Salicylideneserinato Complexes of Vanadium. Crystal Structure of the Sodium Salt of a Complex of Vanadium-(IV) and -(V)‡

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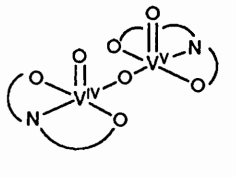
A mixed-valence complex of vanadium-(IV) and -(V), $Na[V_2O_3(\text{DL-salser})_2]\cdot 5H_2O$ (salser = *N*-salicylideneserinate) has been isolated from solutions containing oxovanadium(IV), DL-serine and salicylaldehyde. Its structure has been determined by X-ray diffraction analysis: space group $P2_1/c$, $a = 12.845(5)$, $b = 16.615(4)$, $c = 13.072(0)$ Å, $\beta = 103.53(9)°$, $Z = 4$ and $R = 0.0494$ for 2860 observed reflections. The $V_2O_3^{3+}$ unit in this complex has a V–O–V angle smaller than the usual values and each complex ion contains a D- and a L-serine residue. Each sodium ion is surrounded by seven oxygen atoms in a distorted pentagonal-bipyramidal geometry. The magnetic moment and thermogravimetric analysis are also in accord with the structure.

The biochemical roles of vanadium are not completely understood although some progress has been reported.[1–6] While our awareness of the occurrence of vanadium in biological systems is increasing, an understanding of its structural, functional, and mechanistic properties therein is still a current topic for research. This understanding will depend, in part, on further knowledge of the co-ordination chemistry of vanadium in the +3, +4 and +5 states.

Despite the interest in vanadium complexes of *N*-salicylideneamino acids and derivatives as model systems for pyridoxal-potentiated§ enzymes,[7,8] very few studies have been published concerning the preparation and reactivity of these compounds. Vanadium is one of the most active metal ions in amino acid β-elimination reactions,[9,10] 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.[11,12]

A solid complex has been isolated from solutions containing oxovanadium(IV), DL-serine and salicylaldehyde and it will be shown in this paper that it is a mixed-oxidation-state complex of oxovanadium(IV) and oxovanadium(V) with the Schiff base salicylideneserine (H_2salser), $Na[V_2O_3(\text{DL-salser})_2]\cdot 5H_2O$ **1**. Complexes of Schiff bases derived from the reaction of salicylaldehyde and α-amino acids (glycine, L- and DL-alanine, L-methionine, L-valine, L-leucine, L- and DL-phenylalanine) have been reported previously.[13] The complexes are bluish grey and there is no appreciable interaction between the V atoms.

They have the co-ordination geometry shown in **2**, confirmed in an X-ray study of the L-alanine derivative:[14] the tridentate Schiff base, a water molecule and the O atom of the vanadyl form a square-pyramidal co-ordination geometry around the V^{IV} atom.



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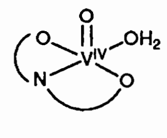

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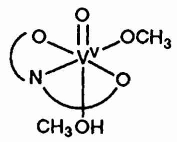

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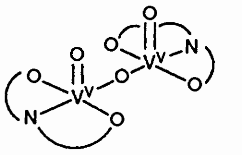

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In complexes **2** one water molecule occupies a basal co-ordination position and 'prevents' dimerization of the compounds assumed to be possible by comparison with similar salicylamine complexes.[15] From a solution containing the salicylidenealaninate (salala) monomeric complex **2** in wet methanol, $[V^VO(\text{L-salala})(OCH_3)(CH_3OH)]$ **3** has been obtained[11] and treatment of **3** with wet dichloromethane yielded deep blue crystals of an EPR-inactive complex $[\{[V^VO(\text{L-salala})]_2O\}_2]\cdot 2CH_2Cl_2$ **4**. The structures of **3** and **4** have also been determined by X-ray techniques[11] and have distorted octahedral co-ordination geometries: in the solid complex **4** the carboxylate O atom of a nearby Schiff-base ligand weakly co-ordinates at the site *trans* to the oxide ion of the vanadyl group.

