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# N-SALICYLIDENEAMINO-ACIDATE COMPLEXES OF OXOVANADIUM(IV)—II. SYNTHESIS, CHARACTERIZATION AND DEAMINATION OF AN N-SALICYLIDENEGLYCYLGLYCINATO COMPLEX

ISABEL CAVACO, JOÃO COSTA PESSOA,* SUSANA M. LUZ
and M. TERESA DUARTE

Centro de Química Estrutural, Complexo I, Instituto Superior Técnico,
1096 Lisboa Codex, Portugal

and

PEDRO M. MATIAS

Instituto de Tecnologia Química e Biológica, 2780 Oeiras, Portugal

and

RUI T. HENRIQUES

ICEN-INETI, Departamento de Química, 2686 Sacavém Codex, Portugal

and

ROBERT D. GILLARD*

School of Chemistry and Applied Chemistry, University of Wales, Cardiff, P.O. Box 912,
Cardiff CF1 3TB, U.K.

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**Abstract**—A vanadium(IV) complex VO(sal-glygly)$(H_2O)_n$ (1) (sal-glygly = N-salicylideneglycylglycinate; $n = 1.5$–3.0) has been isolated from relatively concentrated solutions containing oxovanadium(IV), glycylglycine and salicylaldehyde, and characterized by elemental analysis, thermal (TG and DSC), magnetic and spectroscopic techniques. From similar but dilute solutions the decavanadate, $(NH_4)_4(Na)_2[V_{10}O_{28}] \cdot 10\,H_2O$ (2) was isolated after ageing: its structure has been determined by X-ray diffraction analysis. The $NH_4^+$ cations were formed by deamination of the glycylglycine present in solution.

Several studies concern the preparation and reactivity of vanadium complexes of N-salicylideneamino acids;[1] these may be considered as model systems for some reactions of pyridoxal-potentiated enzymes.[2-6] However, to our knowledge, no such studies with simple peptides have been reported.

The present paper deals with the preparation and characterization by elemental analysis, thermal (TG and DSC), magnetic and spectroscopic methods, of a solid formulated as VO(sal-glygly)$(H_2O)_n$ (1) (sal-glygly = N-salicylideneglycylglycinate; $n = 1.5$–3.0). In attempts to obtain crystals of this complex by slow crystallization

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* Authors to whom correspondence should be addressed.

we obtained a decavanadate, $(NH_4)_4(Na)_2[V_{10}O_{28}] \cdot 10H_2O$ (**2**), characterized by X-ray crystallography. The $NH_4^+$ cations were formed by deamination of the glycylglycine present in solution. This particular decavanadate salt has not been characterized previously.

## EXPERIMENTAL

### *Reagents and apparatus*

Reagent grade salicylaldehyde (Riedel), glycylglycine (Merck), oxovanadium(IV) sulphate pentahydrate (Merck) and sodium acetate (Riedel) were used without further purification. All other reagents were reagent grade.

The IR spectra of KBr discs were recorded on a Perkin–Elmer 683 spectrometer, magnetic susceptibilities were measured in the range 9–300 K using a 7-Tesla Faraday system (Oxford Instruments) coupled to a Sartorius S3D-V microbalance and thermogravimetric (TG) and differential scanning calorimetric curves (DSC) with a Setaram TG DSC92 thermobalance between 20°C and 600°C. The X-band ESR spectrum were recorded at 77 K (on glasses made by freezing solutions in liquid nitrogen) with a Bruker ESR-ER 200 tt connected to a Bruker B-MN C5 ESR spectrometer and to a Bruker ESR data system (linked to an IBM AT computer).

### *Preparation of complex* **1**

Several batches were made; a stream of $N_2$ was maintained throughout the preparations. The reactions were monitored by TLC (see below). Typically glygly (1 g, ~8 mmol) was dissolved in about 15 $cm^3$ of water. Sodium acetate trihydrate (2.1 g, ~16 mmol) and salicylaldehyde (0.9 g, ~8 mmol) in ~20 $cm^3$ of ethanol were added. The solution became yellow due to the formation of the Schiff base. A solution of $VOSO_4 \cdot 5H_2O$ (1.7 g, ~7 mmol) in ~8 $cm^3$ of water was slowly added from a burette; initially the solution became red and darkened as the vanadyl solution was added. Shortly after the addition of the $VOSO_4$ solution a green precipitate formed, which was collected, washed with water, ethanol/water (50%) and diethyl ether, and dried in vacuo. The elemental analyses of several samples gave discordant results, which may be attributed to the formation of different hydrates or to a rapid absorption of water during manipulation. Nevertheless, the analyses clearly confirm the formation of a 1:1 (V:Schiff base) complex, $C_{11}H_{10}N_2O_5V$, with variable water contents as the analytical results from four different preparations varied: C, 37.7–39.6; H, 4.2–4.6; N, 7.9–8.5 (minimum and maximum values indicated), suggesting a variation in the number of $H_2O$ molecules in the range 1.5–3.0. $C_{11}H_{14}N_2O_7V$ ($n_{H_2O} = 2.0$) requires C, 39.2; H, 4.2; N, 8.3%; V, 15.1%. Thermogravimetric measurements (see below) gave for % V: 15.8% assuming $V_2O_5$ as the final product.

Direct analysis for sodium gave a result in the range 0.1–0.2%; inaccuracies in weighing and dissolving/digesting the sample in strong acid at high temperature could account for discrepancies between these and TG measurements (see below).

The solubility of complex **1** was tested with the following solvents: acetonitrile, tetrahydrofuran, benzene, $CHCl_3$, acetone, methanol and butanol. About 2 $cm^3$ of each solvent were added to 2 mg of the complex with ultrasonic dispersion. The complex was practically insoluble in all solvents.

