

# Effects of Protonation in Decavanadates: Crystal Structure of Tetrakis(*n*-hexylammonium) Dihydrogendifcavanadate(v)†

Pascual Román,\*<sup>a</sup> Ana Aranzabe,<sup>a</sup> Antonio Luque,<sup>a</sup> Juan M. Gutiérrez-Zorrilla<sup>a</sup> and Martín Martínez-Ripoll<sup>b</sup>

<sup>a</sup> Departamento de Química Inorgánica, Universidad del País Vasco, Apartado 644, 48080 Bilbao, Spain

<sup>b</sup> Departamento de Cristalografía, Instituto Rocasolano, CSIC, Serrano 119, 28006, Madrid, Spain

The crystal structure of a new dihydrogendifcavanadate(v) of *n*-hexylammonium has been determined by means of X-ray diffraction data. Empirical bond length/bond number calculations have located the protonation sites in two triply-linked oxygen atoms which reinforce theoretical results of relative basicities of the oxygen sites in decavanadate anions. The crystal structure is stabilised by electrostatic forces and an extensive network of hydrogen contacts among anions and cations. The dihydrogendifcavanadate(v) anions are located on the (001) plane and are joined *via* hydrogen bonding,  $d(O \cdots O) = 2.63$  and  $2.64 \text{ \AA}$ , giving evidence of strong  $O \cdots O$  interactions. Infrared spectroscopy and thermoanalytical methods have been applied in order to confirm structural properties.

The structure of the decavanadate(v) anion is well established<sup>1</sup> and has *mmm* ( $D_{2h}$ ) point symmetry. All vanadium atoms have distorted octahedral geometry and the oxygen atoms fall into seven categories, ranging from terminal to six-co-ordinate. Since the structure was elucidated there has been speculation about the sites of protonation which have been determined in several studies.<sup>2–7</sup> The oxygen site B belongs to a close-packed nine-atom array plane, formed by two oxygen sites C, two E, two F, two G and the one referred before as B (see Fig. 1). This plane is particularly appealing to study the conditions that decide the fixation mode of inorganic, organometallic or organic groups to one or several oxygen atoms. In order to delineate the factors, including steric congestion, that influence those incorporation processes it was necessary to decide first what oxygen on this surface is basic enough to serve as a bonding site for small cationic groups. In 1977,<sup>2</sup> a determination of protonation sites by  $^{17}\text{O}$  nuclear magnetic resonance spectroscopy led to the conclusion that the protonation sites observed in  $[\text{V}_{10}\text{O}_{28}]^{6-}$  are correctly predicted by calculating covalent bond strengths using bond lengths observed in the unprotonated anion. The sum of V–O covalent bond strengths at each oxygen site, interpreted as the relative amount of negative charge removed from formally dianionic oxygen, yields the sequence of increasing negative charge  $O_G \approx O_F < O_E < O_D < O_C < O_B < O_A$ . Since  $O_A$  is inaccessible to protons, the sequence correctly predicts  $O_B$  and  $O_C$  to be the most basic oxygens with  $O_B$  more basic than  $O_C$ . In 1992, Kempf *et al.*<sup>7</sup> studied the relative basicities of the oxygen sites in decavanadate anions with an analysis of *ab initio* determined distributions of the electrostatic potential and of the Laplacian of charge density. Their results agreed with the interpretation of the  $^{17}\text{O}$  NMR spectrum proposed by Klemperer and Shum.<sup>2</sup>

However, the crystal structures described in the literature locate the hydrogen atoms of the  $[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-}$  anion in two doubly-linked  $O_C$  type oxygen atoms. Debaerdemakers *et al.*<sup>8</sup> solved the crystal structure of the first dihydrogendifcavanadate anion, tetrakis(4-ethylpyridinium) dihydrogendifcavanadate(v),

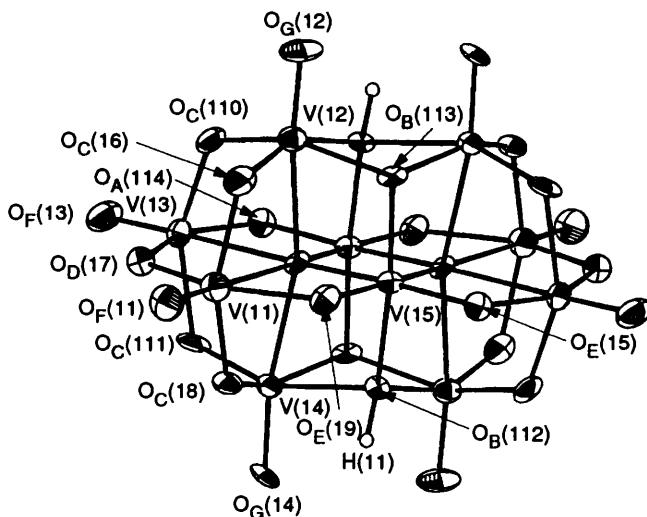


Fig. 1 Structure of the dihydrogendifcavanadate(v) anion I in  $[\text{NH}_3(\text{C}_6\text{H}_{13})][\text{H}_2\text{V}_{10}\text{O}_{28}]$

but no attempt was made to determine the oxygen sites which would carry the hydrogen atoms and to consider the possible role of these atoms in the structure. Evans and Pope<sup>3</sup> using an empirical bond length/bond number calculation,  $s = (R/1.79)^{-5.1}$ , ( $R = \text{V}–\text{O}$  distance;  $s = \text{bond number}$ ) found that the extra proton was attached to the valence deficient, double-linked,  $O_C$  type oxygen atom. They expected that more structure studies of crystals containing the  $[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-}$  species may reveal the protons to be located at other sites. But since then the only protonation sites described in the dihydrogendifcavanadate anion refer to the double-linked oxygen atoms. In 1986 Capparelli *et al.*,<sup>5</sup> following the calculations used by Evans and Pope,<sup>3</sup> reinforced the crystallographic evidence that the hydrogen atoms in the crystal structure of tetrakis(adenosinium) dihydrogendifcavanadate(v) undecahydrate were attached to two double-linked oxygen atoms.