The study of solutions containing VO^{2+}, salicylaldehyde and amino acids by spectroscopic techniques shows evidence for the formation of several complex species.[16] The present paper deals with the preparation and characterization of three solid complexes prepared from solutions containing oxovanadium(IV), salicylaldehyde and serine (L or DL).

Experimental

Reagents and Apparatus.—Reagent-grade salicylaldehyde (Carlo Erba), DL-serine (Sigma), L-serine (BDH), glacial acetic

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‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

§ Pyridoxal = 3-hydroxy-5-hydroxymethyl-2-methylpyridine-4-carbaldehyde.

acid (BDH), 40% tetrabutylammonium hydroxide solution (BDH), vanadyl sulfate pentahydrate (Merck) and sodium acetate trihydrate (BDH Analar) were used without further purification.

The elemental analyses were carried out by standard procedures: C,H,N microanalysis with a Perkin-Elmer analyser (model 240B); vanadium by titration with permanganate and sodium by flame photometry (EL). The IR spectra of KBr disks were recorded on Perkin-Elmer spectrometers (model 457 or 683) and thermogravimetric analysis was carried out on a Stanton Redcroft Thermobalance. Magnetic moments were measured down to liquid-nitrogen temperature using a Faraday balance calibrated by $HgCo(NCS)_4$ as described.[17]

Preparation of the Complex.—*Sodium* μ-*oxo-dioxo-*1κO,2κO-(D-*salicylidene-*1κ²N,O-*serinato-*1κO)(L-*salicylidene-*2κ²N,O-*serinato-*2κO)-1-*vanadium*(IV)-2-*vanadium*(V) *pentahydrate* **1**. DL-Serine (0.2107 g, 2 mmol) was dissolved in water (10 cm^3), salicylaldehyde (0.25 cm^3) in ethanol (7 cm^3) and vanadyl sulfate (0.403 g, 1.6 mmol) in water (5 cm^3). The three solutions were mixed, and sodium acetate (4 mmol) was added. The reddish solution was evaporated at low pressure until it became dark green. On standing, dark green crystals were formed. The product was not recrystallized because it decomposes in solvents to give a yellow solution (Found: C, 35.65; H, 3.80; N, 4.00; Na, 4.00; V, 14.85. Calc. for $C_{20}H_{18}N_2NaO_{11}V_2{\cdot}5H_2O$: C, 35.45; H, 4.15; N, 4.15; Na, 3.40; V, 15.05%).

X-Ray Crystal Structure Determination of Complex **1**.—*Crystal data.* $C_{20}H_{18}N_2NaO_{11}V_2{\cdot}5H_2O$, $M = 677.32$, monoclinic, space group $P2_1/c$, $a = 12.854(5)$, $b = 16.615(4)$, $c = 13.072(0)$ Å, $\beta = 103.53(9)°$, $U = 2714$ Å^3 at room temperature, $Z = 4$, $D_c = 1.66$ g cm^{-3}, $F(000) = 1384$ and $\mu = 7.19$ cm^{-1}.

A dark green, parallelepiped single crystal, dimensions 0.32 × 0.22 × 0.16 mm, was sealed in a Lindemann tube and mounted in a general orientation on an automatic Enraf-Nonius CAD-4 four-circle diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,69$ Å). The unit-cell dimensions and orientation matrix were determined from a least-squares refinement of $\sin^2\theta$ values of 25 reflections in the range $10 < \theta < 25°$; 5184 reflections were measured at room temperature using the θ–2θ scan technique to $\theta_{max} = 26.5°$.

No significant variation in intensities was observed for three standard reflections. Data were corrected for Lorentz and polarization effects; empirical absorption corrections were applied.[18] Equivalent reflections were averaged to give 3892 unique reflections ($R_{int} = 0.0138$) of which 2860 had $F > 3\sigma(F)$.