### *Preparation of the decavanadate* **2**

Decavanadate **2** was obtained in two different batches in attempts to obtain crystals of complex **1**.

In one batch glygly (0.6 g, ~ 4.5 mmol) was dissolved in 15 $cm^3$ of $H_2O$. Salicylaldehyde (0.6 g, ~ 4.5 mmol) in 18 $cm^3$ of ethanol was added. The solution became yellow, and a suspension of solid Schiff base formed; 14 $cm^3$ of an aqueous solution of $VOSO_4 \cdot 5H_2O$ (2 g, ~8 mmol) were slowly added. The solid dissolved and the solution was left to stir for about 1 h. Sodium acetate trihydrate (1.2 g, ~9 mmol) was dissolved in water (8 $cm^3$). The reaction mixture was slowly added to this solution by diffusion through a strip of filter paper. Seven days later an oil had formed. The solution was filtered and diluted 1:2 with ethanol/$H_2O$ 50%. Part of this solution (9 $cm^3$) was allowed to diffuse slowly from a small vial through a strip of filter paper into an aqueous solution (10 $cm^3$) of sodium acetate (0.6 g, ~45 mmol). After 5 weeks, brown crystals of decavanadate **2** had separated.

In the second batch, the solution obtained from the filtration in the preparation of complex **1** was stored at ~5°C for about 1 month. Brown crystals of **2** were obtained.

### *TLC experiments*

These were performed on Merck TLC plates (Art. 5626, 10 × 20 cm) and 1 $\mu l$ samples 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.[7]

When monitoring the reactions, in a typical case, samples containing: glygly, salicylaldehyde and sodium acetate were applied before the addition of the $VOSO_4$ solution, and 15 min and 3 h after the addition. Several experiments were also performed with similar solutions containing 2,2′-bipyridyl in molar amounts equivalent to vanadium.

After development, distinct and clear reddish-brown spots corresponding to glygly were always detected ($R_f \approx 0.22$ and 0.34, for eluents A and B, respectively). Distinct yellow spots corresponding to the Schiff base glygly complex could be detected with eluent A ($R_f \approx 0.72$), but with eluent B only the glygly peak appeared, with extensive fronting, suggesting that the Schiff base complex decomposes during the elution with this acid eluent.

With solutions to which bipy was added, a reddish-brown spot ($R_f \approx 0.63$ and 0.55, for eluents A and B, respectively) could be detected together with the yellow spot of $R_f \approx 0.72$. This result is akin to those obtained with methanolic solutions of [VO(sal-S-ala)($H_2O$)] containing equivalent amounts of bipy, where it is known that [VO(sal-S-ala)(bipy)] forms.[1] Although these TLC results suggest that VO(sal-glygly)(bipy) forms, the C, H, N analyses of solids obtained from such solutions are inconsistent with that formulation.

### *X-ray crystal structure determination of complex* **2**

*Crystal data.* $[V_{10}O_{28}^{6-}][Na^+]_2[NH_4^+]_4 \cdot 10\ H_2O$, $M_r = 1255.8$, triclinic, space group P-1, $a = 8.4943(6)$, $b = 10.4227(9)$, $c = 11.2830(7)$ Å, $\alpha = 68.55(1)^\circ$, $\beta = 87.27(1)^\circ$, $\gamma = 67.12(1)^\circ$, $V = 851.3(1)$ Å$^3$, $Z = 1$, $F_{000} = 620$, $D_c = 2.45$ g cm$^{-3}$, $\mu$ (Mo$K_\alpha$) = 27.1 cm$^{-1}$

*Data collection.* X-Ray measurements were made with an Enraf–Nonius CAD-4 diffractometer and graphite monochromatized Mo-$K_\alpha$ radiation ($\lambda$ 0.71069 Å). Cell dimensions were determined from the measured $\theta$-values for 25 intense reflections with $11.5^\circ < \theta < 16.5^\circ$. The intensities of 4304 reflections $1.5^\circ \leqslant \theta \leqslant 28^\circ$ were measured by the $\omega$–$2\theta$ scan mode giving 3625 independents. The data were corrected for Lorentz, polarization and absorption effects.

*Structure determination and refinement.* The positions of all the vanadium and of most of the oxygen atoms in the decavanadate anion were determined by a direct method with program MITHRIL[8] using the 300 reflections with highest normalized structure factor amplitudes. The atomic positions of the remaining non-hydrogen atoms were found from subsequent difference Fourier synthesis. The analysis of several refinements of the non-hydrogen atomic positions with isotropic thermal motion parameters revealed that a sodium ion was present. Following convergence of the anisotropic refinement, all but one of the hydrogen atoms were located from a difference Fourier synthesis and included in the refinement. It was also discovered at this point that two atoms initially thought to be oxygens were in fact nitrogens, since they had respectively three and four hydrogens attached to them with a geometry consistent with that of ammonia or ammonium ion. No hydrogen atoms were found attached to any of the oxygens in the decavanadate anion and therefore it was assumed that both nitrogen atoms belonged to ammonium ions, the fourth hydrogen in one of them not being located in a peak search of the difference Fourier map probably due to irregular features in the map at its location. This hydrogen, H74n, was therefore placed in a calculated position and included in the refinement. All hydrogens were refined with O—H and N—H bond distances restrained to 0.95(2) Å and individual isotropic thermal motion parameters. The final refinement was carried out with a weighting scheme of the form $w = 1.903/(\sigma^2(F_o) + 0.000624F_o^2)$, and converged to $R(F) = 0.0382$, $R_w(F) = 0.0384$ for 3129 reflections with $F_o > 3\ \sigma(F_o)$ and 316 refined parameters. The structure refinement calculations were carried out using program SHELX-76.[9] Atomic scattering factors were taken from International Tables.[10]

Additional material is available from the Cambridge Crystallographic Data Centre: this comprises fractional atomic coordinates, and thermal motion parameters, together with tables of bond lengths and angles and a list of observed and calculated structure factors.

