4. VANADIUM

D.A. RICE

CONTENTS

INTRODUCTION

This review contains a report on the chemistry of vanadium which appeared during 1980. Certain aspects are largely excluded and these are organometallic chemistry, solid-state chemistry, kinetics and catalysis. The material is organised as in last year's review, except that this year species containing, or formally containing, oxo-anions are discussed in a separate section.

4.1 VANADIUM(V)

4.1.1 Compounds containing vanadium-halogen bonds

The solution chemistry of vanadium pentafluoride has been studied in a wide range of solvents using ^{19}F NMR spectroscopy, and VF$_5$ has been shown to be a weak F$^-$ acceptor even in VF$_5$/AgF/HF mixtures. In the presence of SbF$_5$, it acts as a weak base to give a fluxional polymer [1]. In SO$_2$ClF solution at low temperature, evidence was obtained that suggested VF$_5$ exists as a short linear polymer with *cis* fluorine bridges, the average chain having the formula [(VF$_5$)$_5$] [2]. An oxygen exchange reaction between VF$_5$ and POF$_3$ readily takes place that gives VOF$_3$ and PF$_5$, thus providing evidence for the strength of the

V=O bond. The same oxo-compound, VOF_3, is formed when VF_5 is treated with CF_3CO_2H [3].

Oxovanadium(V) species that also contain halogen atoms are of continuing interest. From the reaction of $V_2O_5/KF/H_2O_2$ mixtures at pH~4, the peroxo anion $[VF(O)(O_2)_2]^{2-}$ was obtained as its potassium salt and characterised by infrared and thermogravimetric measurements [4]. Aryl cyanide adducts of $VOCl_3$ have been the subject of single crystal X-ray studies this year. Cyanobenzene forms 1:1 and 2:1 adducts with $VOCl_3$ giving rise to five- [5] and six- coordinate [6] species respectively. The essential details of both structures are given in Figure 1, where it can be seen that there is disorder present in $[VOCl_3(NCPh)_2]$. It is noticeable that there is a marked difference between the V–N distances in the two structures. A study of the stacking faults in $[VOCl_3(NCPh)_2]$ has also been made [7].

Another $VOCl_3$ adduct whose structure has been examined is $[AsPh_4][VOCl_4]$. The anion has C_{4v} symmetry with an extremely short V–O distance of 1.551(9) Å, a V–Cl distance of 2.256(2) Å, an O–$\hat{V}$–Cl angle of 103.4° and a Cl–$\hat{V}$–Cl angle of 86.9°. The related $[AsPh_4][V(NCl)Cl_4]$ complex has been examined and in its infrared spectrum $\nu(V\equiv N)$ is at 1114 cm^{-1} with $\nu_{as}(VCl_4)$ at 373 cm^{-1}. The related bands in $[VOCl_4]^-$ occur at 970 cm^{-1} {$\nu(V=O)$} and 377 cm^{-1} [8]. Vanadium iodonitrene trichloride exists as a chlorine-bridged centrosymmetric dimer (see Fig. 2) with an I–$\hat{N}$–V angle of 163°. Triple-bond character has been assigned to the vanadium-nitrogen distance, the compound being prepared by the oxidation of VCl_4 by IN_3 [9].

A range of phosphiniminato complexes of vanadium(V), namely $[VCl_2(O)(NPPh_3)]$, $[VCl(O)(NPPh_3)_2]$ and $[VCl_3(NPPh_3)_2]$, have been made from the reaction of the appropriate halo-complex and $Me_3SiN=PPh_3$ [10]. Chloro-azides of vanadium(V) have been prepared in good yield using $SiMe_3(N_3)$ as the source of azide, and the azide products react with PPh_3 to yield phosphiniminatovanadium(V) compounds [11]. Reduction of $VOCl_3$ has been executed both photochemically, and by reaction with hydrogen atoms. Alcoholic solutions of $VOCl_3$, when irradiated in the charge-transfer region, undergo a reaction in which the vanadium is reduced stepwise to vanadium(II) with commensurate oxidation of the alcohol [12]. Infrared chemiluminescence studies of the $H/VOCl_3$ system show that HCl is formed, and from the product distribution it was suggested that a temperature of 3890±250 K was attained [13].

4.1.2 Compounds containing vanadium-oxygen bonds

The reaction of the hydrated $[V(O)_2]^+$ ion with H_2O_2 in the presence of a range of polydentate carboxylic acids {e.g. $edtaH_4$, {$(HOOC)NHCH_2$}$_2$ or $Me_2NCH_2CH_2CH_2N(COOH)_2$} yields species containing hydrated {$VO(O_2)$}$^+$ and the
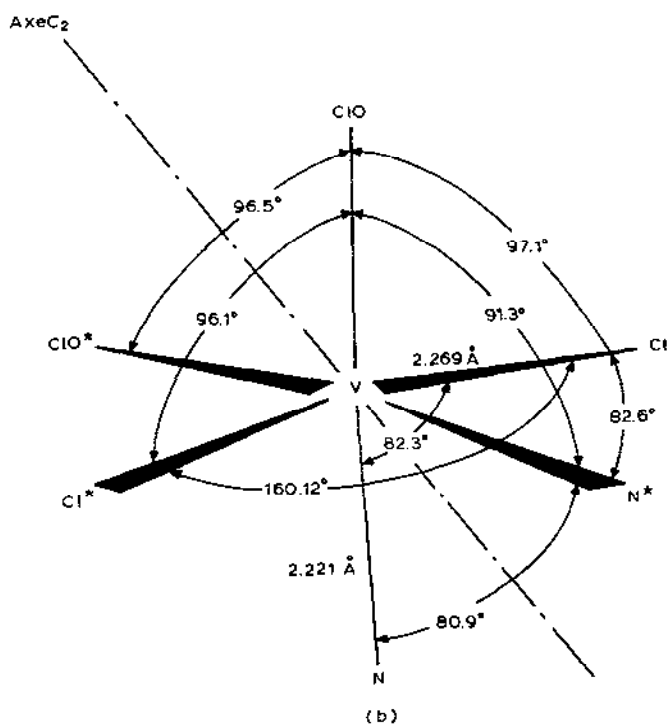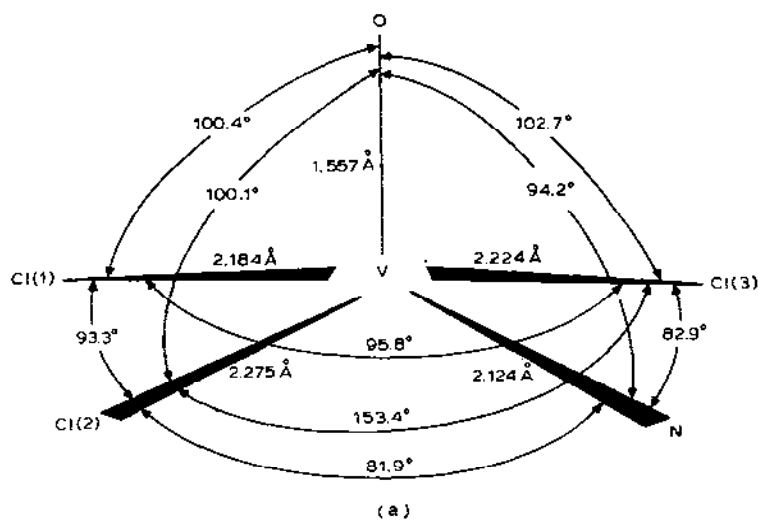
Fig. 1: Comparison of the angles and distances shown by (a) [VOCl₃(NCPh)] and (b) [VOCl₃(NCPh)₂], reproduced with permission from *Acta Crystallogr.*, *Sect. B*, 36 (1980) 312.
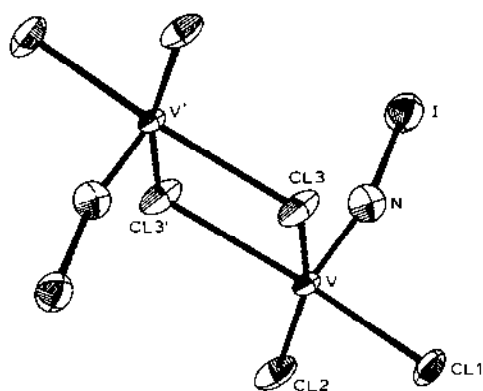
Fig. 2: A view of Cl₃VNI, reproduced with permission from Z. *Naturforsch, Teil B: Anorg. Chem. Org. Chem.*, 35 (1980) 154.