Structure analysis and refinement. The structure was solved by a combination of Patterson, Fourier difference and direct methods and refined by least squares using SHELX 76[19] (calculations run on a VAX/780 computer). Full-matrix least-squares refinement was used with all the non-hydrogen atoms refining anisotropically. A weighting scheme $w = 1.1118/[\sigma^2(F) + 0.0010F^2]$ was used to give satisfactory convergence.

All hydrogens were inserted in idealized positions and allowed group-refined U_{iso} values. Final R and R' values were 0.0494 and 0.0521.

The thermogravimetric analysis shows loss of water starting at temperatures just above room temperature and the high thermal parameters may be due to this instability of the molecule. It may also explain the difference electron-density map which shows residual peaks less than 0.50 e Å^{-3}. Atomic scattering factors were taken from ref. 20.

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

Results and Discussion

The formation of the mixed oxidation-state complex may be explained by the slow diffusion of atmospheric oxygen into the solution and reaction with oxovanadium(IV).

Thermogravimetric Analysis.—The thermogravimetric curve obtained by heating a sample of the sodium salt shows a weight loss from 30 to 80 °C which can be explained by the liberation of five water molecules. Two other weight losses (starting at ≈248 and ≈410 °C) are observed and are due to the thermal decomposition of the complex: the first is probably the decarboxylation of the ligand as observed with the salicylidenealaninatovanadium(IV) complex.[21] The weight of the residue obtained at 560 °C corresponds to NaV_2O_5.

Infrared Spectra.—The broad water band at ≈3400 cm^{-1} shows that there is no water co-ordinated to vanadium which should appear as a band at a lower wavenumber. The shoulder at ≈3200 cm^{-1} is due to the serine OH groups. The Schiff-base nature of the co-ordinated ligand is confirmed by the appearance of a band at 1640 cm^{-1} associated to the C=N group and the absence of bands in the region 2080–2140 cm^{-1} associated with the N–H bond of the amino acid. The C=O band appears as a shoulder on the C=N band. The characteristic V=O band can be observed at 980 cm^{-1}. The band at 545 cm^{-1} is assigned to V–O(aryl), and those at 485 and 465–440 cm^{-1} to the V–N and V–O(carboxyl) bonds.

Magnetic Moments.—The magnetic moment of complex **1** was measured over a large range of temperatures (67.5–297.6 K). The values per molecule were in the range 1.80–1.85 μ_B. The average moment per molecule ($1.83 \pm 0.09\mu_B$) at all temperatures confirms the existence of one unpaired electron per molecule, *i.e.* per two vanadium atoms. This value is slightly greater than the spin-only value of 1.73 μ_B for one unpaired electron, and could be attributed to a small amount of low-molecular weight vanadium(IV) impurity which was not removed because compound **1** could not be recrystallized.

Crystal Structure.—The solid complex **1** was isolated from sodium acetate-containing solutions and its molecular structure is shown by the ORTEP II[22] drawing in Fig. 1. Fractional coordinates are listed in Table 1 and selected bond distances and angles in Table 2.

The hydroxyl side group of serine is not co-ordinated to the metal centre and the two vanadium atoms are joined by an oxo bridge in this mixed-valence (IV,V) binuclear complex. Several other complexes containing the $V_2O_3^{3+}$ group have been reported[23–25] either with localized or delocalized vanadium-(IV) and -(V) centres.