As part of a study on polyoxometalates we have isolated a

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

compound of formula  $[\text{NH}_3(\text{C}_6\text{H}_{13})]_4[\text{H}_2\text{V}_{10}\text{O}_{28}]$ . This work is being done in order to study the protonation sites in the dihydrogencavanadate(v) anion by means of empirical bond length/bond number calculations. In the crystal structure of the tetrakis(*n*-hexylammonium) dihydrogencavanadate(v) the hydrogen atoms have been attached for the first time to two triply linked,  $\text{O}_\text{B}$  type oxygen atoms. Crystallographic effects such as lengthening of V–O distances involving protonated oxygen atoms and strong anion–anion interactions *via* hydrogen bonding give evidence of these unusual protonation sites. The aim of this paper is to describe the syntheses, solid-state characterization and crystal structure of  $[\text{NH}_3(\text{C}_6\text{H}_{13})]_4[\text{H}_2\text{V}_{10}\text{O}_{28}]$ .

## Experimental

**Reagents.**—All reagents were purchased from Merck and were used without further purification.

**Physical Measurements.**—Microanalyses of carbon, nitrogen and hydrogen were performed on a Perkin-Elmer 240 C, H, N-analyser. Vanadium was determined as  $\text{V}_2\text{O}_5$  by thermal decomposition of the compound in an argon–oxygen atmosphere. The densities were measured by flotation in  $\text{CHBr}_3\text{–CCl}_4$ . Infrared spectra were recorded in the 4000–400  $\text{cm}^{-1}$  range on a Nicolet 740 FT-IR spectrometer, and the solid compounds were mixed with fused potassium bromide and pressed into transparent dishes. A Setaram TAG 24 S16 thermobalance was used to obtain the differential thermal analysis (DTA) and thermogravimetric analysis (TGA) curves, simultaneously, in an argon–oxygen atmosphere (4:1) with a heating rate of 5  $^\circ\text{C min}^{-1}$ .

**Preparation of  $[\text{NH}_3(\text{C}_6\text{H}_{13})]_4[\text{H}_2\text{V}_{10}\text{O}_{28}]$  1.**—The *n*-hexylammonium dihydrogencavanadate(v) was obtained according to the following methods: (i) by adding  $\text{CuCl}_2$  (0.30 g, 2.20 mmol) to an aqueous solution (40  $\text{cm}^3$ ) of  $\text{V}_2\text{O}_5$  (2.0 g, 11.0 mmol) and *n*-hexylamine (1.8  $\text{cm}^3$ , 0.013 mmol) and heating with stirring during 30 min, or (ii) from an aqueous solution (pH 4) of  $[\text{NH}_3(\text{C}_6\text{H}_{13})]_6[\text{V}_{10}\text{O}_{28}] \cdot 2\text{H}_2\text{O}$  2<sup>9</sup> and  $\text{CuCl}_2$  (V:Cu = 10:1). This solution was prepared by dissolving the decavanadate salt (3.50 g, 2.18 mmol) in water (30  $\text{cm}^3$ ), adding  $\text{CuCl}_2$  (0.30 g, 2.20 mmol), vigorously stirring until dissolution, and heating for 30 min. Orange single crystals were obtained following method (ii). The first method led to an orange powder identified as the same compound. The crystals were filtered off, washed with diethyl ether and then carefully dried in air. Yield 30% (Found: C, 21.25; H, 4.65; N, 4.05; V( $\text{V}_2\text{O}_5$ ), 66.15; Calc. for  $\text{C}_{24}\text{H}_{66}\text{N}_4\text{O}_{28}\text{V}_{10}$ : C, 21.05; H, 4.85; N, 4.10; V( $\text{V}_2\text{O}_5$ ), 66.50%). IR spectrum:  $\nu(\text{N–H})$  3415m (br), 3405m and 3395m;  $\nu(\text{C–H})$  3215m, 3060m (br) and 2860s;  $\nu(\text{NH}_3^+)$  2930s;  $\delta_{\text{asym}}(\text{NH}_3^+)$  1610vs;  $\delta(\text{N–H})$  1490s;  $\delta_{\text{sym}}(\text{NH}_3^+)$  1200s;  $\gamma(\text{C–C})$  1100s;  $\nu(\text{V–O})$  995s, 965s, 960m and 905s;  $\nu_{\text{asym}}(\text{V–O}_\text{B})$  840s, 815 (sh), 745m and 630m;  $\nu_{\text{sym}}(\text{V–O}_\text{B})$  585m, 525m and 460m;  $\delta(\text{V–O}_\text{B})$  400m  $\text{cm}^{-1}$ .

**Crystallographic Data Collection and Refinement of the Structure.**—**Crystal data.**  $\text{C}_{24}\text{H}_{66}\text{N}_4\text{O}_{28}\text{V}_{10}$ ,  $M = 1368.2$ , triclinic, space group  $\overline{P}\bar{1}$ ,  $a = 10.300(3)$ ,  $b = 16.36(1)$ ,  $c = 16.52(1)$   $\text{\AA}$ ,  $\alpha = 104.56(3)$ ,  $\beta = 71.78(3)$ ,  $\gamma = 89.96(3)^\circ$ ,  $U = 2550(3)$   $\text{\AA}^3$ ,  $D_\text{c} = 1.77$   $\text{g cm}^{-3}$ ,  $D_\text{m} = 1.78(1)$   $\text{g cm}^{-3}$ ,  $Z = 2$ ,  $F(000) = 1380$ ,  $\mu(\text{Cu-K}\alpha) = 156.3$   $\text{cm}^{-1}$ .

**Data collection and processing.** The cell parameters of a prismatic single crystal with dimensions  $0.15 \times 0.20 \times 0.10$  mm were determined on a SEIFERT four-circle diffractometer using graphite-monochromated Cu-K $\alpha$  radiation ( $\lambda = 1.5406$   $\text{\AA}$ ) at 294(1) K, with a standard least-squares routine using 25 reflections measured for both positive and negative Bragg angles. 6084 Reflections were collected using the  $\omega$ –2 $\theta$  scan technique at a 2 $\theta$  scan rate of  $1^\circ \text{ min}^{-1}$  and scan width  $1.0^\circ$ , with Miller indices running from 0 to 11 for  $h$ , from –16 to 16 for  $k$

and from –17 to 17 for  $l$  in the range  $2 \leq \theta \leq 70^\circ$ . During data collection, two reference reflections (2 1 1) and (–1 2 2) were monitored after every 200 reflections to check for drifts in electronics, radiation damage, variations in X-ray tube intensity, crystal stability and counter response. No crystal decay was observed during the data collection process. The intensities were corrected for Lorentz and polarization effects. A total of 3494 reflections with  $I \geq 2\sigma(I)$  were classified as observed and selected for the structure determination. Scattering factors for neutral atoms and anomalous dispersion corrections for V were taken from ref. 10.