## RESULTS AND DISCUSSION

### *Characterization of complex* **1**

*Magnetic moments.*The magnetic susceptibility was measured by the Faraday method at 5 Tesla between 9 and 296 K for VO(sal-glygly)$(H_2O)_n$ (with $n$ = 1.5–3.0). The $\chi_p$ and $\mu_{eff}$ values are shown in Fig. 1. These results are typical for a compound with a spin $\frac{1}{2}$ per formula unit, suggesting that complex **1** is monomeric. In fact, the slight decrease of $\mu_{eff}$ upon cooling, indicates that antiferromagnetic interactions are very weak and if the complex is not monomeric the vanadium(IV) atoms must be quite separated. The diamagnetic correction contributions[11] for $1.5 \leqslant n \leqslant 3.0$ are not significantly different. Taking $n = 2.5$ gives: $\chi_d{}^M = -1.46 \times 10^{-4}$ emu mol$^{-1}$, $\chi_p{}^M(296\ \text{K}) = -1.30 \times 10^{-3}$ emu mol$^{-1}$ and $\mu_{eff} = 1.75$ B.M. The $\mu_{eff}$ is within the range normally found for oxovanadium(IV) complexes (1.68–1.78)[12] with the orbital contribution completely quenched.

*Thermogravimetric analysis.* The TG and DSC curves obtained for one sample formulated as VO(sal-glygly)$(H_2O)_n$ are shown in Fig. 2. The weight loss up to 150 °C is compatible with the loss of 1.75 molecules of $H_2O$ per vanadium. The final weight, if assigned to $V_2O_5$, indicates a molecular weight of 323, rather lower than the value 331 expected if $n = 1.75$. If the solid contained ~0.8% of Na, which is not removed during heating, this would account for the discrepancy. At least three further weight losses starting at ~200, ~240 and ~320°C can be seen in the TG and DSC curves. Comparing these with TG (and DSC) results obtained with [VO(sal-ala)$(H_2O)$],[13] [VO(sal-cys)$(H_2O)$][14] and Na[$V_2O_3$(S,R-sal-ser)$_2$][13] (sal-ala = salicylidene-S-alaninato, sal-ser = salicylidene-S,R-serinato and sal-cys = salicylidene-S-cysteinato) the first two weight losses probably correspond to decarboxylation followed by oxidation of the remaining glygly moiety, and the weight loss from ~320°C probably involves the oxidation of the benzene moiety.

*ESR spectra.* The X-band ESR spectrum of a powdered frozen sample of **1** gave a broad signal with $g = 1.988$, within the range normally found for oxovanadium(IV) compounds.[15] No signal was detected at $g \approx 4$. The spectrum of a frozen methanolic solution of the compound indicates the presence of two species in solution that will be designated by A and B ($A_\parallel$ (A) < $A_\parallel$ (B)). The spin-Hamiltonian parameters were calculated using the correct equations[16] based on Chasteen's method.[17] We have analysed the spectra as a superposition of two axial spectra. Coincident perpendicular lines had to be assumed for the two species because these were insufficiently resolved. The parallel lines are relatively close to each other, species A and B are clearly detected, but the exact positions of the $M_I = 5/2$ and $7/2$ lines cannot be determined, especially for B which apparently is a minor species. The values obtained were $A_\parallel = 160$ (A) and 170 (B) $\times 10^{-4}$ cm$^{-1}$, $g_\parallel = 1.950$ (A) and 1.954 (B) $A_\perp = 60.1$ (A) and 59.5 (B) $\times 10^{-4}$ cm$^{-1}$, $g_\perp = 1.980$ (A) and 1.978 (B).

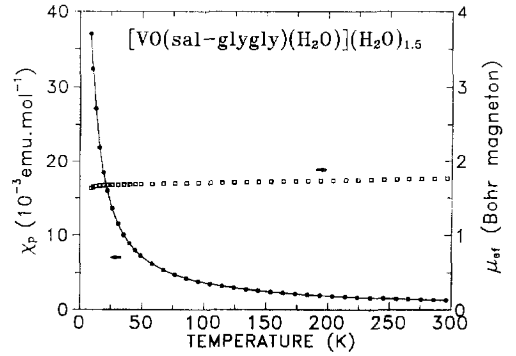


Fig. 1. Temperature dependence of the magnetic susceptibility and $\mu_{eff}$ of **1** at 5 Tesla between 4.2 and 300 K. The data were corrected from the diamagnetic contribution ($\chi_d{}^M = -1.46 \times 10^{-4}$ emu mol$^{-1}$)

To sort out the nature of species A and B detected in the frozen solution ESR spectra, Chasteen's[17] table of vanadium-51 hyperfine coupling constants for additivity calculations may be used. However Chasteen's table does not include values for groups such as Ph—CH═N—CHR and —N—(amide); they certainly differ from those for ═N(bipy) or —$NH_2$(en) donor groups which are the basis of Chasteen's parameters for nitrogen donors. We have previously estimated[1] for $A_\parallel$ (═N—, Schiff base) values in the range $166–174 \times 10^{-4}$ cm$^{-1}$, with $171 \times 10^{-4}$ cm$^{-1}$ being reasonable. To estimate $A_\parallel$(—N—(amide)) one needs a well characterized oxovanadium(IV) complex including this donor group: to our knowledge only the paper of Kabanos and coworkers[18] includes ESR studies on complexes including an N(amide) donor characterized by X-ray analysis. These complexes have the following donor groups in the equatorial plane: N (py), N(amine), N(amide) and O(ketone). The results of back calculations of the hyperfine coupling constants of N(amide) for these complexes depend on the values assumed for the O(ketone) donor group, which Chasteen's[17] table also lacks. If it is assumed that $A_\parallel$(O-ketone) = $A_\parallel(COO^-)$ then one obtains $A_\parallel$(N-amide) $\approx 114 \times 10^{-4}$ cm$^{-1}$; if $A_\parallel$(O-ketone) = $A_\parallel(R—O^-)$ then one estimates $A_\parallel$(N-amide) $\approx 144 \times 10^{-4}$ cm$^{-1}$, i.e. the magnitude of $A_\parallel$ is probably comparable to complexes with either sulphur or nitrogen/sulphur donors, being in the range $130–144 \times 10^{-4}$ cm$^{-1}$. Values of $A_\parallel$ lower than for $R\text{-}S^-$ are unlikely.