The oxo-bridge between the vanadium atoms has several interesting features. The V(1)–O(0) and V(2)–O(0) bond lengths are different, suggesting that the vanadium atoms have different oxidation states. The V–O–V angle is 146.6°, smaller than the angles usually found for the $V_2O_3^{3+}$ unit,[26] and probably indicates a weak electronic interaction. This may be explained by the compound having localized vanadium-(IV) and -(V) centres. In $[V_2O_3(S\text{-peida})_2]^-$ **5** {*S*-peida = (*S*)-[1-(2-pyridyl)ethyl]iminodiacetate}[23] the corresponding angle is 179.5° but the V=O groups are roughly 'antiparallel' and the V atoms are inequivalent. The complexes $[V_2O_3(nta)_2]^{3-}$ **6** (nta = nitrilotriacetate)[24] and $[V_2O_3(pmida)_2]^-$ **7** [pmida = (pyridylmethyl)iminodiacetate][25] both contain the $V_2O_3^{3+}$ core but with V=O bonds *cis* to the bridge but *trans* to each other. The oxygen bridge is nearly linear (175.3° for **7**, not specified in **6**). This leads to good overlap between the d_{xy} orbitals, consequently the properties of these mixed-valence compounds are very near to those of fully delocalized systems.

The two V=O groups in complex **1** are roughly parallel [angle 11.6(2)°] and are *cis* to the bridge and to each other. The V–N bond lengths (2.07 and 2.12 Å) are slightly longer than in

Table 1 Fractional atomic coordinates (× 10^4) for complex **1**

Atom	*x*	*y*	*z*
O(0)	6 378(3)	5 538(2)	1 231(3)
V(1)	6 494(1)	6 230(1)	250(1)
V(2)	6 819(1)	5 250(1)	2 646(1)
O(1)	7 975(2)	5 887(2)	288(2)
O(2)	5 005(2)	6 284(2)	9 587(3)
O(3)	6 706(3)	7 067(2)	835(3)
C(1)	8 442(4)	6 021(3)	9 535(4)
O(6)	5 341(3)	5 114(2)	2 663(3)
O(7)	8 093(3)	4 750(2)	2 298(3)
O(8)	7 266(3)	6 022(2)	3 325(3)
C(4)	8 657(4)	4 231(3)	2 925(4)
C(8)	4 974(4)	7 172(3)	8 131(4)
C(9)	4 484(4)	6 794(3)	8 859(4)
C(10)	3 398(4)	6 948(3)	8 804(4)
C(11)	2 836(4)	7 476(3)	8 062(4)
C(12)	3 317(4)	7 849(3)	7 350(5)
C(13)	4 363(4)	7 702(3)	7 376(4)
C(15)	5 362(4)	4 151(3)	4 036(4)
C(16)	4 858(4)	4 748(3)	3 327(4)
C(17)	3 798(4)	4 948(3)	3 302(4)
C(18)	3 252(5)	4 546(3)	3 946(5)
C(19)	3 725(5)	3 940(4)	4 611(4)
C(20)	4 765(5)	3 750(3)	4 656(4)
N(1)	6 727(3)	6 604(2)	8 772(3)
C(2)	7 780(4)	6 425(4)	8 559(4)
C(3)	8 360(5)	7 124(5)	−1 758(6)
C(7)	6 050(4)	7 002(3)	8 067(4)
N(2)	7 113(3)	4 280(2)	3 661(3)
C(5)	8 201(4)	3 963(3)	3 838(4)
C(6)	8 908(4)	4 265(3)	4 884(4)
C(14)	6 447(4)	3 923(3)	4 121(4)
O(4)	9 357(3)	5 807(2)	−433(3)
O(5)	8 601(4)	7 697(3)	−887(5)
O(9)	9 500(3)	3 962(2)	2 795(3)
O(10)	8 571(3)	3 947(2)	5 758(3)
Na(1)	9 352(2)	4 860(1)	1 135(1)
O(11)	8 228(3)	4 100(2)	−332(3)
O(12)	3 843(3)	5 208(3)	728(3)
O(13)	10 612(4)	5 855(3)	2 003(3)
O(14)	19 039(4)	2 618(3)	505(4)
O(15)	9 777(5)	7 404(3)	1 361(4)