**Structure analysis and refinement.** The position of the vanadium atoms were obtained by direct methods using the SIR 88<sup>11</sup> program; the remaining non-hydrogen atoms of the structure were located on successive Fourier syntheses. Anisotropic refinement was carried out by full-matrix least-squares analysis. A convenient weighting scheme<sup>12</sup> of type  $w = w_1 w_2$  with  $w_1 = k_1/(a + b|F_0|)^2$  and  $w_2 = k_2/[c + d(\sin \theta/\lambda)]$  was used so as to give no trends in  $\langle w\Delta^2 F \rangle$  vs.  $\langle F_0 \rangle$  and vs.  $\langle \sin \theta/\lambda \rangle$ . Hydrogen-atom positions were not discernible from electron density difference maps; those belonging to the cations were generated at geometrically fixed positions. Last cycles of refinement gave the discrepancy indices  $R = 0.093$ ,  $R' = 0.098$  for 403 parameters; goodness of fit = 1.2103; maximum shift/error in the final cycle 0.40 and the largest positive peak on a final Fourier difference synthesis was 1.40 e  $\text{\AA}^{-3}$ . Most calculations were carried out using the XRAY 76<sup>13</sup> system running on a MicroVAX II computer.

A structure solution has been attempted in the alternative (body-centred monoclinic) space group, and has been found to be unsatisfactory. The lattice shows pseudo-centred monoclinic symmetry and the heavy atoms positions taken alone suggest space group  $I2/a$ , but the actual intensity data did not exhibit Laue symmetry  $2/m$ , nor was a satisfactory refinement possible on this basis.

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

## Results and Discussion

**Syntheses and Spectroscopic Characterization.**—Isolation of polyanions from solution is generally achieved by addition of an appropriate counter ion, commonly an alkali metal, ammonium or tetraalkylammonium. We have reported previously the use of alkylamines and aromatic amines as counter ions in polyanions in order to vary the chemical properties of the polyanion salts.<sup>9,14–19</sup> Due to the interesting disposition of oxygen atoms in polyanions as coplanar closest-packed oxygen surfaces, the study of the different protonation sites in these surfaces as basic oxygen atoms may be an important feature in the study of co-ordination chemistry. We have used *n*-hexylamine in order to study the stability of the polyanion,  $[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-}$ . Neither stoichiometric direct reaction between the vanadium pentoxide and the hexylamine in water nor the dilution of the  $[\text{NH}_3(\text{C}_6\text{H}_{13})]_6[\text{V}_{10}\text{O}_{28}] \cdot 2\text{H}_2\text{O}$  in water (acidified with HCl until pH 4) leads to the expected compound. As it can be seen in the literature<sup>20</sup> metallic halides are used as reactants in the synthesis of some polyoxoclusters of vanadium. In our synthesis the addition of  $\text{CuCl}_2$  in both preparative methods leads to the dihydrogencavanate of *n*-hexylammonium. The presence of  $\text{CuCl}_2$ , presumably, avoids the formation of the unprotonated decavanadate salt which is highly insoluble. Single crystals of the product were obtained and the crystal structure is reported.

Infrared spectroscopy was a good method to identify the type of polyanion, its protonated state and the presence of protonated organic cations. As expected on the basis of the literature the bands corresponding to the isopolyanions are detectable in the range 1000–400  $\text{cm}^{-1}$  and the presence of well differentiated V–O linkages in polyanions structures indicates

**Table 1** Fractional atomic coordinates for non-hydrogen atoms. Where no estimated standard deviation (e.s.d.) is quoted, the atom has been placed in a fixed site