Assuming structure **I** for species A detected in the frozen solution ESR spectrum, and taking: $A_\parallel(Ph—O^-) = 155.5$,[17] $A_\parallel(COO^-) = 170.9$.[17] $A_\parallel$(═N—, Schiff base) = 171[1] and $A_\parallel$(N-amide) = 130 or $144 \times 10^{-4}$ cm$^{-1}$, gives $A_\parallel$ (**I**) ~ 157 or 160, respectively. This suggests that **I** is a plausible structure for complex **1**.

If one assumes structure **II** for species B detected in the ESR spectrum, and taking:

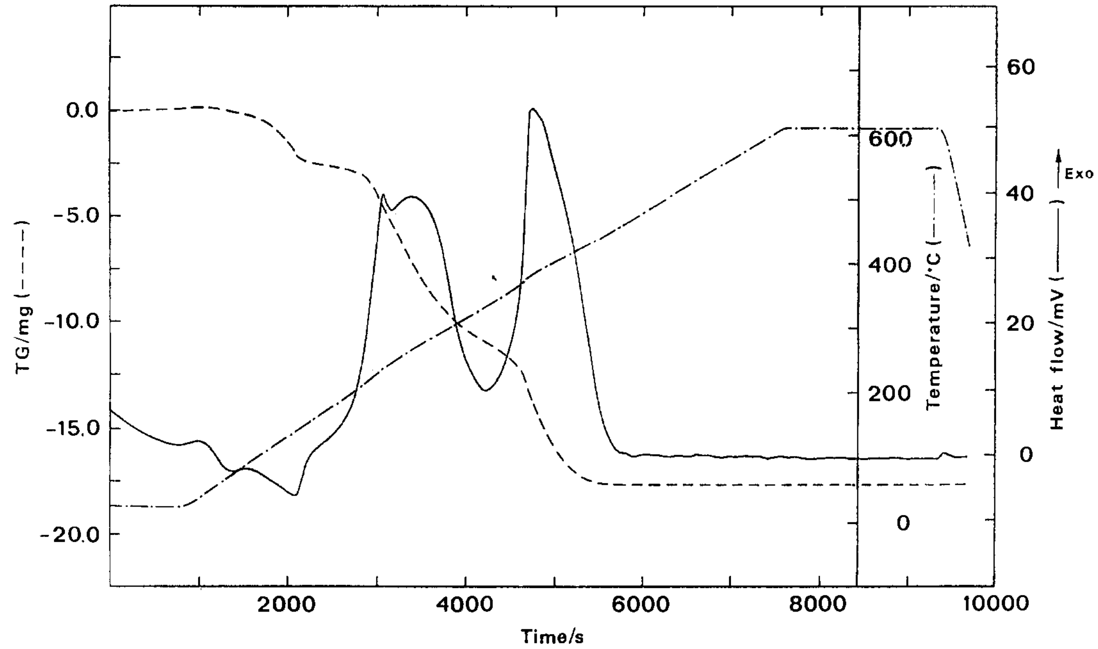
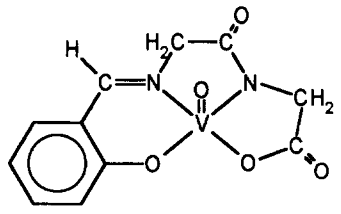
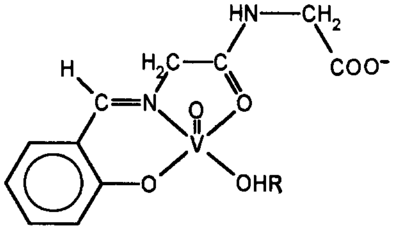


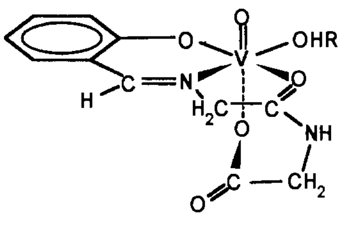
Fig. 2. Thermogravimetric (TG) and DSC curves for VO(sal-glygly)(H$_2$O)$_n$. The curves were corrected with a blank measurement, using an empty crucible.



(I)



or



(IIa)

(IIb)

$A_{\parallel}(\text{Ph—O}^-) = 155.5$,[17] $A_{\parallel}$(O-ketone) ≈ $A_{\parallel}(\text{COO}^-) = 170.9$,[17] $A_{\parallel}$(=N—, Schiff base) = 171[1] and $A_{\parallel}$(ROH) = 182.6 (= $A_{\parallel}(H_2O)$), one obtains $A_{\parallel}$(**II**) ~ 170, which agrees remarkably well with the value obtained for $A_{\parallel}$(B). In **II** the coordination of COO$^-$ in axial position cannot be ruled out although models suggest this would involve some strain in the glygly moiety.