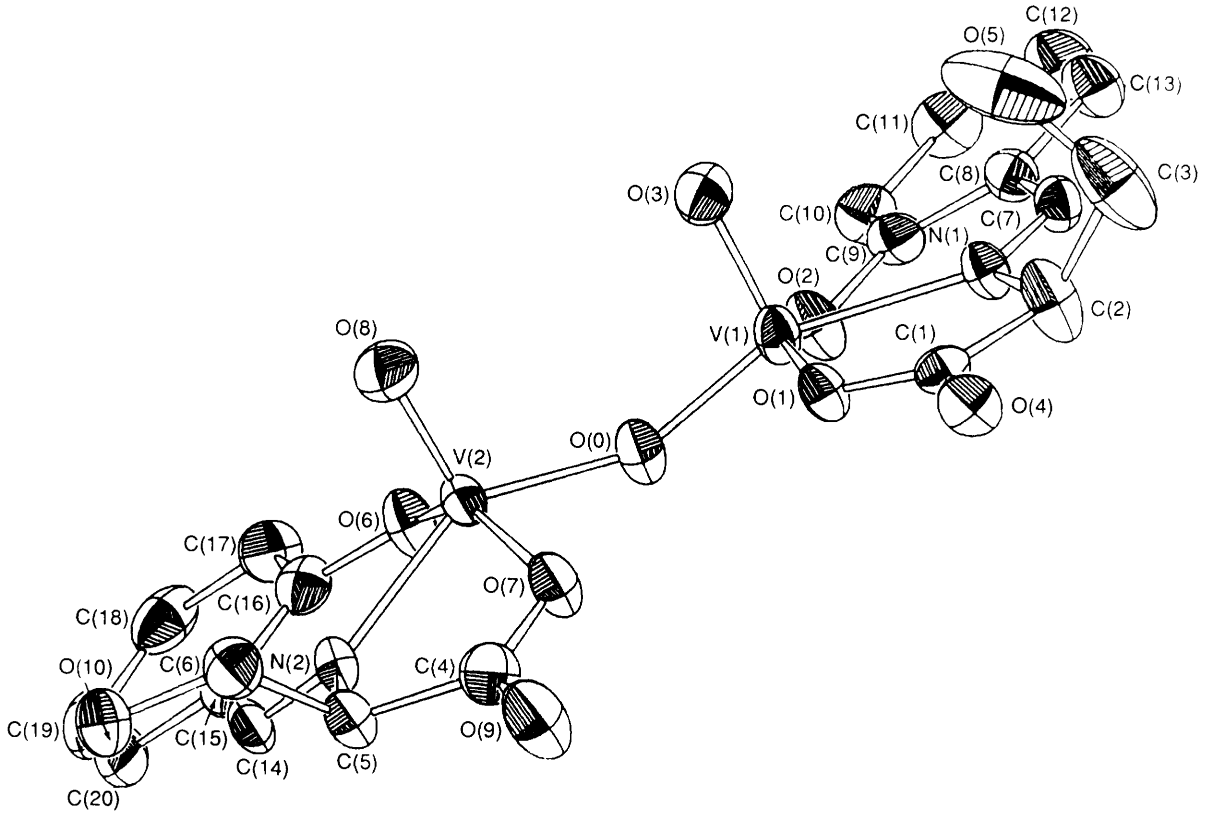

Fig. 1 ORTEP II[22] diagram of $[V_2O_3(\text{DL-salser})_2]^-$ with thermal ellipsoids at 50% probability, showing the atom labelling scheme

$[V^{IV}O(\text{L-salala})(H_2O)]$ **2** (2.05 Å)[14] but comparable to those found in **3** (2.10 Å) and **4** (1.99, 2.10, 2.10 and 2.12 Å).[11] The V–N bond lengths in **1** and **4** are, with one exception, longer then the corresponding distance in **2** and in other vanadium(IV) complexes, owing to the *trans* influence of the oxygen of the bridge in $V_2O_3^{3+}$. The equatorial V–O bond lengths reported for *N*-salicylidenealaninato complexes of V^{IV} (1.91–2.00 Å)[14] and V^V (1.78–1.95 Å)[11] are comparable with those measured in this work (1.92–1.98 Å). The V–N and V–O bond lengths in **1** confirm the inequivalence of the two vanadium centres: the V^{IV} atom shows shorter V–N and longer V–O than those at V^V.