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>
V(11)	0.6633(3)	-0.1502(2)	0.0525(2)	O(211)	1.3004(12)	0.5971(8)	0.0158(9)
V(12)	0.7720(3)	0.0081(2)	-0.0105(2)	O(212)	1.1315(11)	0.3932(7)	0.0064(7)
V(13)	0.6026(3)	0.0253(2)	0.1844(2)	O(213)	0.9124(12)	0.4694(8)	-0.1146(7)
V(14)	0.3649(3)	-0.0720(2)	0.1355(2)	O(214)	1.1047(12)	0.5300(8)	-0.0465(7)
V(15)	0.5511(3)	-0.0897(2)	-0.0754(2)	N(11)	0.9370(14)	0.1727(9)	0.1302(10)
O(11)	0.7434(15)	-0.2398(9)	0.0416(11)	C(12)	0.9360(39)	0.1796(25)	0.2247(25)
O(12)	0.9131(12)	0.0437(8)	-0.0579(9)	C(13)	1.0429(52)	0.2154(33)	0.2463(34)
O(13)	0.6257(15)	0.0662(9)	0.2767(8)	C(14)	1.0285(50)	0.1927(32)	0.3473(34)
O(14)	0.2256(12)	-0.1047(9)	0.1816(8)	C(15)	1.0430	0.1019	0.3429
O(15)	0.5097(12)	-0.1172(7)	-0.1660(8)	C(16)	1.1148	0.0948	0.4188
O(16)	0.8126(11)	-0.0964(7)	-0.0125(7)	C(17)	1.2405	0.1265	0.4133
O(17)	0.6807(13)	-0.0840(9)	0.1533(10)	N(21)	0.4047(15)	0.3521(10)	0.1624(10)
O(18)	0.4870(12)	-0.1662(7)	0.1020(9)	C(22)	0.3354(36)	0.3682(24)	0.2574(25)
O(19)	0.6246(12)	-0.1783(7)	-0.0679(9)	C(23)	0.3711(75)	0.3280(52)	0.3042(57)
O(110)	0.7508(12)	0.0565(9)	0.1045(10)	C(24)	0.4739	0.3428	0.3402
O(111)	0.4232(12)	-0.0181(9)	0.2194(8)	C(25)	0.5450	0.3464	0.3923
O(112)	0.3594(10)	-0.1073(7)	0.0052(7)	C(26)	0.6792	0.3783	0.3971
O(113)	0.6998(10)	-0.0299(7)	-0.1107(8)	C(27)	0.6434	0.3586	0.4926
O(114)	0.5596(10)	-0.0267(8)	0.0496(7)	N(31)	0.4360(14)	0.6747(9)	0.1291(10)
V(21)	1.2865(3)	0.4749(2)	-0.1840(2)	C(32)	0.3329(56)	0.6934(39)	0.2207(39)
V(22)	1.0007(3)	0.5718(2)	-0.1358(2)	C(33)	0.2897(51)	0.6313(35)	0.2445(35)
V(23)	1.2158(3)	0.6511(2)	-0.0529(2)	C(34)	0.1495(57)	0.6774(39)	0.3378(41)
V(24)	1.2617(3)	0.4925(2)	0.0113(2)	C(35)	0.0786	0.6075	0.3499
V(25)	1.0244(3)	0.4100(2)	-0.0750(2)	C(36)	-0.0653	0.6176	0.4146
O(21)	1.4021(14)	0.4322(10)	-0.2785(9)	C(37)	-0.0707	0.5335	0.4237
O(22)	0.9053(16)	0.6042(10)	-0.1825(10)	N(41)	1.0622(14)	0.1497(9)	-0.1604(10)
O(23)	1.2838(16)	0.7385(9)	-0.0423(10)	C(42)	1.0965(31)	0.1303(20)	-0.2591(21)
O(24)	1.3512(12)	0.4583(9)	0.0608(10)	C(43)	1.1884(59)	0.1790(36)	-0.3021(38)
O(25)	0.9427(12)	0.3207(7)	-0.0658(9)	C(44)	1.3112(63)	0.1840(38)	-0.3092(39)
O(26)	1.1469(14)	0.5168(9)	-0.2221(10)	C(45)	1.4142	0.1365	-0.4064
O(27)	1.3359(12)	0.5835(7)	-0.1551(8)	C(46)	1.5376	0.1580	-0.3922
O(28)	1.3534(12)	0.4464(8)	-0.1004(8)	C(47)	1.6296	0.1192	-0.4930
O(29)	1.1623(13)	0.3804(8)	-0.1703(8)	H(1)	0.3230	-0.1684	0.0164
O(210)	1.0875(13)	0.6661(7)	-0.1021(9)	H(2)	1.2101	0.3509	-0.0039

**Table 2** Bond-number calculations for all the oxygen atoms in the two crystallographically independent  $[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-}$  polyanions

Polyanion I		II			
Atom	$\Sigma_{\text{si}}$	$\Sigma_{\text{si}}^*$	Atom	$\Sigma_{\text{si}}$	$\Sigma_{\text{si}}^*$
O(11)	1.67(10)	1.99(10)	O(21)	1.67(5)	1.67(5)
O(12)	1.72(5)	1.93(5)	O(22)	1.84(10)	1.84(10)
O(13)	1.84(5)	1.84(5)	O(23)	1.84(6)	2.17(6)
O(14)	1.96(6)	1.96(6)	O(24)	1.84(10)	2.04(10)
O(15)	2.10(5)	2.10(5)	O(25)	1.79(4)	1.98(4)
O(16)	1.81(3)	2.06(3)	O(26)	1.74(3)	1.74(3)
O(17)	1.85(5)	2.03(5)	O(27)	1.77(2)	1.97(2)
O(18)	1.87(2)	2.11(2)	O(28)	1.91(4)	2.15(4)
O(19)	1.81(4)	1.98(4)	O(29)	1.77(4)	1.77(4)
O(110)	1.80(5)	2.05(5)	O(210)	1.83(4)	2.05(4)
O(111)	1.88(4)	1.88(4)	O(211)	1.71(3)	1.94(3)
O(112)	1.39(1)	1.39(1)	O(212)	1.40(1)	1.40(1)
O(113)	2.07(2)	2.07(2)	O(213)	1.97(2)	1.97(2)
O(114)	2.04(1)	2.04(1)	O(214)	2.04(1)	2.04(1)

\* Contribution of adjacent hydrogen atoms from hydrogen bondings are included.

the possibility of a great number of internal vibrations. The spectrum is characterized by strong bands at 995, 965 and 905  $\text{cm}^{-1}$  assigned to the stretching of the terminal V–O bonds, and other strong peaks between 840 and 460  $\text{cm}^{-1}$  attributable to the stretching of V–O<sub>b</sub> bonds. The bands which appear at higher frequencies between 840 and 630  $\text{cm}^{-1}$  correspond to asymmetrical stretching vibrations whereas symmetrical stretches are in the range 585–400  $\text{cm}^{-1}$ . The band associated with the deformation mode of the V–O<sub>b</sub> group appears at 400  $\text{cm}^{-1}$  as a medium intensity band. There are two specific bands

characteristic of protonated decavanadate anions. At 995  $\text{cm}^{-1}$  there is a sharp band which can be assigned to some V–O bonds which are shortened due to the elongation of the V–O<sub>b</sub> bonds which involve the protonated oxygen atoms the stretches of which are seen as a medium broad band at 630  $\text{cm}^{-1}$ .

**Crystal Structure Determination.**—Atomic coordinates are listed in Table 1. The crystal structure contains four crystallographically independent *n*-hexylammonium cations and two crystallographically independent centrosymmetric dihydrogendifavanadate anions (I and II).

Although, as can be seen in the literature, protonation in decavanadates always takes place at double-linked oxygen atoms, the hydrogen atoms in compound 1 are located in both anions at the triply-linked O<sub>B(n12)</sub> oxygen atom and its corresponding centrosymmetric one. We have carried out empirical bond length/bond number calculations similar to those described by Evans and Pope.<sup>3</sup> Calculations based on all the oxygen atoms for both polyanions show that for the O<sub>A</sub> type oxygen atoms, the bond number is 2.04, for the O<sub>C</sub> type oxygen atoms it is in the range 1.71–1.91 and for the O<sub>B(n12)</sub> oxygen atoms they are 1.39 (I) and 1.40 (II), respectively (Table 2). These calculations were made prior to allowance for any O···H interactions. Table 2 also lists the bond number for all the oxygen atoms considering the contribution of the adjacent hydrogen atoms from O···H–N (ref. 21) and O···H–O (ref. 22) interactions.