*IR spectra.* The spectrum of **1** is quite complex. However, a few assignments are helpful to structural work. In the free (impure) Schiff base, the broad band with a clear maximum at 3300 cm$^{-1}$ can be assigned to $\nu_{N-H}$. Complex **1** lacks this band: a broad band due to $\nu_{O-H}$ of water is detected instead, with maxima at 3580 (sharp) and ~3350 (broad). A broad band at 3215 cm$^{-1}$ may well correspond to $\nu_{N-H}$(amide). The sharp band at 2910 cm$^{-1}$ may be assigned to $\nu_{as}(CH_2)$. Of the several bands in the region 1700–1200 cm$^{-1}$, that at ~1660 cm$^{-1}$ probably corresponds to $\nu_{C=N}$; bands at

$\sim 1640$ and $\sim 1520$ cm$^{-1}$ may perhaps be assigned as the amide II and III, but the strong absorption at $\sim 1415$ cm$^{-1}$ could be assigned to a C—N (amide) stretching mode, indicating the presence of a deprotonated amide complex.[19] A strong band at 950 cm$^{-1}$ can be assigned to $\nu_{V=O}$.

### *Characterization of complex* 2

Decavanadate **2** was obtained in attempts to obtain crystals of complex **1** suitable for X-ray diffraction when similar but dilute solutions were used. Cell parameters confirmed the formation of the same solid in different batches. Apparently the same decavanadate was obtained from similar dilute solutions which were expected to yield [VO(sal-thr)($H_2O$)][14] and a different polyvanadate from solutions containing [VO(sal-ala)($H_2O$)].[14]

Magnetization measurements performed as a function of temperature in the range 9–296 K did not show any significant variation of the magnetic susceptibility with temperature, indicating that we are not in the presence of a vanadium(IV) compound, for which a $1/T$ dependence would be expected.

The formation of a compound of vanadium(V) may be explained by the oxidation of oxovanadium(IV) by atmospheric oxygen. The $NH_4^+$ cations are presumably formed by deamination of the glygly present in solution. This process may have involved an oxidative deamination catalysed by salicylaldehyde and the metal ion.[20]

The structure of many decavanadates has been studied by X-ray crystallography (e.g. refs 22–26), and the $V_{10}O_{28}^{6-}$,[25] $HV_{10}O_{28}^{5-}$,[26] $H_2V_{10}O_{28}^{4-}$[23] and $H_3V_{10}O_{28}^{3-}$[24] anions have been characterized in the solid state. Our particular decavanadate salt has not been characterized previously. A molecular diagram[21] presenting the numbering scheme is shown in Fig. 3; selected bond distances are listed in Tables 1 and 2.

Since the starting material was a compound of vanadium(IV) and only two $Na^+$ cations are present in decavanadate **2**, the possibility of the compound being a mixed valence or a protonated polyvanadate anion existed. Magnetic moment measurements as a function of temperature indicated that it only included vanadium(V) atoms. However, on refinement of X-ray data, the calculated difference Fourier synthesis were not completely clear in deciding the location of the four protons then necessarily present to compensate for the charge of the decavanadate core.

If the $V_{10}O_{28}^{6-}$ ion were protonated, there would be significant differences in length between some of the V—O bonds in compound **2** and its counterpart $Na_6V_{10}O_{28}\cdot 18H_2O$[25] which is certainly unprotonated. Such differences would help in locating the protons in **2**: although X-ray crystal structure determinations have been performed for several

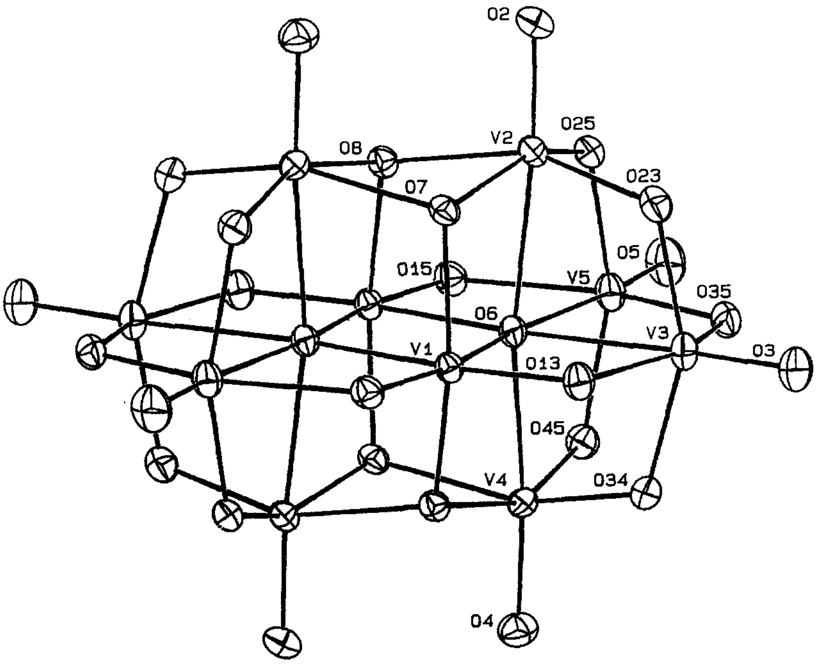


Fig. 3. ORTEP-II[21] diagram of $V_{10}O_{28}^{6-}$ in $(NH_4)_4(Na)_2(V_{10}O_{28})\cdot 10H_2O$ (**2**). The thermal motion ellipsoids are drawn at the 50% probability level.