relationship of the rate expression to the nature of the acid has been evaluated [14]. In a related study on sodium vanadate(V)/hydrogen peroxide mixtures, the equilibrium constants for the formation of the red hydrated $[VO(O_2)]^+$ ion from hydrated $[V(O)_2]^+$ {$K = (3.7\pm0.4) \times 10^4$ mol dm^{-3} at 25 °C in 0.3 M Na[ClO₄]} and the yellow anion $[VO(O_2)_2]^-$ from hydrated $[VO(O_2)]^+$ {$K = 0.6\pm0.1$ mol dm^{-3} at 25 °C in 0.3 M Na[ClO₄]} have been determined. The kinetics of the reduction of these ions by aqueous iodide have been interpreted in terms of nucleophilic attack by I$^-$ on the various protonated form of the hydrated $[VO(O_2)]^+$ and $[VO(O)_2]^-$ ions [15]. A range of salts containing the $[VO(O_2)_2]^-$ moiety have been prepared, namely K$[VO(O_2)_2(H_2O)]$, K$_3$$\{VO(O_2)_2(CO_3)\}$, K$_3$$[VO(O_2)_2(C_2O_4)]$ and K$_2$$[VO(O_2)(C_2O_4)_2]$.H$_2$O, and on the basis of their infrared spectra it was suggested that the anions are monomeric with a pentagonal pyramidal or pentagonal bipyramidal structure [16].

The structure of tetraphenylphosphonium dioxo{4-(2-pyridylazo)resorcinolato}-vanadate(V) has been determined by X-ray methods (see Fig. 3). The vanadium atom has a coordination sphere consisting of two *cis* terminal oxygen atoms {$r(VO) = 1.625(2)$, 1.615(2) Å}, a phenolic oxygen atom {$r(VO) = 1.943(2)$ Å}, a pyridine nitrogen atom {$r(VN) = 2.081(2)$ Å} and one of the nitrogen atoms from the azo group {$r(VN) = 2.141(2)$ Å}. It is noticeable that coordination has caused a lengthening of the nitrogen-nitrogen distance in the azo group [17].

The dissociation in solution of the dimeric vanadium(V) compounds $[V_2O_3(L)_4]$ {L = 8-quinolinato or isopropyltropolonato} has been studied photometrically and the equilibrium constants for reaction (1) determined [18].

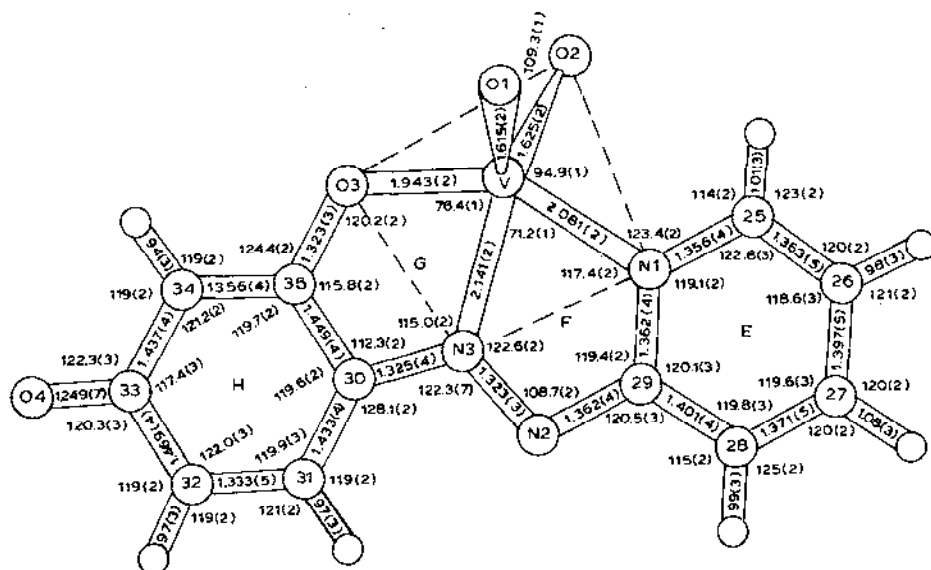$$[V_2O_3(L)_4] + H_2O \rightleftharpoons 2[V(O)_2L] + 2HL \qquad (1)$$
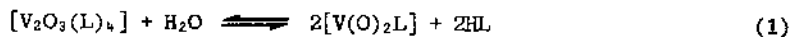
Fig. 3: A schematic diagram of the dioxo 4-(2-pyridylazo)resorcinolato)vanadate(V) anion, reproduced with permission from *Acta Crystallogr.*, *Sect. B*, 36 (1980) 2933.

Four interesting studies have reported aspects of the chemistry of $[VO(E)_3]$ (E = uninegatively charged species). The low-energy photoelectron spectrum of $[VO(NO_3)_3]$ in the gas phase has three regions (like the spectra of $[Co(NO_3)_3]$ and $[Cu(NO_3)_2]$) that are associated with the molecular orbitals of the $[NO_3]^-$ ion. The spectrum of $[VO(NO_3)_3]$ shows a closer resemblance to that of $KNO_3(g)$ than does $[Ti(NO_3)_4]$, thus indicating that the $[NO_3]^-$ molecular orbitals are less perturbed in the vanadium than in the titanium compound [19]. The oxo-compound $[VO(NPh_2)_3]$ has been synthesised from $[V(NPh_2)_3]$ by oxidation with NO in tetrahydrofuran [20], while attack by pentane-2,4-dione on $[VO(OEt)_3]$ in CCl_4 or EtOH has been studied spectrophotometrically and shown to yield $[VO(acac)_2(OEt)]$ [21]. The carboxylates $[VO(O_2CR)_3]$ (R = alkyl) are readily prepared by the reaction $VOCl_3$ with an excess of $Ag[O_2CR]$ in CH_2Cl_2, or by the depolymerisation of $\{VO_2(O_2CR)\}_n$ in $(RCO)_2O$. These carboxylates form 1:1 adducts with 2,2'-bipyridine or 1,10-phenanthroline, where the vanadium atom is six coordinate and the carboxylate groups are monodentate and take up a *meridional* configuration [22].

4.1.3 Compounds formally containing oxo-anions

In this section all the chemistry of species containing oxo-anions irrespective of the valence state of vanadium are discussed; also included are

oxo-vanadium-phosphorus, oxo-vanadium-molybdenum and oxo-vanadium-tungsten species.

The vibrational spectra of a range of metavanadates AVO_3 (A = $[NH_4]$, $[ND_4]$, K, Rb or Cs) have been measured and the results for aqueous solution measurements on KVO_3 interpreted as showing the polymeric $\{VO_3\}_n^{n-}$ ion, with C_{2v} symmetry, being present in solution [23]. The nature of the isomorphic substitution of Ca, Ba or Sr ions in the $Sr_3(VO_4)_2/M_3(VO_4)_2$ system and that of $Ca_3(VO_4)_2/Ba_3(VO_4)_2$ has been investigated, and the variation in unit cell parameters for the solid solutions examined [24]. Three solid phases in the system $Li_xV_2O_5$ ($0.1<x<1.0$) have been synthesised and characterised by X-ray measurements. Examination of the compounds in electrical cells suggest homogeneous phases exist in three regions: I, $0<x<0.1$; II, $0.35<x<0.5$ and III, $0.9<x<1.0$ [25].