Typical structures for decavanadate anions consist of 10 vanadium atoms and 28 oxygen atoms arranged in a highly condensed system of ten VO<sub>6</sub> octahedra sharing corners and edges. It can be described as a section of cubic close-packed oxygen atoms with vanadium atoms in the octahedral holes.

**Table 3** Distance (Å) from the respective ring plane of the oxygen and vanadium atoms

Atom	(1)/I	(1)/II	(2)	(3)	Atom	(1)/I	(1)/II	(2)	(3)
O <sub>G</sub> (n2)	-0.004	0.032	-0.037	0.020	O <sub>G</sub> (n2)	0.782	0.814	-0.887	-0.941
O <sub>G</sub> (n4')	0.050	-0.003	-0.010	-0.083	O <sub>G</sub> (n4')	0.804	0.798	-0.901	-0.991
O <sub>C</sub> (n6)	-0.038	-0.050	0.041	-0.021	O <sub>C</sub> (n6)	0.865	0.827	-0.824	-0.963
O <sub>C</sub> (n13)	-0.113	-0.092	0.076	-0.073	O <sub>C</sub> (n13)	0.753	0.795	-0.825	-0.824
O <sub>C</sub> (n11')	-0.037	-0.006	0.040	0.004	O <sub>C</sub> (n11')	0.804	0.905	-0.899	-0.844
O <sub>F</sub> (n1)	0.019	0.009	-0.036	-0.024	O <sub>F</sub> (n1)	1.036	0.976	-0.912	-0.955
O <sub>E</sub> (n9)	0.041	0.003	0.031	-0.037	O <sub>E</sub> (n9)	1.024	0.988	-0.883	-0.920
O <sub>E</sub> (n5)	-0.012	0.010	-0.038	0.021	O <sub>E</sub> (n5)	0.937	1.009	-0.989	-0.814
O <sub>F</sub> (n3')	0.006	-0.007	-0.016	-0.032	O <sub>F</sub> (n3')	0.930	1.013	-1.006	-0.816
V(n1)	-0.962	-0.951	0.886	0.934	V(n1)	0.006	-0.004	0.004	0.013
V(n2)	-0.857	-0.832	0.860	1.004	V(n2)	-0.011	0.007	-0.007	0.064
V(n3')	-0.915	-0.983	0.963	0.891	V(n3')	-0.006	0.004	-0.003	0.076
V(n4')	-0.799	-0.867	0.915	0.818	V(n4')	0.011	-0.007	0.006	0.068
V(n5)	-0.755	-0.780	0.831	0.784	V(n5)	0.184	0.182	-0.095	0.085
O <sub>G</sub> (n2')	0.045	0.011	-0.017	-0.082	O <sub>G</sub> (n2')	1.011	0.961	-0.939	-0.958
O <sub>G</sub> (n4)	-0.022	0.040	-0.028	0.008	O <sub>G</sub> (n4)	0.955	0.981	-0.937	-0.867
O <sub>C</sub> (n8)	-0.041	-0.044	0.040	0.024	O <sub>C</sub> (n8)	0.880	0.854	-0.865	-0.834
O <sub>C</sub> (n12)	-0.065	-0.080	0.086	0.069	O <sub>C</sub> (n12)	0.849	0.826	-0.831	-0.795
O <sub>C</sub> (n10')	-0.014	-0.034	0.034	0.004	O <sub>C</sub> (n10')	0.889	0.878	-0.894	-0.861
O <sub>F</sub> (n1)	0.081	0.077	-0.045	-0.086	O <sub>F</sub> (n1)	0.950	0.932	-0.945	-0.938
O <sub>E</sub> (n9)	0.016	-0.053	0.019	-0.011	O <sub>E</sub> (n9)	0.875	0.808	-0.893	-0.864
O <sub>E</sub> (n5)	-0.090	0.010	-0.007	0.024	O <sub>E</sub> (n5)	0.760	0.880	-0.931	-0.830
O <sub>F</sub> (n3')	0.069	0.043	-0.030	-0.038	O <sub>F</sub> (n3')	0.911	0.920	-0.967	-0.893
V(n1)	-0.880	-0.874	0.910	0.832	V(n1)	0.003	-0.005	0.006	-0.023
V(n2')	-0.929	-0.936	0.935	0.781	V(n2')	0.005	-0.008	0.012	-0.088
V(n3')	-0.865	-0.883	0.925	0.917	V(n3')	-0.003	0.004	-0.009	0.059
V(n4)	-0.951	-0.912	0.900	0.952	V(n4)	-0.005	0.008	-0.006	0.083
V(n5)	-0.908	-0.914	0.831	0.824	V(n5)	-0.040	-0.040	-0.087	-0.032

Fig. 1 shows the corner and edge-sharing octahedra of the decavanadate anion with atom labelling. As it has been pointed out previously, oxygen site B is located on a close-packed nine-atom plane. The plane in which O<sub>B</sub>(n13) oxygen atom is placed consists of the following nine oxygen atoms: O<sub>G</sub>(n2), O<sub>G</sub>(n4'), O<sub>C</sub>(n6), O<sub>B</sub>(n13), O<sub>C</sub>(n11'), O<sub>F</sub>(n1), O<sub>E</sub>(n9), O<sub>E</sub>(n5) and O<sub>F</sub>(n3') while the O<sub>B</sub>(n12) plane comprised O<sub>G</sub>(n2'), O<sub>G</sub>(n4), O<sub>C</sub>(n8), O<sub>B</sub>(n12), O<sub>C</sub>(n10'), O<sub>F</sub>(n1), O<sub>E</sub>(n9), O<sub>E</sub>(n5) and O<sub>F</sub>(n3') oxygen atoms. These planes have been evaluated for **1** and for the corresponding unprotonated decavanadate salt, **2**, in order to study the deviation of planarity in both the protonated and the unprotonated state. Table 3 indicates the location of the oxygen atoms and five vanadium atoms from the respective planes in compounds **1** and **2**. These vanadium atoms are lying on a plane parallel to the nine-oxygen atom ones, occupying the octahedral holes just behind them. It is noteworthy that in the unprotonated anion the longest distances are those involving the triply-linked oxygen atoms, and the rest of the atoms form a perfect plane. For the protonated anions a distortion effect can be observed in the nine-atom array plane involving the protonated oxygen atom O(n12). This triply linked oxygen atom involved in the protonation lies closer to the plane which in turn is distorted from planarity. It is important to notice the effect created in the location of the vanadium atoms. Whenever a triply-linked oxygen atom is not protonated the corresponding five-vanadium atoms plane behind it has the V(5) atom located out of the plane (Table 3). However if protonation takes place in a triply-linked oxygen atom, the V(5) vanadium gets closer to the plane and it attains planarity. *tert*-Butylammonium dihydrogendifcavanadate(v) **3**<sup>23</sup> has been studied in order to observe the effect when protonation takes place in an O<sub>C</sub> type doubly linked oxygen atom (Table 3).