Table 1. Bond lengths (Å) for the $V_{10}O_{28}^{6-}$ anion

| | | | |
|---|---|---|---|
| V1—O6 | 2.097(3) | V1—O6[a] | 2.115(4) |
| V1—O7 | 1.920(4) | V1—O8[a] | 1.916(3) |
| V1—O13 | 1.683(4) | V1—O15[a] | 1.697(3) |
| V2—O2 | 1.618(4) | V2—O6 | 2.244(4) |
| V2—O7 | 2.000(4) | V2—O8 | 1.989(4) |
| V2—O23 | 1.820(4) | V2—O25 | 1.819(3) |
| V3—O3 | 1.602(4) | V3—O6 | 2.290(4) |
| V3—O13 | 2.056(3) | V3—O23 | 1.867(4) |
| V3—O34 | 1.886(4) | V3—O35 | 1.825(4) |
| V4—O4 | 1.619(4) | V4—O6 | 2.225(3) |
| V4—O7[a] | 1.995(3) | V4—O8[a] | 2.021(3) |
| V4—O34 | 1.809(4) | V4—O45 | 1.816(4) |
| V5—O5 | 1.598(4) | V5—O6 | 2.358(3) |
| V5—O15 | 2.019(4) | V5—O25 | 1.874(3) |
| V5—O35 | 1.850(4) | V5—O45 | 1.891(4) |

[a] Symmetry-related atom by $-x, 1-y, 2-z$.

Table 2. Distances between adjacent vanadium atoms in $[Na^+]_2[NH_4^+]_4\,[V_{10}O_{28}^{6-}]\cdot 10H_2O$

| | Symmetry operation[a] | Distance, Å |
|---|---|---|
| V1 ··· V1 | $[-x, 1-y, 2-z]$ | 3.266(1) |
| V1 ··· V2 | $[x, y, z]$ | 3.162(1) |
| V1 ··· V2 | $[-x, 1-y, 2-z]$ | 3.154(1) |
| V1 ··· V3 | $[x, y, z]$ | 3.062(1) |
| V1 ··· V4 | $[x, y, z]$ | 3.167(1) |
| V1 ··· V4 | $[-x, 1-y, 2-z]$ | 3.151(1) |
| V1 ··· V5 | $[-x, 1-y, 2-z]$ | 3.085(1) |
| V2 ··· V3 | $[x, y, z]$ | 3.089(1) |
| V2 ··· V4 | $[-x, 1-y, 2-z]$ | 3.073(1) |
| V2 ··· V5 | $[x, y, z]$ | 3.124(1) |
| V3 ··· V4 | $[x, y, z]$ | 3.105(1) |
| V3 ··· V5 | $[x, y, z]$ | 3.076(1) |
| V4 ··· V5 | $[x, y, z]$ | 3.122(1) |

[a] This symmetry operation applies to the coordinates of the second atom.

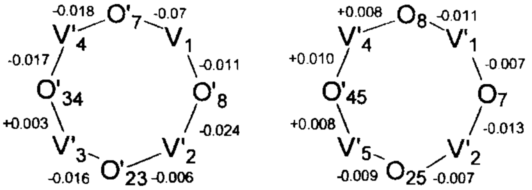


Fig. 4. Differences (Å) between the distances of individual bonds in decavanadate **2** and $Na_6V_{10}O_{28}\cdot 18H_2O$[25] for $V_4O_4$ rings.

salts of $V_{10}O_{28}^{6-}$, the determination for $Na_6V_{10}O_{28}\cdot 18H_2O$[25] is probably the most accurate[24] and will therefore be used for comparisons. However, the very small differences found in the eight-membered $V_4O_4$ rings (Fig. 4) and the spacings between the approximately planar layers of negatively-charged and closed-packed oxygen atoms, separated by layers of cationic vanadium centres in both $V_{10}O_{28}^{6-}$ cores (Fig. 5), suggest that the decavanadate **2** is not protonated.

In decavanadate **2** each sodium ion is surrounded by six oxygen atoms as shown in Fig. 6. In this $[Na^+]_2\cdot 10H_2O$ cluster, O1w occupies a bridging position between the two neighbouring sodium ions. The Na—O distances listed in Table 3 are comparable with those found in hydrated sodium salts.[27] In the crystal structure, the bulkier $V_{10}O_{28}^{6-}$ anions form layers in the *ac*-plane, and these 3 layers stack along the *b*-axis direction, one anion from one layer lying over the cavity formed by four adjacent anions in the layers above and below it. The $[Na^+]_2\cdot 10H_2O$ clusters occupy these cavities and thus each cluster is surrounded by six $V_{10}O_{28}^{6-}$ anions. This packing arrangement can be appreciated in Fig. 7. In view of the fact that there is a large number of donor and acceptor groups, it is not surprising that there are many hydrogen bonds in this crystal structure (see Table 4). Since the donor groups are the water molecules in the $[Na^+]_2\cdot 10H_2O$ clusters and the ammonium ions, and the acceptor groups are mainly oxygen atoms in the $V_{10}O_{28}^{6-}$ anion, this hydrogen bonding plays an important role in stabilizing this crystal structure.

*IR spectra.* Vibrational spectra of the decavanadates obtained in several batches are similar to those previously described in refs 23, 24 and 28. The presence of well differentiated V—O linkages indicates the possibility of a great number of internal vibrations.

The bands between 985 and 900 $cm^{-1}$ can be assigned to the symmetrical stretching of the terminal V—O bonds, while the antisymmetric ones possibly correspond to the band at 810 $cm^{-1}$. Anti-

Table 3. Selected contact distances in the $[Na^+]_2\cdot 10H_2O$ cluster

| | Symmetry operation[a] | Distance, Å |
|---|---|---|
| $Na^+$ ··· $Na^+$ | $[1-x, 1-y, 1-z]$ | 3.404(3) |
| $Na^+$ ··· O1w | $[x, y, z]$ | 2.414(5) |
| $Na^+$ ··· O1w | $[1-x, 1-y, 1-z]$ | 2.436(5) |
| $Na^+$ ··· O2w | $[x, y, z]$ | 2.335(6) |
| $Na^+$ ··· O3w | $[1-x, 1-y, 1-z]$ | 2.379(6) |
| $Na^+$ ··· O4w | $[1-x, 1-y, 1-z]$ | 2.342(6) |
| $Na^+$ ··· O5w | $[x, y, z]$ | 2.352(5) |

[a] This symmetry operation applies to the coordinates of the second atom.