Recently a stereospecific synthesis of mixed-metal polyanions has been developed and this process can be used to investigate the electronic interaction between adjacent metal atoms in a polyanion. The EPR spectra of $[\alpha,1,2-SiV_2W_{10}O_{40}]^{6-}$ and $[\alpha,1,2,3-SiV_3W_9O_{40}H]^{6-}$ in their reduced forms, namely $[\alpha-SiV^{IV}V^VW_{10}O_{40}]^{7-}$ (1) and $[\alpha-SiV^{IV}(V^V)_2W_9O_{40}H_x]^{8-x}$ (2), show that there is an interaction of the electron on the V(IV) atom with the other vanadium nuclei. For (1) a fifteen line spectrum was obtained, indicating that the electron is delocalised over the two vanadium atoms (see Figure 4), while for (2) a forty line spectrum is obtained
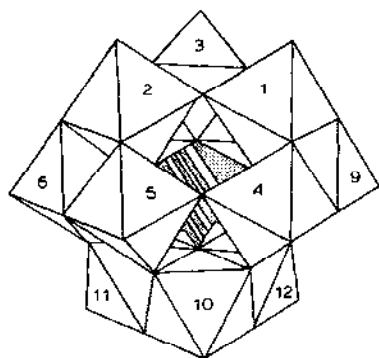
Fig. 4: A polyhedral representation of the Keggin structure with the proposed I.U.P.A.C. numbering scheme for the metal atoms, reproduced with permission from *J. Am. Chem. Soc.*, 102 (1980) 6865. Complexes $[\alpha,1,2-SiV_2W_{10}O_{40}]^{6-}$ and $[\alpha,1,2,3-SiV_3W_9O_{40}H]^{6-}$ contain vanadium atoms in sites 1 and 2 and sites 1, 2 and 3, respectively.

and this has been shown to indicate that the electron is trapped on one of the vanadium atoms, but spends 17% of its time on each of the other two [26].

A 1:14 vanadophosphate $[PV_{14}O_{42}]^{9-}$ anion has been isolated as its guanidinium

salt. It was prepared from a H_3PO_4/$NaVO_3$ mixture (molar ratio 1:4), with nitric acid being used to attain pH 2.7 in the presence of an excess of guanidinium hydrochloride. The position of the phosphorus atom can be seen from Figures 5 and 6, the central {PO_4} tetrahedron sharing its oxygen atoms with four {V_3O_{13}} groups [27].

Fig. 5: The polyhedral model of the $[PV_{14}O_{42}]^{9-}$ anion, reproduced with permission from *J. Am. Chem. Soc.*, 102 (1980) 6571.

Two heteropolyanions in which there are central {VO_4} tetrahedra are $[Mo_8V_5O_{40}]^{7-}$ and $[(V_2Mo_{10})VO_{40}]^{6-}$. Both these species have been the subject of single crystal X-ray studies and their structure are represented in Figures 7 and 8. From Figure 7 it can be seen that in $[Mo_8V_5O_{40}]^{7-}$ (which is not a Keggin
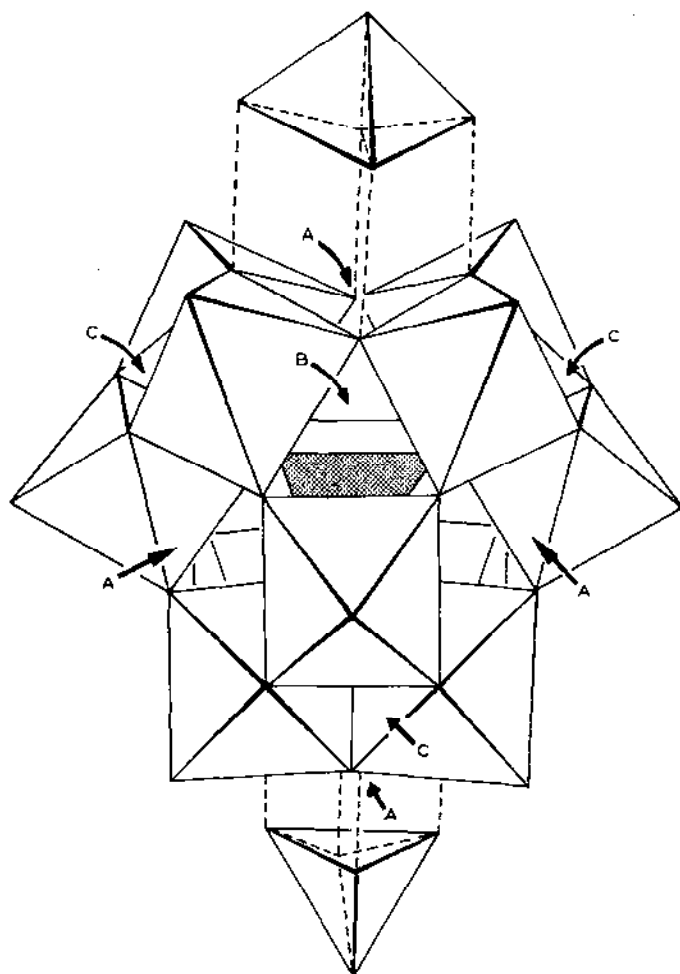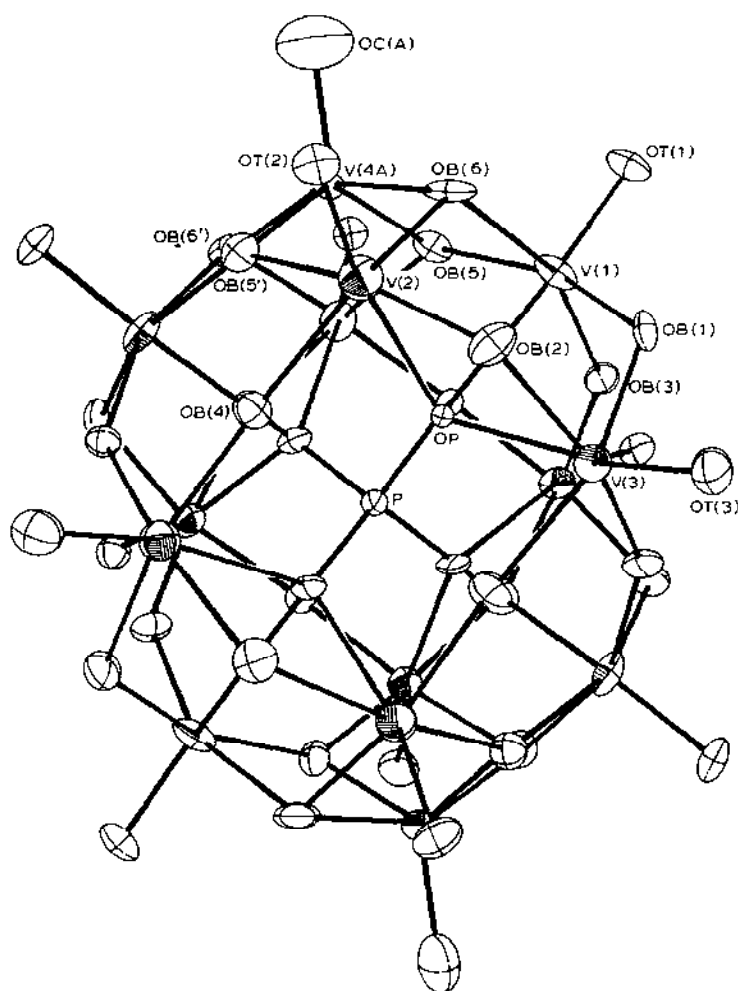
Fig. 6: The geometry of the $[PV_{14}O_{42}]^{9-}$ anion, reproduced with permission from *J. Am. Chem. Soc.*, 102 (1980) 6571.

structure), besides the unique {VO$_4$} tetrahedron, there are present four {VO$_5$} square pyramids and eight {MoO$_6$} octahedra [28]. Two of the vanadium atoms and the ten molybdenum atoms are randomly distributed over twelve sites in the $[(V_2Mo_{10})VO_{40}]^{6-}$ anion: the EPR results suggest that it is a one electron heteropoly blue, best formulated as $[(V^{IV}V^VMo^{VI}_{10})V^VO_{40}]^{6-}$ [29].

Dodecavanadophosphoric acid was obtained as a violet-red solid by evaporation of the aqueous solution in which it had been formed through a cation-exchange process using $Li_2H_5(PV_{12}O_{36})$. The acid was examined by titrimetric and infrared methods [30]. A vanadium(III) cyclotetraphosphate was isolated by a

Fig. 7: A representation of the $[Mo_8V_5O_{40}]^{7-}$ anion, reproduced with permission from *Acta Crystallogr. Sect. B*, 36 (1980) 1533.