In the two crystallographically independent anions of **1** there are two oxygen atoms which lie within the [V<sub>10</sub>O<sub>28</sub>]<sup>6-</sup> group each of which link six weak O-V bonds; four oxygen atoms on the surface co-ordinated to three vanadium atoms each; fourteen oxygen atoms co-ordinated to two vanadium atoms and eight oxygen atoms lie on the outer corners and co-ordinate to only one vanadium atom. The V-O bond distances can be

classified in three different groups: short 1.57(1)–1.61(1) (I), 1.59(2)–1.70(1) Å (II); medium, 1.72(1)–2.10(1) (I), 1.75(1)–2.11(1) Å (II) and long, 2.10(1)–2.35(1) (I), 2.13(1)–2.40(1) Å (II). Each octahedron has a short distance to a terminal oxygen atom, four medium distances and one long distance with the six-co-ordinate vanadium atom. The two octahedra situated in the centre of the [V<sub>10</sub>O<sub>28</sub>]<sup>6-</sup> group show two short distances, three medium ones and only one long one which is smaller than the other long distances. Table 4 lists V-O bond distances for the unprotonated decavanadate anion<sup>9</sup> and the two crystallographically independent dihydrogendifcavanadate anions.

It is noteworthy that the V-O distances for the triply-linked oxygen atoms, O(112) and O(212) are in the range 2.05(1)–2.11(1) Å. A clear lengthening of these V-O(n12) distances can be seen in the diprotonated anion, the average V-O(n12) distances in the unprotonated anion being 1.987(6) Å. In accordance with earlier findings concerning these protonated bonding distances,<sup>5</sup> bonds between vanadium and protonated oxygen atoms are significantly longer than bonds between vanadium and unprotonated oxygen atoms. The lengthening of these bonding distances causes a shortening of the respective *trans* bonds.

The distinguishing feature of compound **1** is its extensive hydrogen bond network among anions and cations. Dihydrogendifcavanadate anions are located at *z* = 0 [symmetry centres (0, 1/2, 0) and (1/2, 0, 0)]. The *n*-hexylammonium cations occupy the space among these anion levels with the nitrogen atoms forming hydrogen bonds with the oxygen atoms of the polyanions giving a sequence ... accacc ... (a = anion, c = cation). The hydrogen-bonding interactions between anions in the same *z* level and among cations and anions together with the electrostatic interactions stabilize the structure. The hydrogen contacts distances N-H...O are in the range 2.74(2)–3.32(2) Å (Table 5). In the structure there also are some relatively short C-H...O hydrogen contacts; such contacts are common in this class of compounds, but in our case, only some of them can be evaluated due to the high thermal motion of the carbon atoms, whose atomic coordinates were fixed. The C-H...O contacts indicate some degree of polarization and the role of

**Table 4** Bond distances (Å) in the two crystallographically independent dihydrogendifcavanadate anions and in the unprotonated  $[V_{10}O_{28}]^{6-}$ 

	$[H_2V_{10}O_{28}]^{4-}$ (I) $n = 1$	$[H_2V_{10}O_{28}]^{4-}$ (II) $n = 2$	$[V_{10}O_{28}]^{6-}$
V(n1)–O(n1)	1.62(2)	1.62(1)	1.589(6)
V(n1)–O(n6)	1.93(1)	1.93(2)	1.856(5)
V(n1)–O(n7)	1.80(2)	1.84(1)	1.852(6)
V(n1)–O(n8)	1.79(1)	1.88(2)	1.901(6)
V(n1)–O(n9)	2.09(2)	2.02(1)	2.021(6)
V(n1)–O(n14)	2.30(1)	2.40(1)	2.374(5)
V(n2)–O(n2)	1.61(1)	1.59(2)	1.620(5)
V(n2)–O(n6)	1.75(1)	1.77(1)	1.787(5)
V(n2)–O(n10)	1.81(2)	1.84(1)	1.840(5)
V(n2)–O(n12)*	2.08(1)	2.08(1)	2.036(5)
V(n2)–O(n13)	1.98(1)	1.96(1)	1.966(5)
V(n2)–O(n14)	2.24(1)	2.30(1)	2.235(4)
V(n3)–O(n3)	1.59(1)	1.59(1)	1.620(6)
V(n3)–O(n7)	1.84(1)	1.83(1)	1.805(5)
V(n3)–O(n10)	1.85(1)	1.80(2)	1.859(5)
V(n3)–O(n5')	2.03(1)	2.07(1)	2.105(6)
V(n3)–O(n11)	1.95(1)	1.99(2)	1.893(5)
V(n3)–O(n14)	2.35(1)	2.30(1)	2.300(5)
V(n4)–O(n4)	1.57(1)	1.59(2)	1.612(5)
V(n4)–O(n8)	1.84(1)	1.75(1)	1.824(5)
V(n4)–O(n11)	1.72(1)	1.75(1)	1.831(5)
V(n4)–O(n13')	1.98(1)	2.02(1)	2.018(5)
V(n4)–O(n12)	2.10(1)	2.11(1)	1.993(5)
V(n4)–O(n14)	2.31(1)	2.27(1)	2.250(5)
V(n5)–O(n5)	1.64(1)	1.70(1)	1.682(5)
V(n5)–O(n9)	1.69(1)	1.72(1)	1.692(5)
V(n5)–O(n13)	1.84(1)	1.87(1)	1.932(4)
V(n5)–O(n14')	2.09(1)	2.02(1)	2.082(5)
V(n5)–O(n12)	2.07(1)	2.05(1)	1.933(4)
V(n5)–O(n14)	2.09(1)	2.13(1)	2.141(5)

\* Centrosymmetric atoms: symmetry code for primed atoms  $-x + 1, -y, -z$  (for  $n = 1$ );  $-x + 2, -y + 1, -z$  (for  $n = 2$ ).

