varepsilon|$. For this band, the Cotton effects increase with the bulk of the amino acid side chain {the same occurs for the [VO(sal-L-aa)(bipy)] complexes in solution}. This may reflect a corresponding evolution of the conformation from δ to λ (see below) and/or from *exo* to *endo*, as the bulk of the side chain increases. Alternatively (or simultaneously) this may imply different contributions from the asymmetric deviation of ligating atoms from regular polyhedra in complexes **2–6**, this effect therefore making a contribution
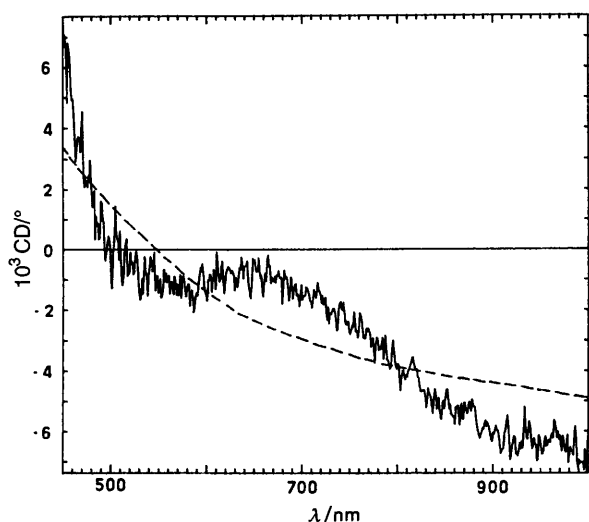
Fig. 5 Circular dichroism spectrum of a sample of [VO(naph-L-val)H₂O] dispersed in Nujol (two pairs of microscope slides, average of six spectra, see Experimental section)

Fig. 6 Circular dichroism spectra in the UV range for methanolic solutions of complexes 2 (−·−·), 3 (—), 4 (−−−), 5 (—) and 6 (---)

to the CD spectra in the visible range (d–d bands). This contribution could in fact be quite important and the recent preparation and determination[10] of the crystal and molecular structure of [V^{V}O(sal-L-phe)(hquin)] corroborates this. Chakravorty and co-workers[10] found that the absolute configuration of the vanadium co-ordination sphere is C,[50] which corresponds to isomer **VIa** (the complex therefore has CS configuration), and the amino acid side group is *endo*. No evidence was found for the presence of the AS diastereoisomer. In CDCl₃ the ¹H NMR spectrum of the complex showed that the absolute configuration is also CS in solution[10] just as it is in the crystalline state. We have previously found that for the VO²⁺ complex [V^{IV}O(sal-L-ala)(bipy)] the two diastereoisomers **VIa**, **VIb** coexist in equal proportions in the solid state. A similar situation regarding the chirality at the V was found[12] in the case of [VO(naph-L-ala)(OBu^s)(Bu^{s}OH)]. Therefore a possible explanation for the CD spectra in Fig. 4(*b*) might be that the diastereoisomeric stability varies in these systems and as the bulk of the side chain varies, one diastereoisomer predominates over the other. More systems need to be examined in order to define the controlling factors.

The Cotton effect measured for [V^{IV}O(naph-L-val)(H₂O)] **7** dispersed in Nujol mulls is weaker and apparently corresponds to a different CD spectrum (Fig. 5) from that of the corresponding salicylaldehyde derivative. However, as mentioned above, in these CD spectra the position of the baseline is not known; if it corresponded to the dashed line the general pattern of all spectra would be similar. We do not expect the co-ordination geometry in **7** to differ from that in **2–6**, which corresponds to structure **I**. What may differ in these complexes is either the proportion of enantiomers **VIa** and **VIb** and/or the relative importance of *exo* and *endo* isomers in **2–6** and **7**.

CD and absorption spectra: UV range

The CD and absorption spectra for the present series of VO chelates of amino acid Schiff bases are summarized in Table 5, and some spectra are included in Fig. 6. In general, the complexes derived from salicylaldehyde possess a low-energy absorption band around 373 (CD) or 375 nm (absorption), which can be attributed to a π ⟶ π* transition originating mainly in the azomethine chromophore. These bands display Cotton effects of negative sign in the CD spectra, as found for the related zinc,[30] copper[51] and cobalt(II)[52] chelates. The intense absorption and CD bands occurring at higher energy
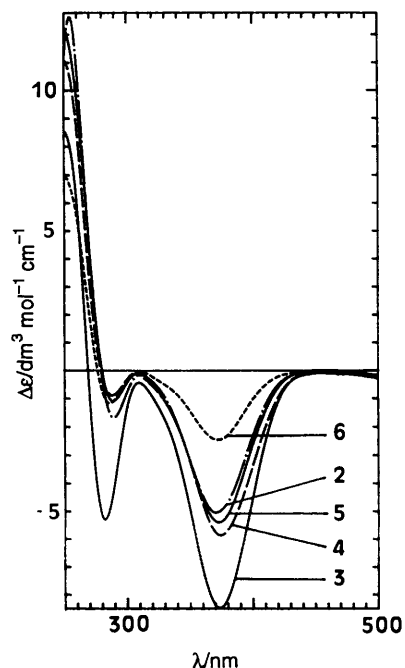
[absorption ≈ 230 and CD ≈ 255 (Δε > 0) and ≈ 220 nm (Δε > 0)] are probably associated with benzene ring π ⟶ π*[52] and charge-transfer[53] transitions. The imine bands are flanked by prominent shoulders at 280–295 nm, but these apparently correspond to relatively weak CD activity. For this band Δε < 0 and for the nearby higher-energy bands (at ≈255 nm) Δε > 0, so the correct positions of the λmax and their true order of magnitude cannot be obtained.