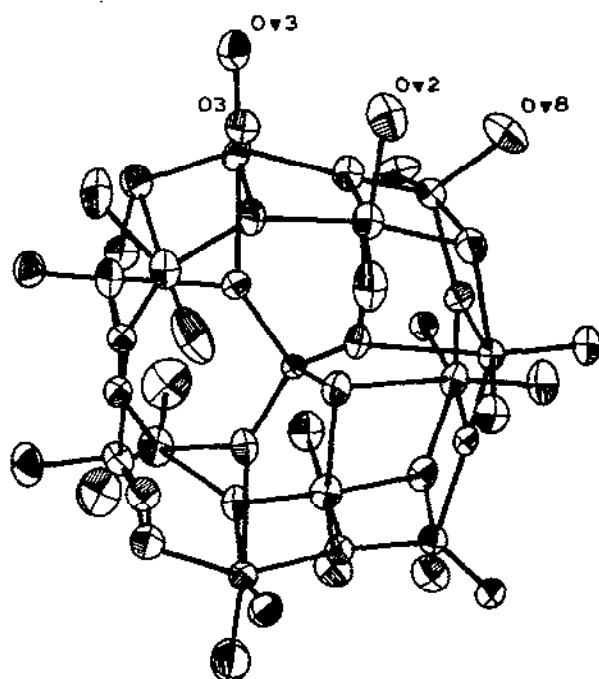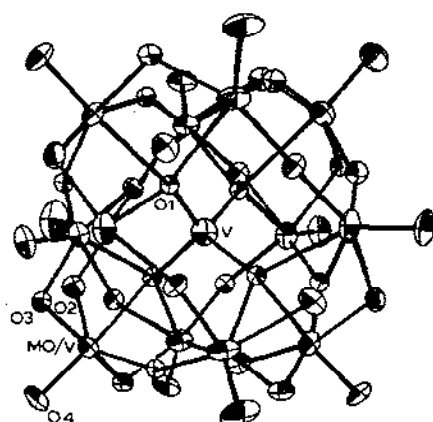Fig. 8: A representation of the $[(V_2Mo_{10})VO_{40}]^{6-}$ anion, reproduced with permission from *Acta Crystallogr. Sect. B*, 36 (1980) 1020.

condensation reaction involving H_3PO_4/V_2O_5 (with a 6:1 P:V ratio): the crystalline product contains the cyclic $[P_4O_{12}]^{4-}$ anion [31]. The species $V_2(HPO_3)_3.7H_2O$ has been prepared from the reaction of $V(ClO_4)_3$ with ammonium phosphite. The EPR spectrum of the product shows hyperfine splitting arising from the electron's interaction with the ^{51}V nucleus. Attack of phosphorus acid on $V(O_2CMe)_3$ yields $VH_3P_2O_6$ [32]. Related to the above compounds is $V(H_2PO_3)_3$, which is obtainable by the reduction of V_2O_5 powder in molten H_3PO_3 at 200 $^\circ$C [33], and the same research group have prepared $V(PO_4)$ by the thermal decomposition under inert gas of $[NH_4]_2(VO)_2(HPO_4)_2(C_2O_4).5H_2O$ or by the reduction of $(VO)_2P_2O_7$ with SO_2 at 100 $^\circ$C: the product is isostructural with β-$CrPO_4$ [34]. French workers prepared $V(PO_4)$ by the reduction of $VOPO_4$ in a N_2/H_2 mixture at 750 $^\circ$C, a process that can be reversed by heating the product in dioxygen [35]. Both groups who have prepared $V(PO_4)$ assign to it the same space group and unit cell parameters [34,35].

The structure of $InVO_4$ consists of a cation chain of $\{InO_6\}$-*pseudo*-octahedra linked by $\{VO_4\}$ tetrahedra to give a complex network structure (Figure 9). The

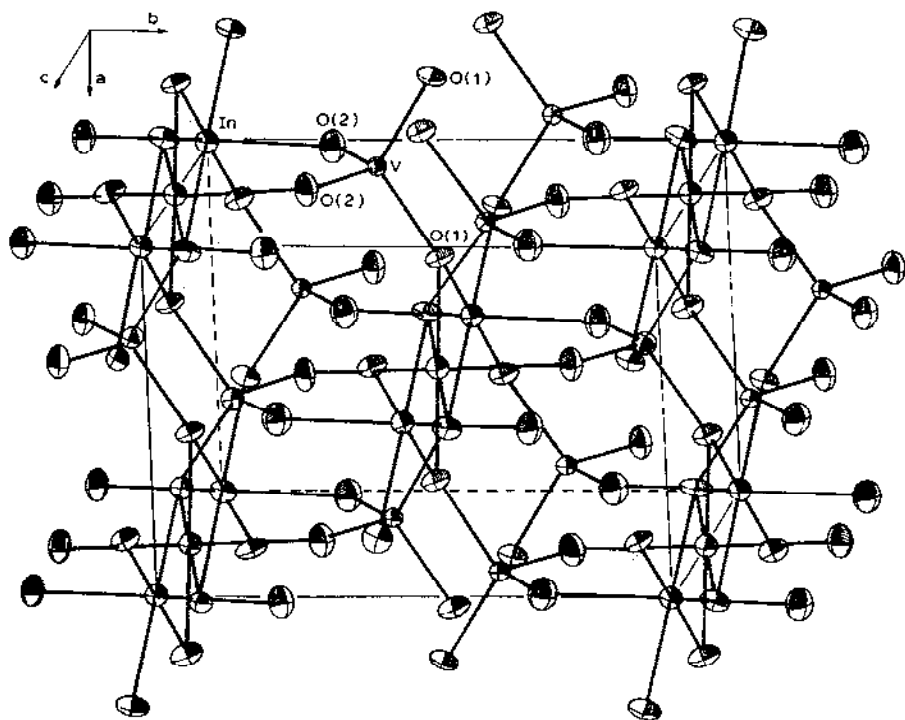Fig. 9: A view of the lattice structure of $InVO_4$, reproduced with permission from *Acta Crystallogr. Sect. B*, 36 (1980) 243.

In-O bonds are (within experimental error) all equivalent (2.160 Å), but in the {InO$_6$} fragment not all angles (subtended at In) between adjacent oxygen atoms are 90°. The {VO$_4$} moiety contains two V-O distances of 1.662 and 1.791 Å [36]. The mixed V(III)/V(II) compound BaV$_{10}$O$_{15}$, which was prepared by the reduction of BaO/V$_2$O$_5$ mixtures with dihydrogen at high temperatures, has an interesting structure in which the vanadium atoms are octahedrally coordinated and there is a cuboctahedron of oxygen atoms around the barium ions [37].

4.2 VANADIUM(IV)

4.2.1 Compounds containing vanadium-halogen bonds

The coordination of the fluoride ion to VOF$_2$ has been shown to lead to the formation of [VOF$_4$]$^{2-}$ [38,39], and [VOF$_5$]$^{3-}$ [40]. The guanidinium salt of [VOF$_5$]$^{3-}$ is isostructural with [C(NH$_2$)$_3$]$_3$[MnF$_6$] which has a NaCl type structure [40]. Structural studies on [NH$_4$]$_2$[VOF$_4$] have revealed that the vanadium atom is octahedrally coordinated by five fluorine atoms {r(V-F) = 1.910 to 2.224 Å} and one oxygen atom {r(V-O) = 1.612 Å}. The anions form an infinite chain being linked by cis fluorine atoms [38].

Structural studies on liquid VCl$_4$ using neutron diffraction have been made [41] and the complexes it forms with PEt$_3$ and benzofuroxane studied [42]. The EPR spectrum of [VCl$_4$(PEt$_3$)$_2$] shows hyperfine structure due to the interaction of the electron with the ^{51}V nucleus, and superhyperfine splitting caused by the two ^{31}P atoms was noted. For [VCl$_4$(PEt$_3$)$_2$], $g_\perp > g_{||}$, while for the related niobium(IV) and tantalum(IV) species the situation was reversed [42]. EPR and vibrational spectroscopic measurements on the bis(benzofuroxane) adduct of VCl$_4$ indicate a trans disposition is adopted by the ligands, and that coordination is through the oxygen atom of the NO group [43].