Each molecule of complex **1** contains a D- and a L-serine residue. This may explain why the formation of crystals from solutions containing DL-serine is easier than from solutions of L-serine.

The Na–O distances listed in Table 2 are comparable with those found in hydrated sodium salts[27] and this is another example of sodium ion co-ordinated by a metal complex ion acting as a ligand:[28] an unusual co-ordination number (seven) was found instead of the normal four, five or six. Each sodium ion is surrounded by seven oxygen atoms in a distorted pentagonal-bipyramidal geometry as shown in Fig. 2: two water molecules [O(11) and O(13)], the four carboxyl oxygen atoms of a complex ion [O(1), O(4), O(7), O(9)] and another carboxyl oxygen of a neighbouring complex. A pair of sodium ions is bound to a pair of complex ions and four water molecules form

Table 2 Selected bond lengths (Å) and angles (°) for complex **1**

V(1)–O(0)	1.754(6)	V(2)–O(0)	1.866(5)
O(1)–V(1)	1.977(5)	O(2)–V(1)	1.908(5)
O(3)–V(1)	1.580(6)	N(1)–V(1)	2.117(6)
O(6)–V(2)	1.918(5)	O(7)–V(2)	1.982(6)
O(8)–V(2)	1.589(6)	N(2)–V(2)	2.066(6)
Na(1)–O(1)	2.520(5)	Na(1)–O(7)	2.473(8)
Na(1)–O(4)	2.585(8)	O(13)–Na(1)	2.405(9)
Na(1)–O(9)	2.605(8)	O(11)–Na(1)	2.462(9)
Na(1)–O(4m)	2.354(7)	Na(1) ··· Na(1m)	3.757(9)
V(2)–O(0)–V(1)	146.6(2)	O(1)–V(1)–O(0)	92.2(2)
O(2)–V(1)–O(0)	96.6(3)	O(2)–V(1)–O(1)	151.9(1)
O(3)–V(1)–O(0)	105.0(3)	O(3)–V(1)–O(1)	100.7(3)
O(3)–V(1)–O(2)	102.7(3)	N(1)–V(1)–O(0)	156.1(2)
N(1)–V(1)–O(1)	76.5(2)	N(1)–V(1)–O(2)	85.0(2)
N(1)–V(1)–O(3)	97.9(3)	O(6)–V(2)–O(0)	88.3(2)
O(7)–V(2)–O(0)	87.4(2)	O(7)–V(2)–O(6)	145.8(1)
O(8)–V(2)–O(0)	109.5(3)	O(8)–V(2)–O(6)	108.6(3)
O(8)–V(2)–O(7)	104.8(3)	N(2)–V(2)–O(0)	143.6(2)
N(2)–V(2)–O(6)	86.2(3)	N(2)–V(2)–O(7)	77.5(3)
N(2)–V(2)–O(8)	106.4(3)		

Symmetry operation relating designated atoms to reference atoms at (x, y, z): m 2.0 − x, 1.0 − y, −z.

Table 3 Hydrogen bond lengths (Å) for complex **1**

H(17) ··· O(8a)	1.801	H(22) ··· O(2b)	2.022
H(21) ··· O(6)	1.897	O(15) ··· H(23)	1.936
H(26) ··· O(5c)	2.286	H(28) ··· O(9d)	1.936
H(24) ··· O(10e)	2.173	O(13) ··· H(19h)	2.015
O(12) ··· H(20i)	1.924	H(25) ··· O(4c)	2.340
O(14) ··· H(18f)	1.794		

Symmetry operations relating designated atoms to reference atoms at (x, y, z): a x, 1.5 − y, −0.5 + z; b x, y, −1.0 + z; c 3.0 − x, 1.0 − y, −z; d 2.0 − x, 0.5 + y, 0.5 − z; e 2.0 − x, 1.0 − y, 1.0 − z; f 1.0 + x, 0.5 − y, −0.5 + z; h 2.0 − x, 1.0 − y, −z; i 1.0 − x, 1.0 − y, −z.