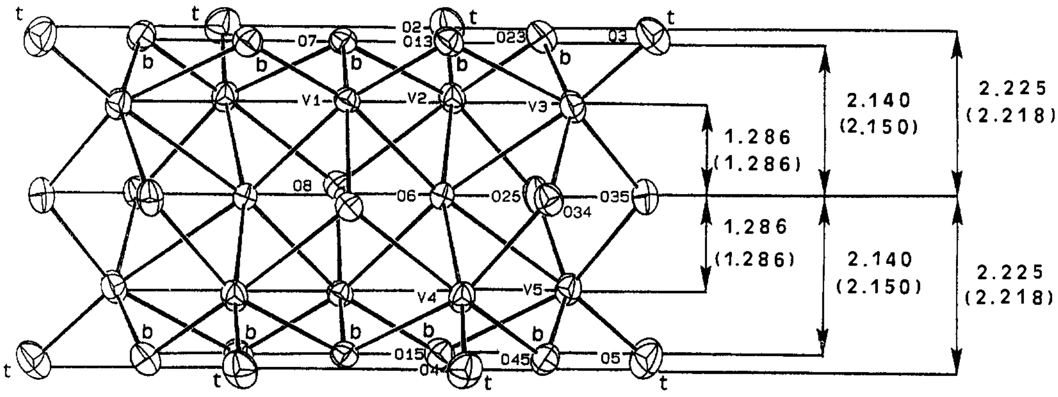


Fig. 5. View of the decavanadate anion showing the different layers of atoms, and the spacings between these in decavanadate **2** and $Na_6V_{10}O_{28}\cdot 18H_2O$.[25] In both anions, the plane containing six doubly-bridging, two triply-bridging, and two six-coordinate oxygen atoms may be used as a reference plane from which spacings to other nearly parallel layers may be measured.[24] In both anions, three types of atoms may be considered to lie in planes above and below the reference plane: two sets of four terminal oxygen atoms ($O_t$), two sets of four doubly-bridging and one triply-bridging oxygen atoms ($O_b$) and two sets of five vanadium atoms (V), these are displaced from the reference plane by the values shown (values for $Na_6V_{10}O_{28}\cdot H_2O$[25] indicated between brackets).

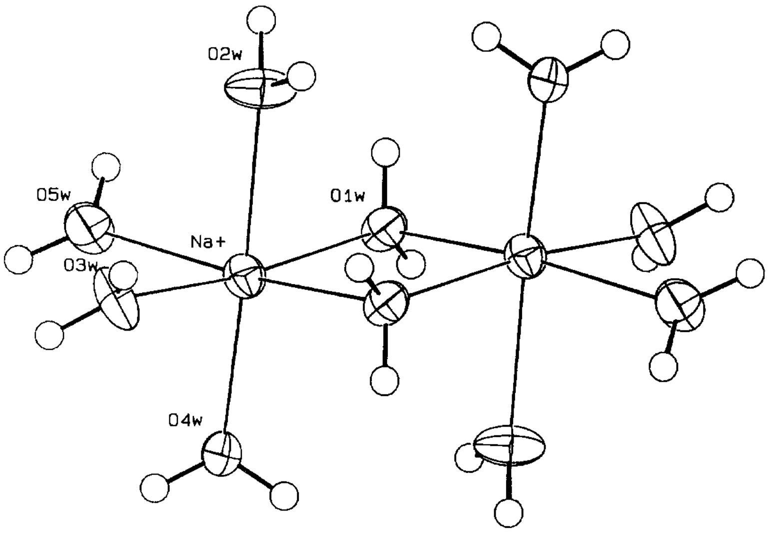


Fig. 6. ORTEP-II[21] diagram of $[Na^+]_2\cdot 10H_2O$ in $(NH_4)_4(Na)_2(V_{10}O_{28})\cdot 10H_2O$ (**2**). The thermal motion ellipsoids are drawn at the 50 % probability level. For clarity, the hydrogen atoms have been drawn with the same arbitrary isotropic temperature factor.

symmetric and symmetric bridge vibrations are probably in the 840–740 and 600–400 cm$^{-1}$ ranges, respectively.

The spectra confirm the presence of the ammonium cations, as bands in the region 3000–3300 and 1400 cm$^{-1}$ are clearly seen. $H_2O$ shows a characteristic broad strong band between 3600 and 2900 cm$^{-1}$ and a band of medium intensity around 1630 cm$^{-1}$.