Dichloro(oxo)vanadium(IV) forms a bis(triphenylphosphine) adduct in which the vanadium atom is five-coordinate, and 0.55 Å above the plane formed by the two oxygen atoms (from the ligand molecules) and the two chlorine atoms [44a]. The two chlorine atoms were shown to be trans in the base of the square pyramid thus confirming [44a] the assignment of a structure to [VOCl$_2$(OPPh$_3$)$_2$] on the evidence of vibrational spectroscopy [44b]. This species has also been the subject of polarised electronic absorption spectroscopic studies, as have [VOCl$_2$(tmtu)$_2$], [VOCl$_2$(hmpa)$_2$], K$_3$[VO(CN)$_5$], [NH$_4$]$_3$[VOF$_5$] and [NMe$_4$][VO(NCS)$_4$(OH$_2$)], while single crystal studies were made on [VOX$_2$(tmu)$_2$] (X = Cl or Br), [NEt$_4$]$_2$[VOCl$_4$] and [AsPh$_4$][VO(NCS)$_2$]. For all the five coordinate complexes, all of the expected d-d type transitions occur below 30000 cm^{-1} {3d$^*_{xy}$ → (3d$^*_{xz}$,3d$^*_{yz}$) in the range 12800 to 15100 cm^{-1}; 3d$^*_{xy}$ → 3d$^*_{z}$ in the range 21000 to 22600 cm^{-1}; 3d$^*_{xy}$ → 3d$^*_{x^2y^2}$ varies with changes in the in-plane ligands}. For the six

coordinate complexes, the first two bands occur below 30000 cm^{-1} [45]. By the reaction of $[VO(acac_2en)]$ $(acac_2enH_2$ = Schiff's base from pentane-2,4-dione and 1,2-diaminoethane) or $[VO(tropolonate)_2]$ with an excess of $SOCl_2$, dichloro species are obtained of the type $[VCl_2(acac_2en)]$ or $[VCl_2(tropolonate)_2]$. The EPR spectra indicate a $d_{x^2-y^2}$ ground state for $[VCl_2(acac_2en)]$ and a d_{z^2} ground state for $[VX_2(tropolonate)_2]$ (X = Cl or Br). The change in ground state for the tropolonates is believed to be caused by the presence of the five membered V-O-C-C-O rings which cause distortions [46].

4.2.2 Compounds containing the $\{VO\}^{2+}$ or $\{VS\}^{2+}$ fragment

Compounds containing the $\{VO\}^{2+}$ moiety and also halogen atoms are covered in the previous section.

Two single crystal X-ray studies on hydrates of $VOSO_4$ have shown that in both $\{VO_6\}$ octahedra exist. In this hexahydrate, the asymmetric unit contains one free molecule of water, an isolated $\{SO_4\}^{2-}$ and a $\{VO_6\}$ octahedron $\{r(V=O) = 1.586(2)$ Å; $r(V-O)_{trans\ to\ V=O} = 2.160(2)$ Å; the remaining $r(V-O)$ distances = 2.004(2) to 2.029(2) Å} [47]. The β form of the pentahydrate has $r(V=O) = 1.591(5)$ Å, $r(V-O)_{trans\ to\ V=O} = 2.218(5)$ Å, with the remaining V-O distances spanning the range 2.018(4) to 2.031(3) Å [48].

Well resolved triplet-state EPR spectra have been obtained for $[NEt_4]_4[(VO)_2\{(+)-C_4H_2O_6\}\{(-)-C_4H_2O_6\}].8H_2O$. Single crystal X-ray studies on this material have shown it to possess a dimeric structure and thus to exist as a binuclear tetra-negative centrosymmetric anion with a vanadium-vanadium distance of 3.985(1) Å. The bond lengths in the anions do not vary significantly from those reported previously for the related sodium salt. The essential features of the anion are given in Figure 10 [49].

The optical absorption spectra of $\{VO\}^{2+}$ in a $K_2C_2O_4.H_2O$ matrix at 77 K show a vibronic progression with a step of 755 cm^{-1} on the 15384 cm^{-1} d-d band. All the observed d-d bands have been interpreted using MO and CF theories while radiation damage on $\{VO\}^{2+}/K_2C_2O_4.H_2O$ induces the formation of VO_2 [50]. The nitrilotriethanoate ion forms a 1:1 complex anion with $\{VO\}^{2+}$ which is blue in colour and has the oxo group trans to the tertiary amine atom. The anion also has a coordinated water molecule $[V(O)\{N(CH_2COO)_3\}(OH_2)]^-$ whose replacement by $[NCS]^-$ and $[N_3]^-$ has been studied by means of kinetic measurements. The $[NO_2]^-$ ion oxidises $[V(O)\{N(CH_2COO)_3\}(OH_2)]^-$ to $[V(O)_2\{N(CH_2COO)_3\}(OH_2)]^{2-}$ and these two complex vanadium anions interact to yield an anion containing one V(IV) and one V(V) centre [51]. The same research group has studied the acid hydrolysis of $[V(O)\{N(CH_2COO_3\}(OH_2)]^-$ and aquaoxo{N-(2-pyridylmethyl)iminodiethanoate}-vanadium(IV) [52]. The species $\{VO\}^{2+}$ forms complexes with vanillamandelic, mandelic, and thiolatic acids that contain bidentate chelating groups as shown
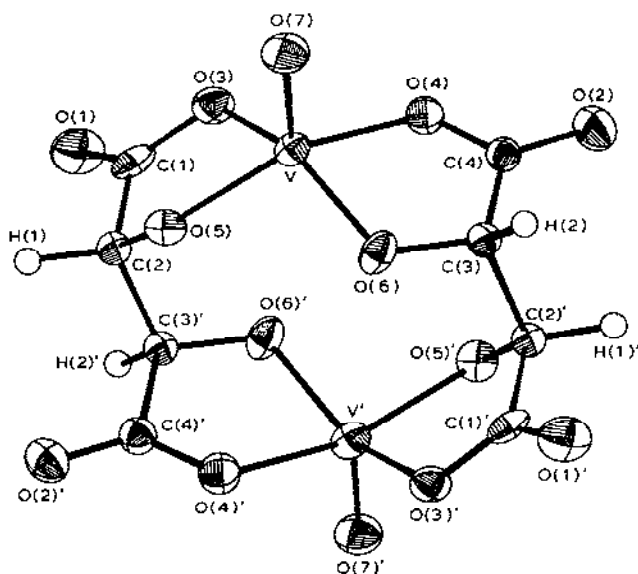
Fig. 10: The $[(VO)_2\{(+)-C_4H_2O_6\}\{(-)-C_4H_2O_6\}]^{4-}$ anion, reproduced with permission from *Acta Crystallogr. Sect. B*, 36 (1980) 1788.

by the observation that two protons are liberated on complex formation [53]. The thiomalate $V(O)(C_4H_4O_4S).2H_2O$ has been prepared and shown to contain a coordinated sulphur atom [54].

The reaction of $Na[BPh_4]$ with N,N'-ethylenebis(salicylideniminato)oxovanadium(IV), $[VO(sal_2en)]$, yields $[Na\{VO(sal_2en)\}_2][BPh_4]$ in which all the oxygen atoms in a $[VO(sal_2en)]$ unit are coordinated to a sodium ion. Each sodium ion is six coordinate and bonded to four different $[VO(sal_2en)]$ complexes (see Figure 11) [55].

Last year, brief mention was made of the synthesis of the $\{VS\}^{2+}$ group which was obtained by reaction of $[V(O)L]$ (L = Schiff's base) with B_2S_3 [56] and now full details of the preparative route and the spectroscopic properties of the products are available. These oxo-Schiff's base species $[V(O)L]$ also react with Ph_3PBr_2 to give $[VBr_2L]$ [57].