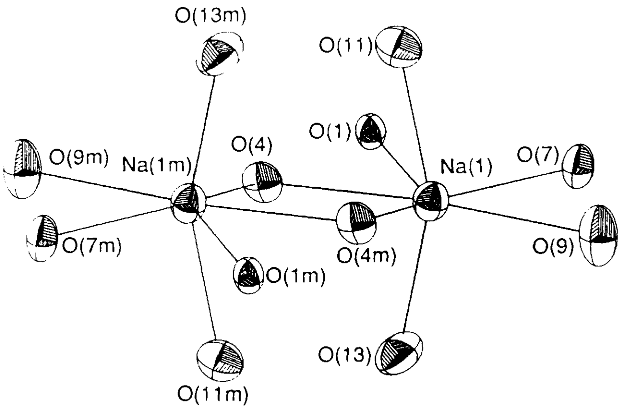

Fig. 2 ORTEP II[22] diagram showing the sodium ion environment with thermal ellipsoids at 50% probability and the atom labelling scheme

a neutral group. A hydrogen bond between the two water molecules [O(11) and O(13m)] may contribute to the stabilization of this group.

The structure may be stabilized by a complex system of hydrogen bonding and the relevant bond distances are listed in Table 3. Using the numbers of the water oxygen atoms in order to refer the water molecules, the hydrogen-bonding system may be tentatively described as follows. The hydroxyl groups of the serine residues [O(5) and O(10)] are bound to water molecules [O(13) and O(14)]. The oxo group of the vanadium(IV) centre [O(8)] may also form a hydrogen bond with the hydroxyl [O(5)]. The molecules are linked by hydrogen bonding through the phenolate oxygen atoms [O(2) and O(6)] of two neighbouring complex ions forming hydrogen bonds with a water molecule [O(12)]. Each carboxyl oxygen not co-ordinated to vanadium [O(4) and O(9)] is bound to a water molecule [O(14) and O(15) respectively]. There is hydrogen bonding between pairs of water molecules [O(11), O(12); O(11), O(13); and O(13), O(15)].

As shown in Fig. 1 the β-carbon and the hydroxyl oxygen of one serine residue have higher thermal parameters. Higher thermal parameters are also found for the water molecules [O(14) and O(15)] located near this position.

The different nature of the two vanadium atoms is also confirmed by the geometry of the co-ordinated atoms. The co-ordination around V(1) is a distorted square pyramid and the deviation of the vanadium atom from the least-squares basal plane is 0.583 Å, comparable with other vanadium(IV) complexes. The co-ordination around V(2) is also a distorted square pyramid but different from that of V(1): V(2) deviates from the least-squares basal plane by 1.17 Å and the angle of the V(2)=O bond to this plane is 88.4°.

The stability of the complexes of the $V_2O_3^{3+}$ unit is now quite well established.[24] This work and Nakajima's report[11] suggest that such complexes could act as intermediates on oxidation of V^{IV} to V^{V}, but to confirm this and to check the reversibility of the reaction more extensive studies are needed. Diamantis *et al.*[29] emphasized that solutions containing VO^{2+} and dinegative tridentate ligands of the type $^-$O–N–O$^-$ are easily oxidized to the corresponding vanadium(V) complexes. Vanadium(IV) complexes may only be stable upon isolation if insoluble.

The results reported in this work may give a few clues to explaining the reactivity of vanadium complexes of *N*-salicylideneamino acids and derivatives as model systems for pyridoxal-potentiated enzymes. However, they show that in order to understand the catalytic role of vanadium, the rich redox chemistry of this type of complex should be taken into account.

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