The CD spectra of the [VO(sal-L-aa)(bipy)] complexes are similar but the imine band and its shoulder are shifted to the red by *ca.* 10 (imine band) and *ca.* 20–40 nm (shoulder). Owing to the very high absorption for λ < 280 nm, the CD spectra are recorded with a high degree of noise, but apparently these bands are also shifted to the red by *ca.* 30–50 nm.

As found for spectra in the visible range, the CD spectra in the UV range are more informative than the corresponding absorption spectra. Comparison of the CD spectra of the [VO(sal-L-aa)X] (X = H₂O or bipy) complexes shows that the sign pattern of the Cotton effects associated with the absorption bands near 375, 290 and 230 nm (two bands) is constant within the two series. The electronic transition-moment vector of the C=N chromophore may conjugate with the aromatic part of the ligand and also mix with metal orbitals,[54] but the common pattern observed may reflect the adoption of a common conformation by the ligands. It has been suggested for salicylidene- and pyridoxylidene-amino acidato complexes[30] that the amino acid chelate ring of the co-ordinated Schiff base is in a puckered λ conformation when the amino acid has the L absolute configuration. In this conformation the amino acid side chain is in a pseudo-axial position and shows least steric interaction with the azomethine hydrogen atom. In solution the complexes can undergo a conformational inversion such that the amino acid side chain will occupy either a pseudo-axial (λ conformation) or -equatorial (δ conformation) position. For oxovanadium(IV) complexes, as mentioned above, the presence of the oxo group implies the existence of two enantiomers **VIa**, **VIb** and the possibility of steric interaction of the amino acid side chain with the oxygen (oxo) atom. Besides, the V atom is normally above the plane of the equatorially co-ordinated ligands by *ca.* 0.3–0.4 Å. The similarity of the solution CD spectra within the entire [VO(sal-L-aa)X] (X = H₂O or bipy)

Table 5 Circuclar dichroism UV/VIS spectral data and UV electronic absorption data for methanolic solutions of complexes 1–10 and 12

Complex*	CD–UV λ_{max}/nm ($\Delta\varepsilon_{max}$/cm² mmol⁻¹)	CD–VIS λ_{max}/nm ($\Delta\varepsilon_{max}$/cm² mmol⁻¹)	UV absorption λ_{max}/nm (ε_{max}/cm² mmol⁻¹)
2	372 (−5.0), 289 (−1.7)	532 (−0.41), 650 (+0.25), 861 (−0.15)	277 (8934), 375 (3362)
9	382 (−6.8), 312 (−4.3)	544 (−0.33), 684 (+0.31), 848 (−0.22)	390 (3695)
3	373 (−8.5), 281 (−5.3)	534 (−0.61), 646 (+0.22), 832 (−0.20)	275 (8673), 375 (3465)
10	384 (−10.0), 321 (−4.9)	540 (−0.41), 660 (+0.07), 780 (−0.20), 960 (+0.02)	390 (3812)
4	373 (−5.8), 288 (−0.88)	536 (−0.45), 654 (+0.12), 840 (−0.16)	275 (9075), 377 (3458)
8	386 (−7.3), 322 (−3.8)	545 (−0.25), 668 (+0.10), 825 (−0.20)	390 (3822)
6	372 (−2.5), 286 (−1.2)	535 (−0.17), 640 (+0.08), 830 (−0.10)	275 (9600), 377 (3511)
12	379 (−4.0), 323 (−4.1)	545 (−0.14), 666 (+0.08), 830 (−0.10)	390 (3811)
5	372 (−5.4), 289 (−1.1)	532 (−0.33), 662 (+0.28), 869 (−0.12)	278 (9734), 376 (3734)
[VO(sal-L-ile)(bipy)]	385 (−7.4), 320 (−4.4)	540 (−0.21), 688 (+0.43), 852 (−0.25)	390 (4088)
7	403 (−6.4), ≈300 (+ ≈ 3.9)	530 (−0.39), 636 (+0.32), 856 (−0.15)	326 (10 463), 398 (7504)
[VO(naph-L-val)(bipy)]	405 (−8.3), 320 (−6.0)	541 (−0.78), 701 (+0.59), 863 (−0.11)	339 (sh) (12 800), 410 (7793)

* The [VO(sal-aa)(bipy)] solutions were prepared by adding an excess of 2,2-bipyridine (mol ratio VO:bipy ≈ 1:5) to methanolic solutions of the corresponding complexes [VO(sal-aa)(H₂O)].

series, the similar sign pattern of the CD bands near 373, 290 and 230 nm(two bands), with the corresponding bands of the [Zn(sal-L-aa)(H₂O)] complexes,[30] and the increasing magnitude of the Cotton effects at ≈373nm, with increasing bulk of the amino acid side chain [also as for the zinc(II) complexes[30]] indicate that these complexes in solution possibly prefer the λ conformation and the formation of the *endo* isomer.

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