The oxovanadium(IV) phthalocyanine, $[VO(Pc)]$, has been the subject of patents, as it has been found to be useful in photoelectric and xerographic imaging. The compound can exist in at least three solid phases, and the structure of the so-called phase II has been determined. The essential features of the structure are given in Figure 12, and the way the molecule stacks reveals the absence of discrete dimers in the solid state of phase II as had been postulated on the basis of solid state optical absorption measurements [58].

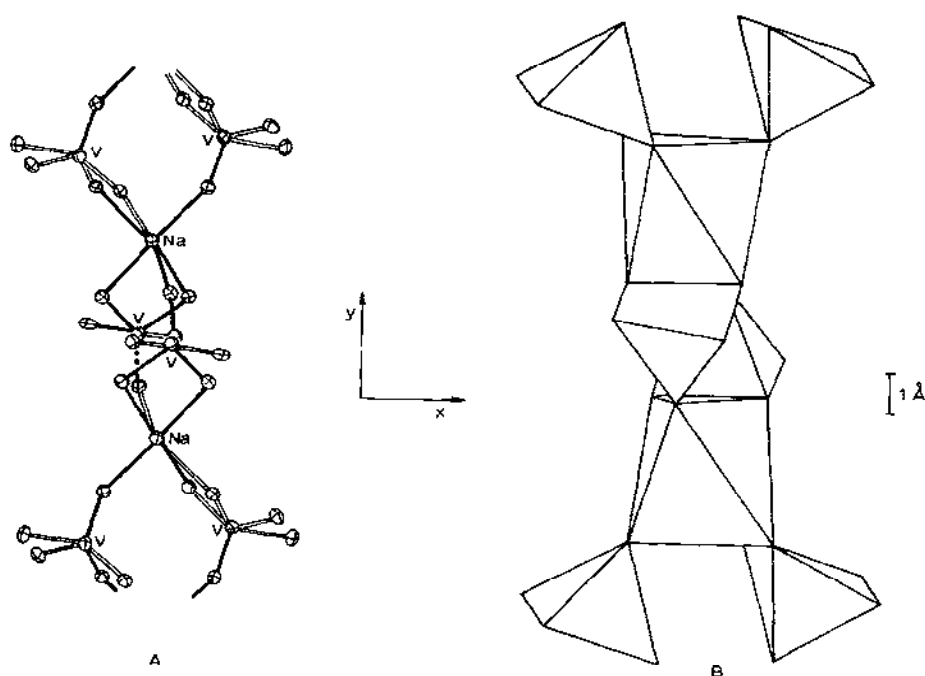A number of studies have appeared this year concerned with oxovanadium(IV)

Fig. 11: Two representations of the coordination polyhedra around vanadium and sodium along the chain of $[Na\{VO(sal_2en)\}_2]_n^+$ cations, reproduced with permission from *Inorg. Chem.*, 19 (1980) 1200.

porphyrins. The EPR spectra of the oxovanadium(IV) compounds formed with etioporphyrin(II) and octaethylporphyrin have been measured at 77 K in frozen CH_2Cl_2 solution and the results are best interpreted by invocation of a dimeric model [59]. The coordination ability of oxovanadium(IV) porphyrinates has been studied with variation in temperature and concentration. As expected, lowering the temperature promotes complex formation and, for example, with N_2H_4 100% conversion takes place at -196 °C with $[N_2H_4] = 10^{-2}$ mol dm^{-3} [60]. Oxovanadium(IV) etioporphyrin reacts with DX/HX (X = Cl or Br) mixtures not to give the expected demetallated product, but yielding a carbonium-type protonated species. Proton exchange with the methyne groups was also observed [61]. Demetallation of oxovanadium(IV) etioporphyrin, a process of importance in the refining of some crude oils, has been studied over a $CoO/MoO_3/Al_2O_3$ catalyst in the presence of dihydrogen. A kinetic model was proposed that accounted for the removal of 90% of the vanadium [62].

A vast number of publications concerning the preparation and characterisation (by infrared and UV-VIS spectroscopy) of oxovanadium(IV) coordination compounds has appeared this year. The following are among the most interesting. The
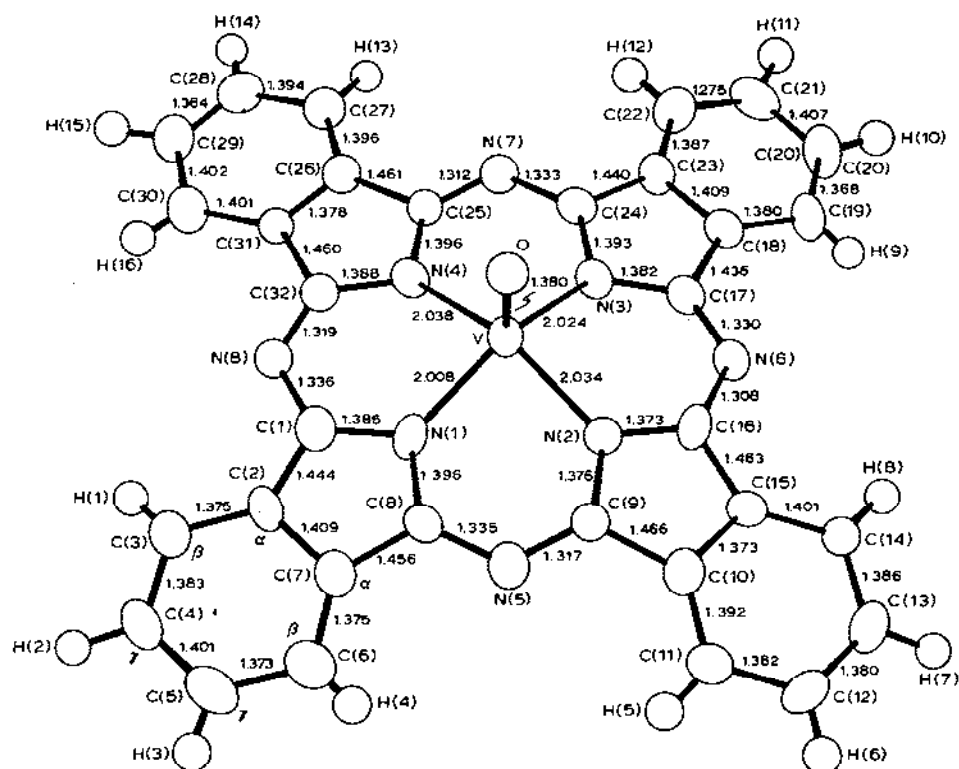
Fig. 12: A perspective view of oxovanadium(IV) phthalocyanine with interatomic distances, reproduced with permission from *J. Chem. Soc., Dalton Trans.*, (1980) 2301.

β-diketone oxovanadium(IV)benzoylacetanlide and benzoyl-3-nitroacetanilide complexes have been shown (contrary to previous reports) to be magnetically dilute [63] and an interesting bis(β-diketone), namely 1,1'-(1,3-phenylene)-bis(butane-1,3-dione), has been synthesised and with it a number of complexes prepared including one containing $\{VO\}^{2+}$ [64]. A binuclear species containing $\{VO\}^{2+}$ has been prepared with the ligand thiouracil (L). It has the formulation $[\{VO(L)(H_2O)\}_2][SO_4]$ and is diamagnetic with the ligand coordinating through a deprotonated nitrogen atom and a sulphur atom [65]. Dimeric species having two square-pyramidal units joined through phenolic or enolic oxygen bridges $[\{VOL\}_2]$ have been prepared for a number of Schiff's bases derived from S-Me-dithiocarbazate and a range of β-diketones (*e.g.* benzoylacetone) [66]. Stepwise stability constants have been determined for complex formation between $\{VO\}^{2+}$ and dithiodiethanoic acid, digycolic acid, thiodiethanoic acid, thiodipropanoic acid or imino-ethanoic acid [67,68].