**Table 5** Hydrogen contacts

Contact type	X–H	X...O	H...O	$\angle X\text{--H}\cdots O$
N(11)–H(111)…O(16 <sup>l</sup> )	0.98	2.76(2)	1.80	165.3
N(11)–H(112)…O(210 <sup>ll</sup> )	1.00	2.81(2)	1.82	167.4
N(11)–H(113)…O(110)	1.01	2.75(2)	1.85	147.0
N(21)–H(211)…O(19 <sup>iii</sup> )	1.00	2.95(2)	1.96	167.8
N(21)–H(212)…O(23 <sup>ii</sup> )	0.99	3.31(2)	2.60	128.2
N(21)–H(212)…O(27 <sup>ii</sup> )	0.99	2.85(2)	1.89	159.4
N(21)–H(213)…O(24 <sup>iv</sup> )	1.00	2.86(2)	1.87	166.7
N(31)–H(311)…O(211 <sup>iv</sup> )	1.00	2.74(2)	1.73	175.3
N(31)–H(312)…O(28 <sup>l</sup> )	0.99	2.78(2)	1.81	166.8
N(31)–H(313)…O(18 <sup>v</sup> )	1.01	2.77(2)	1.79	161.3
N(41)–H(411)…O(25)	0.98	2.89(2)	1.93	166.6
N(41)–H(412)…O(11 <sup>l</sup> )	1.00	3.32(2)	2.53	135.9
N(41)–H(412)…O(17 <sup>l</sup> )	1.00	2.90(2)	1.99	151.1
N(41)–H(413)…O(12)	1.00	2.84(2)	1.85	166.4
O(112)–H(1)…O(23 <sup>vi</sup> )	1.10	2.64(2)	1.71	138.2
O(212)–H(2)…O(11 <sup>l</sup> )	1.01	2.63(2)	1.78	140.5
C(13)–H(131)…O(22 <sup>ii</sup> )	1.01	3.36(6)	2.52	165.9
C(17)–H(172)…O(111 <sup>vii</sup> )	1.01	3.44(1)	2.45	167.5
C(22)–H(221)…O(22 <sup>viii</sup> )	0.98	3.18(5)	2.45	130.2
C(33)–H(332)…O(24 <sup>iv</sup> )	1.07	3.48(5)	2.55	145.3
C(42)–H(421)…O(14 <sup>iii</sup> )	1.01	3.23(3)	2.46	132.0
C(43)–H(431)…O(29)	1.07	3.42(5)	2.57	135.7
C(44)–H(441)…O(17 <sup>l</sup> )	1.05	3.40(7)	2.42	155.3
C(44)–H(442)…O(29)	1.05	3.47(5)	2.73	126.9

Symmetry operations: I  $2 - x, -y, -z$ ; II  $-x, 1 - y, -z$ ; III  $1 - x, -y, -z$ ; IV  $x - 1, y, z$ ; V  $x, 1 + y, z$ ; VI  $x - 1, y - 1, z$ ; VII  $x + 1, y, z$ ; VIII  $-x + 1, -y + 1, -z$ .

this type of interactions in a series of compounds has also been examined in the literature.<sup>24,25</sup>

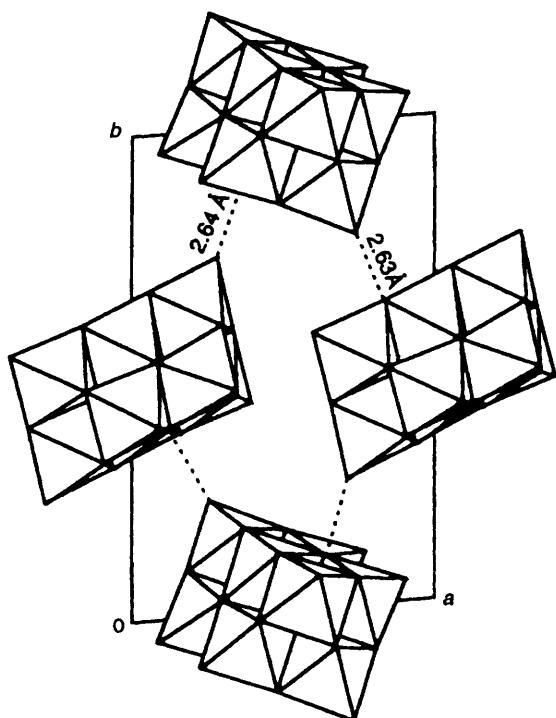
The crystal packing of the structure is also an important feature in locating the protonation sites in these dihydrogendifcavanadate anions (Fig. 2). The closest-approach distances that are suitably oriented to permit hydrogen contacts between the

dihydrogendifcavanadate(v) anions are (i) between the protonated triply-linked, O<sub>B</sub> type oxygen atom O(112) from anion I and the terminal oxygen atom O(23) from anion II, O...O 2.64(2) Å; (ii) between the triply-linked oxygen atom O(212) from anion II and the terminal oxygen atom O(11) from anion I, O...O 2.63(2) Å. These hydrogen bondings connect

**Table 6** Steps, initial and final temperature (°C), partial and total weight loss, enthalpy (endothermic or exothermic) and maximum peak for each step in the thermal decomposition of compounds **1** and **2**

Ar + O <sub>2</sub>				Ar			
Step	T <sub>i</sub> –T <sub>f</sub>	T <sub>m</sub>	%Δm	Step	T <sub>i</sub> –T <sub>f</sub>	T <sub>m</sub>	%Δm
<b>1</b>							
1	180–210	184(–)	14.65	1	180–220	190(–)	9.45
2	210–320		3.12	2	220–320	180(–)	14.65
3	320–420	390(+)	9.49	3	320–420	380(–)	7.10
			34.47 (33.49)*	4	420–600		39.06
<b>2</b>							
1	70–115	104(–)	2.32	1	85–120	115(–)	2.28
2	130–190	180(+)	14.51	2	135–220	140(+)	14.65
3	190–270	241(+)	9.31	3	220–310	225(+)	7.10
4	370–425	418(+)	9.79	4	310–600		
5	425–500		43.06 (43.36)*				48.06

\* Theoretical V<sub>2</sub>O<sub>5</sub> mass percent.