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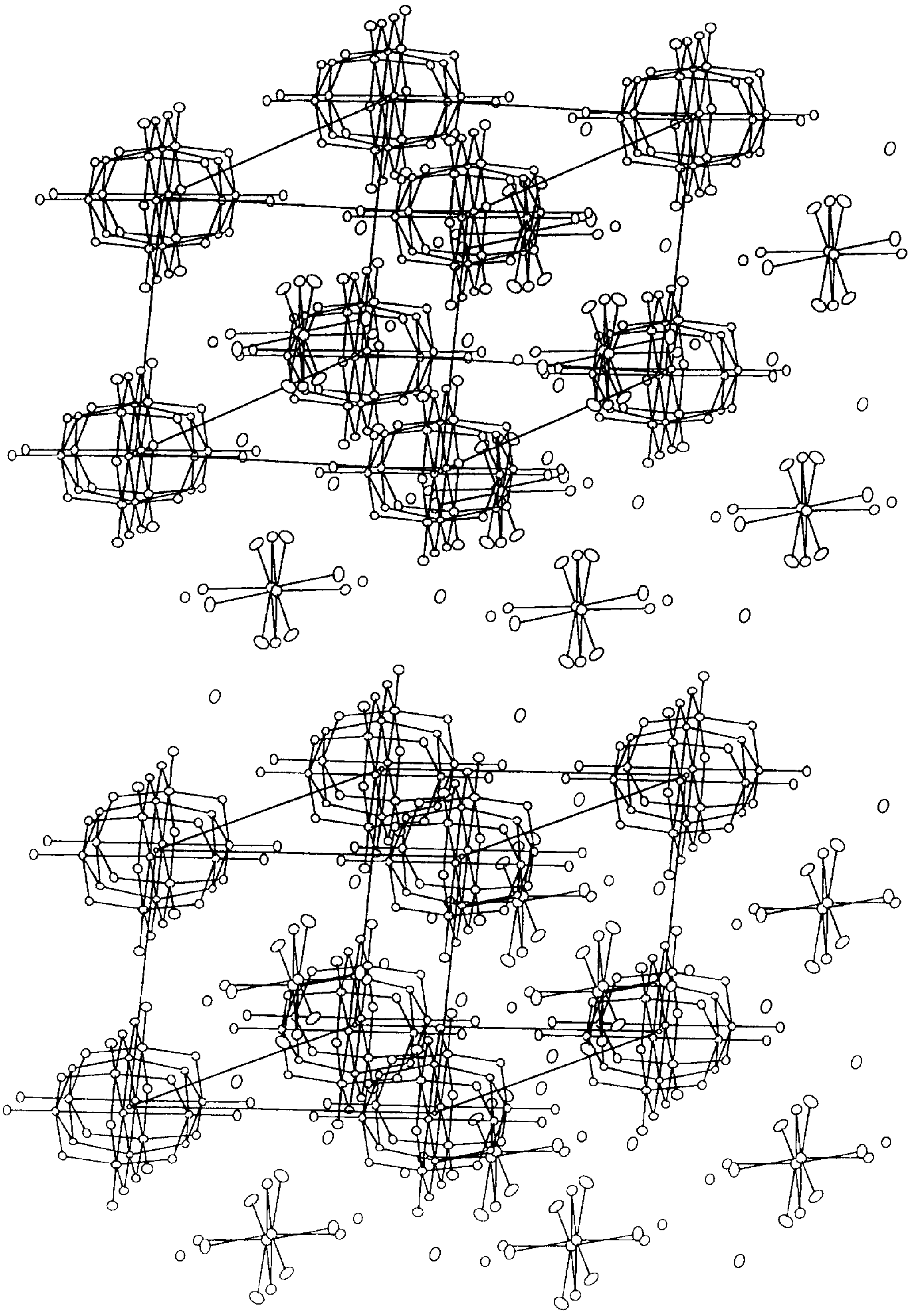

Fig. 7. ORTEP-II[21] stereo diagram of the crystal packing in $(NH_4)_4(Na)_2(V_{10}O_{28}) \cdot 10H_2O$ **(2)**. The origin of the unit cell depicted in this diagram is not that used in the structure refinement. The origin is located in the lower right corner, the crystal *a*-axis is vertical, the *b*-axis in horizontal and the *c*-axis goes towards the back of the figure.

Table 4. Hydrogen bond geometrical data for $[V_{10}O_{28}^{6-}][Na^+]_2[NH_4^+]_4 \cdot 10H_2O$

| D—H···A[a] | Symmetry operation[b] | $r$(H···A), Å | $\alpha$(D—H···A), (°) |
|---|---|---|---|
| O1w—H11w···O45 | $[-x, 1-y, 2-z]$ | 1.94(8) | 163(3) |
| O1w—H12w···O4 | $[x, y, z-1]$ | 2.15(6) | 160(3) |
| O2w—H21w···O15 | $[-x, 1-y, 2-z]$ | 1.93(8) | 175(3) |
| O2w—H22w···O34 | $[1-x, 1-y, 2-z]$ | 1.93(7) | 162(3) |
| O3w—H31w···O25 | $[x, 1-y, z-1]$ | 1.88(5) | 174(2) |
| O3w—H32w···O2 | $[-x, 1-y, 1-z]$ | 2.34(8) | 134(3) |
| O3w—H32w···O4 | $[x, y, z-1]$ | 2.19(8) | 141(4) |
| O4w—H41w···O35 | $[x, 1+y, z-1]$ | 1.88(5) | 168(3) |
| O4w—H42w···O3 | $[1-x, 1-y, 2-z]$ | 2.34(8) | 126(2) |
| O5w—H51w···O7 | $[x, y, z]$ | 2.05(7) | 161(3) |
| O5w—H52w···O23 | $[1-x, -y, 2-z]$ | 2.00(6) | 151(3) |
| N6—H61n···O13 | $[x, y, z]$ | 2.01(9) | 149(4) |
| N6—H62n···O8 | $[1+x, y, z]$ | 2.06(9) | 155(3) |
| N6—H63n···O2 | $[1-x, -y, 2-z]$ | 1.99(5) | 165(2) |
| N6—H64n···O5w | $[x, y, z]$ | 2.11(11) | 168(4) |
| N7—H71n···O4 | $[-x, 1-y, 2-z]$ | 2.00(7) | 174(3) |
| N7—H72n···O3 | $[1-x, -y, 2-z]$ | 2.30(7) | 122(2) |
| N7—H72n···O5 | $[-x, -y, 2-z]$ | 2.37(7) | 149(3) |
| N7—H73n···O4w | $[1-x, 1-y, 1-z]$ | 2.08(7) | 168(3) |
| N7—H74n···O34 | $[x, y, z-1]$ | 2.40(7) | 130(2) |
| N7—H74n···O35 | $[x, y, z-1]$ | 2.40(8) | 130(2) |
| N7—H74n···O45 | $[x, y, z-1]$ | 2.28(9) | 155(3) |

[a] D stands for donor and A for acceptor atom.

[b] This symmetry operation applies to the coordinates of the acceptor atom.

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