4.3 VANADIUM(III)

4.3.1 *Compounds containing vanadium-halogen bonds*

The reaction of vanadium(III) chloride with tertiary butylisocyanide has been shown to yield $[VCl_3(CNCMe_3)_3]$ and not insertion products as previously claimed. The ^1H NMR spectrum of this complex contains two resonances at room temperature that are in the ratio 2:1: above 60 $^\circ$C the two resonances coalesce. These NMR observations indicate that at room temperature a *meridional* geometry is adopted and this has been confirmed by an X-ray crystal structure (see Figure 13). The
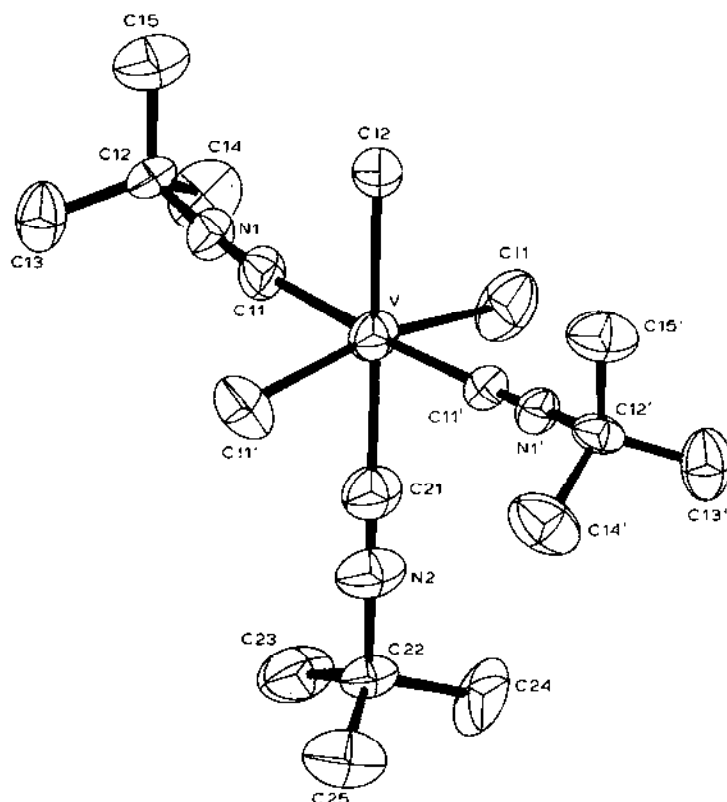
Fig. 13: The geometry of $[VCl_3(CNCMe_3)_3]$, reproduced with permission from *Inorg. Chem.*, 19 (1980) 3381. Atoms Cl(2), V, C(21), N(2) and C(22) lie on a crystallographically required two-fold symmetry axis.

two types of V-C distance (*trans* to V-Cl or *trans* to V-C) are equivalent within experimental error, but ligand exchange reactions indicate that the ligand *trans* to V-Cl is selectively exchanged thus showing the *trans* effect to be

$Cl^->CNCMe_3$. Addition of an excess of Me_3CNC to $[VCl_3(CNCMe_3)_3]$ gives $[V(CNCMe_3)_6]^{2+}$, a species that can also be formed directly from vanadium(III) chloride and an excess of the ligand [69].

4.3.2 Compounds containing vanadium-oxygen bonds

Analysis of X-ray absorption edge data has enabled a structural study on the vanadium complex in living Ascidian blood cells to be carried out. Only trace amounts of $(VO)^{2+}$ were detected and analysis of the EXAFS data established that in living cells the vanadium(III) ion is present, and that the best fit for the data is obtained by postulating a six oxygen atom environment with a V-O distance of 1.99 Å [70]. Among the vanadium-carboxylic acid studies reported recently is the crystal structure of a salt of $[V_3O(OOCCH_2Cl)_6(H_2O)_3]^+$. From the size of the vanadium-vanadium distance it is apparent no direct metal-metal interaction is present [71]. The complexing of vanadium(III) by some hydroxy-carboxylic acids has been studied by NMR relaxation techniques. By determination of the T_1 and T_2 relaxation times as a function of vanadium concentration, formation constants for the 1:1, 1:2 and 1:3 complexes formed by mandelic (120±5, 180±5, 70±5) and lactic acids (110±5, 180±5, 90±5) were obtained [72]. The oxidation of vanadium(II) to vanadium(III) by an α-ketocarboxylic acid occurs in two stages. Initially a complex is formed between the vanadium(II) ion and the acid. This step is followed by the reduction of the acid [73].

4.4 VANADIUM(II)

The preparation, structure and properties of the vanadium(II) halides and the complexes they form have been reviewed [74], as have the relationship between structure and properties exhibited by the lower vanadium fluorides [75,76].

What is claimed to be the first efficient semiconductor-liquid junction solar cell based on a p-type semiconductor has been reported. It has a 9.4% efficiency for the solar-to-electrical energy conversion and contains vanadium(II) and vanadium(III) chlorides (e.g. p-InP/VCl_3-VCl_2-HCl/C) [77]. The reaction of 1,1'-methylenedipyrazole (H_2Cpzl_2) and 1,1'-methylenebis(3,5-dimethylpyrazole) ($H_2Cdmpzl_2$) with a range of vanadium(II) salts lead to the formation of the species $[VX_2(H_2Cpzl_2)]$ (X = Cl, Br or NCS) and $[VX_2(H_2Cdmpzl_2)]$ (X = Br or NCS), which are six-coordinate and monomeric. Five-coordinate ionic species of the type $[VX(L)]^+$ are obtained if the reactions are carried out in the presence of $[BPh_4]^-$. Cationic six-coordinate complexes containing $[V(HCpzl_3)]^{2+}$ are obtained with tris(1-pyrazoyl)methane [78].

From measurements of infrared spectra it was judged that in the salts

containing the $[V(NCS)_6]^{4-}$ ion (cation = $[NMe_4]^+$, $[NEt_4]^+$ or $[pyH]^+$, the vanadium atom is in a six-coordinate all-nitrogen environment. This suggestion is supported by the positions of the bands in the d-d spectra. All the complexes were shown to obey the Curie law and $[NEt_4]_4[V(NCS)_6]$ is isomorphous with the analogous nickel(II) salt [79].