**Fig. 2** View on the (001) plane of the two crystallographically independent dihydrogendifcavanadate(V) anions. Hydrogen contacts between polyanions are represented by dotted lines

polyanions lying in the same *z* level and according to Gilli *et al.*,<sup>26</sup> this type of hydrogen bonding is strong,  $2.50 \leq d(\text{O} \cdots \text{O}) \leq 2.65 \text{ \AA}$ .

**Thermal Analysis.**—Table 6 lists thermoanalytical data for compounds **1** and **2** in an argon and argon–oxygen atmosphere.

Thermal decomposition of **1** in an argon–oxygen atmosphere starts at 180 °C. As can be seen in Table 6, the unprotonated decavanadate salt due to its hydrated state shows less stability and initial decomposition occurs at 70 °C. It is well known that the presence of water molecules leads to lower stability in polyanion salts, but it is interesting to compare the stability of the corresponding anhydrous salts. In compound **2** the endothermic step ceases at 115 °C and the anhydrous

compound is stable up to 130 °C. It is important to notice that compound **1** is more stable than the anhydrous unprotonated decavanadate. This same effect is observed if we study the thermoanalytical data in the decomposition processes of other organoammonium salts.<sup>27</sup> The unprotonated and diprotonated decavanadate anhydrous pyridinium salts start their decomposition processes at 92 and 182 °C respectively, *i.e.* the diprotonated decavanadate salt is more stable. In the 4-methylpyridinium salts the same effect is observed. The thermal decomposition of the anhydrous decavanadate salt of 4-methylpyridinium starts at 129 °C and for the dihydrogen-decavanadate salt, after the corresponding dehydration step between 129 and 153 °C, the anhydrous compound is stable up to 161 °C. If we compare anhydrous protonated and unprotonated decavanadate salts a clear effect of increasing stability can be observed as protonation takes place. Additionally a smaller number of organic cations and the presence of anion–anion interactions *via* hydrogen bonding imply an increase in the thermal stability of polyanion salts.

In order to study possible differences in the thermal behaviour of the alkylammonium decavanadates the thermal decomposition in argon as an inert atmosphere was performed; no difference in the thermal stability of compound **1** was observed but for compound **2**<sup>16</sup> the dehydration step was shifted to higher temperature. The thermal decomposition was not complete until 600 °C. The final solid product was identified as a mixture of vanadium-(III) and -(IV) oxides.

#### Acknowledgements

We thank Iberdrola, S. A. and Universidad del País Vasco/Euskal Herriko Unibertsitatea (Grant No. 169.310-EA004/93) for financial support. We also thank the referees for their valuable comments.

#### References

- 1 H. T. Evans, *Inorg. Chem.*, 1966, **5**, 967.
- 2 W. G. Klemperer and W. Shum, *J. Am. Chem. Soc.*, 1977, **99**, 3544.
- 3 H. T. Evans and M. T. Pope, *Inorg. Chem.*, 1984, **23**, 501.
- 4 V. W. Day, W. G. Klemperer and D. J. Maltbie, *J. Am. Chem. Soc.*, 1987, **109**, 2991.
- 5 M. V. Capparelli, D. M. L. Goodgame, P. B. Hayman and A. C. Skapski, *J. Chem. Soc., Chem. Commun.*, 1986, 776.
- 6 M. I. Khan, J. Zubietta and P. Toscano, *Inorg. Chim. Acta*, 1992, **193**, 17.

7 J.-Y. Kempf, M.-M. Rohmer, J. M. Poblet, C. Bo and M. Bénard, *J. Am. Chem. Soc.*, 1992, **114**, 1136.

8 T. Debaerdemeker, J. M. Arrieta and J. M. Amigó, *Acta Crystallogr., Sect. B*, 1982, **38**, 2465.

9 P. Román, A. Aranzabe, A. Luque and J. M. Gutiérrez-Zorrilla, *Mater. Res. Bull.*, 1991, **26**, 731.

10 D. T. Cromer, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, p. 72.

11 M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna and D. Viterbo, *J. Appl. Crystallogr.*, 1989, **22**, 389.

12 M. Martínez-Ripoll and F. H. Cano, Programa PESOS, Instituto Rocasolano, CSIC, Madrid, 1975.

13 J. M. Stewart, P. A. Machin, C. W. Dickinson, H. L. Ammon, H. Heck and H. Flack, The XRAY 76 System, Technical report TR-446, Computer Science Center, University of Maryland, College Park, MD, 1976.

14 P. Román, A. Aranzabe, A. Luque and J. M. Gutiérrez-Zorrilla, *Mater. Res. Bull.*, 1991, **26**, 19.

15 P. Román, R. Macías, A. Luque and J. M. Gutiérrez-Zorrilla, *Mater. Res. Bull.*, 1992, **27**, 573.

16 P. Román, A. Aranzabe and A. Luque, *Thermochim. Acta*, 1992, **206**, 61.

17 P. Román, R. Macías, A. Luque and C. Guzmán-Miralles, *Thermochim. Acta*, 1992, **209**, 135.

18 P. Román, R. Macías, A. Luque and C. Guzmán-Miralles, *Thermochim. Acta*, 1992, **209**, 189.

19 P. Román, A. San José, A. Luque and J. M. Gutiérrez-Zorrilla, *Inorg. Chem.*, 1993, **32**, 775.

20 M. I. Khan, Q. Chen, D. P. Goshorn and J. Zubietta, *Inorg. Chem.*, 1993, **32**, 672.

21 G. Donnay and R. Allmann, *Am. Miner.*, 1970, **55**, 1003.

22 I. D. Brown, *Chem. Soc. Rev.*, 1978, **7**, 359.

23 A. San José, personal communication, 1994.

24 R. Taylor and O. Kennard, *J. Am. Chem. Soc.*, 1982, **104**, 117.

25 G. R. Desiraju, *Acc. Chem. Res.*, 1991, **24**, 290.

26 P. Gilli, V. Bertolasi, V. Ferretti and G. Gilli, *J. Am. Chem. Soc.*, 1994, **116**, 909.

27 J. M. Arrieta, *Polyhedron*, 1992, **11**, 3045.

Received 13th December 1994; Paper 4/07584F