REFERENCES

1   B.R. Fowler and K.C. Moss, *J. Fluorine Chem.*, 14 (1979) 485.
2   S. Brownstein, *J. Fluroine Chem.*, 15 (1980) 539.
3   B.R. Fowler and K.C. Moss, *J. Fluorine Chem.*, 15 (1980) 67.
4   G.V. Jere and S.M. Kaushik, *Synth-React. Inorg. Met-Org. Chem.*, 10 (1980) 255.
5   A. Gourdon and Y. Jeannin, *Acta Crystallogr. Sect. B*, 36 (1980) 304.
6   J.C. Daran, A. Gourdon and Y. Jeannin, *Acta Crystallogr. Sect. B*, 36 (1980) 309.
7   A. Gourdon and Y. Jeannin, *Acta Crystallogr. Sect. A*, 36 (1980) 328.
8   G. Beindorf, J. Strähle, W. Leibelt and K. Dehnicke, *Z. Naturforsch., Teil B: Anorg. Chem. Org. Chem.*, 35 (1980) 522.
9   G. Beindorf, J. Strähle, W. Liebelt and K. Dehnicke, *Z. Naturforsch., Teil B: Anorg. Chem. Org. Chem.*, 35 (1980) 153.
10   R. Choukroun, D. Gervais and J.R. Dilworth, *Transition Met. Chem. (Weinheim, Ger.)*, 4 (1979) 249.
11   R. Choukroun and D. Gervais, *J. Chem. Soc., Dalton Trans.*, (1980) 1800.
12   A.V. Korzah and Y.S. Kuchmii [*Chem. Abstr.*, 93 (1980) 159067].
13   J.P. Sung, D.W. Setser and H. Heydtmann, *Ber. Bunsenges Phys. Chem.*, 83 (1979) 1272.
14   S. Funahashi, T. Midorikawa and M. Tanaka, *Inorg. Chem.*, 19 (1980) 91.
15   F. Secco, *Inorg. Chem.*, 19 (1980) 2722.
16   P. Schwendt, P. Petrovic and D. Uskert, *Z. Anorg. Allg. Chem.*, 466 (1980) 232.
17   N. Galesic and M. Siroki, *Acta Crystallogr. Sect. B*, 35 (1979) 2931.
18   A. Yuchi, H. Muranaka, S. Yamada and M. Tanaka, *Bull. Chem. Soc. Jpn.*, 53 (1980) 1560.
19   C.D. Garner, R.W. Hawksworth, I.H. Hillier, A.A. MacDowell and M.F. Guest, *J. Am. Chem. Soc.*, 102 (1980) 4325.
20   H.O. Froehcich and W. Reomild, *Z. Chem.*, 20 (1980) 154.
21   S.Y. Kuchmii, V.S. Kuts and I.A. Kryukov, *Teor. Eksp. Khim.*, 15 (1979) 739 [*Chem. Abstr.*, 93 (1980) 36075].
22   F. Preuss, W. Towae and J. Woitschach, *Z. Naturforsch. Teil B: Anorg. Chem. Org. Chem.*, 35 (1980) 817.
23   S. Onodera and Y. Ikegami, *Inorg. Chem.*, 19 (1980) 615.
24   V.D. Zhuravlev and A.A. Fotiev, *Zh. Neorg. Khim.*, 25 (1980) 2560.
25   P.G. Dickens, S.J. French and A.T. Hight, *Mater. Res. Bull.*, 14 (1979) 1295.
26   M.M. Mossoba, C.J. O'Connor, M.T. Pope, E. Sinn, G. Herve and A. Teze, *J. Am. Chem. Soc.*, 102 (1980) 6865.
27   R. Kato, A. Kobayashi and Y. Sasaki, *J. Am. Chem. Soc.*, 102 (1980) 6571.
28   A. Björnberg, *Acta Crystallogr. Sect. B*, 36 (1980) 1530.
29   A. Björnberg and B. Hedman, *Acta Crystallogr. Sect. B*, 36 (1980) 1018.
30   E. Hagenbruch and H. Hahn, *Z. Anorg. Allg. Chem.*, 467 (1980) 126.
31   K. Schlesinger and G. Ladwig, *Z. Chem.*, 19 (1979) 349.
32   M. Ebert and L. Kavan, *Collect. Czech. Chem. Commun.*, 44 (1979) 2737.
33   K. Schlesinger and G. Ladwig, *Z. Chem.*, 20 (1980) 33.
34   G. Ladwig, K.H. Jost and K. Schlesinger, *Z. Chem.*, 19 (1979) 386.
35   J. Tudo and D. Carton, *C.R. Hebd. Seances Acad. Sci. Ser. C*, 289 (1979) 219.
36   M. Toboul and P. Tolédano, *Acta Crystallogr. Sect. B*, 36 (1980) 240.

37   D.C. de Beaulieu and H. Muller-Buschbaum, Z. Naturforsch., Teil B: Anorg. Chem. Org. Chem., 35 (1980) 669.

38   P. Bukovec and L. Golic, Acta Crsytallogr. Sect. B, 36 (1980) 1925.

39   A.K. Sengupta, B.B. Dhaumik and R.K. Chattopadhyay, Indian J. Chem. Sect. A, 17 (1979) 527.

40   A. Demsar and P. Bukovec, Vestn. Slov. Kem. Drus., 26 (1979) 401.

41   I.P. Gibson and J.C. Dore, Mol. Phys., 37 (1979) 1281.

42   G. Labauze, E. Samuel and J. Livage, Inorg. Chem., 19 (1980) 1384.

43   V. Fernandez and C. Muro, Z. Anorg. Allg. Chem., 466 (1980) 209.

44a   M.R. Caira and B.J. Gellatly, Acta Crystallogr. Sect. B, 36 (1980) 1198.

44b   J. Cave, P.R. Dixon and K.R. Seddon, Inorg. Chim. Acta, 30 (1978) L349; K.R. Seddon, Report 1980, AD-A088311.

45   D. Collison, B. Gahan, C.D. Garner and F.E. Mabbs, J. Chem. Soc., Dalton Trans., (1980) 667.

46   A. Jesierski and B.J. Raynor, Inorg. Chim. Acta, 44 (1980) L153.

47   M. Tachez and F. Theobald, Acta Crystallogr. Sect. B, 36 (1980) 249.

48   M. Tachez and F. Theobald, Acta Crystallogr. Sect. B, 36 (1980) 1757.

49   R.B. Oreega and C.F. Campana and R.E. Tapscott, Acta Crystallogr. Sect. B, 36 (1980) 1786.

50   S. Radhakrishna, B.V.R. Chowdari and M. Salagram, J. Chem. Phys., 72 (1980) 1908.

51   M. Nishizawa and K. Saito, Inorg. Chem., 19 (1980) 2284.

52   M. Nishizawa and K. Saito, Bull. Chem. Soc. Jpn., 53 (1980) 664.

53   T.M. Che and K. Kustin, Inorg. Chem., 19 (1980) 2275.

54   P.R. Patil and V. Krishnan, Indian J. Chem. Sect. A, 19 (1980) 555.

55   M. Pasqualli, F. Marchetti, C. Floriani and M. Cesari, Inorg. Chem., 19 (1980) 1198.

56   K.P. Callahan, P.J. Durand and P.H. Rieger, J. Chem. Soc., Chem. Commun., (1980) 75.

57   K.P. Callahan and P.J. Durand, Inorg. Chem., 19 (1980) 3211.

58   R.F. Ziolo, C.H. Griffiths and J.M. Troup, J. Chem. Soc., Dalton Trans., (1980) 2300.

59   A.I. Vrublevskii and Yu.V. Glazor, Dokl. Akad. Nauk SSSR, 24 (1980) 503.

60   V.A. Starodubova, V.A. Maslov, T.I. Burnistrova and V.I. Titov, Koord. Khim., 5 (1979) 1806.

61   A.G. Vinogradskii and A.N. Sidorov, Zh. Fiz. Khim., 54 (1980) 1239.

62   Chi-Wen Hung and J. Wei, Ind. Eng. Chem. Process Des. Dev., 19 (1980) 250.

63   A. Syamal and K.S. Kale, Indian J. Chem. Sect. A, 17 (1979) 518.

64   D.E. Fenton, C.M. Regan, U. Casellato, P.A. Vigato and M. Vidali, Inorg. Chim. Acta , 44 (1980) L105.

65   K. Srivastava and M.N. Srivastava, Natl. Acad. Sci. Lett. (India), 2 (1979) 328.

66   S.K. Sahni and R.K. Kapoor, Indian J. Chem. Sect. A, 18 (1979) 456.

67   R.K. Baweja, S.N. Dubey and D.M. Puri, J. Indian Chem. Soc., 57 (1980) 244.

68   R.K. Baweja, S.N. Dubey and D.M. Puri, Acta Cienc. Indica (Ser.) Chem., 6 (1980) 67.

69   L.D. Silverman, J.C. Dewan, C.M. Giandomenico and S.J. Lippard, Inorg. Chem., 19 (1980) 3379.

70   T.D. Tullius, W.O. Gillum, R.M.K. Carlson and K.O. Hodgson, J. Am. Chem. Soc., 102 (1980) 5670.

71   T. Glowiak, M. Kubiak, T. Szymanska-Buzar and B. Jezowska-Trzebiatowska, Int. Semin. Cryst. Chem. Coord. Organomet. Compd. [Proc.], 3 (1977) 211.

72   A.A. Popel, A.N. Glebov, Y.I. Salnikov and N.E. Zhuravleva, Zh. Neorg. Khim., 25 (1980) 2175.

73   J. Konstantatos, E. Vrachnou-Astra, N. Katsaros and D. Katakis, J. Am. Chem. Soc., 102 (1980) 3035.

74   C. Cros, Rev. Inorg. Chem., 1 (1979) 163.

75   Y.S. Hong, R.F. Williamson and W.O.J. Boo, J. Chem. Educ., 57 (1980) 583.

76   R.F. Williamson and W.O.J. Boo, Inorg. Chem., 19 (1980) 31.

77   A. Heller, B. Miller, H.J. Lewerenz and K.J. Bachmann, J. Am. Chem. Soc., 102 (1980) 6555.

78   F. Mani, *Inorg. Chim. Acta*, **38** (1980) 97.
79   L.F. Larkworthy and B.J. Tucker, *J. Chem. Soc., Dalton Trans.*, (1980) **2042**.