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New chemistry of vanadium(II) [1]

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Contents

Abstract

The synthetic routes to vanadium(II) complexes from metallic vanadium and from compounds in higher oxidation states, comprising both chemical and electrochemical methods, are reviewed. The reduction of vanadium(III) chloride by Zn seems to be the simplest entry to useful starting materials such as trichlorohexakis(tetrahydrofuran)divanadium(1+), dichlorobis(tetramethylethylenediamine)vanadium and diiodotetrakis(tetrahydrofuran)vanadium. The chemistry is not dominated by a single ligand type, and O-, N- and P-donors are all used. Few dinitrogen complexes of vanadium-(II) and -(III) have been reported and all contain bridging dinitrogen. The protonation of these compounds yields ammonia only from vanadium(II); the higher oxidation state regenerates dinitrogen. The extensive chemistry of trinuclear vanadium(II) complexes now being revealed may also be relevant to vanadium(II)–catechol–methoxide nitrogen-fixing systems.

Keywords: Polynuclear compounds; Vanadium(II) compounds

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1. Introduction

Joseph Chatt started his renowned exploration of platinum chemistry using phosphines as ligands and determining how simple halide complexes could be synthesized and characterized. This work was all done essentially at The Frythe. Also at The Frythe he started to move through the Transition Series, upwards and to the left, through Pd, Ni, Ir, Co, Ru, Os, Fe and even into Re (with a brief incursion into Ti) [1].

Once the Unit of Nitrogen Fixation was established at the University of Sussex, we quickly adopted a similar approach, expanding considerably the work on Os and Re [2], and discovering similar routes to phosphine complexes of Mo and W halides [3]. As we expected, dinitrogen complexes of Os, Ru, Re, Mo and W were all eventually isolated, and all from the UNF laboratory contained phosphines [4].

Although the chemistry of such N_2 complexes was very stimulating, in some ways the most interesting dinitrogen chemistry has arisen from vanadium, principally from the work of Shilov's group in "soups" containing vanadium(II). These can generate ammonia and/or hydrazine, sometimes catalytically, and sometimes in protic environments [5].

Despite our reluctance in those early days to push our researches into transition metal Group 5, developments in nitrogenase chemistry have persuaded us that the time is right for us to explore this area with more care. One might not expect phosphines to be the best ligands for exploiting the chemistry of vanadium in low oxidation states, because Group 5 elements are not generally regarded as being particularly electron rich, so that other kinds of ligand needed to be considered. Because the available routes to vanadium(II), and the vanadium(II) compounds themselves, were not particularly versatile and useful [6], we decided to follow the old pattern, that is, to explore the chemistry of vanadium(II) before attempting to unravel the dinitrogen chemistry.

This review aims to summarize the synthetic pathways which lead into the chemistry of vanadium(II), before describing recent developments in our own and in other laboratories, and the unexpected results that have accrued. Our own programme was conceived very much in the original pattern of Chatt, and we submit it as a token of our respect for the man and his work. It shows how much we still owe to him, but also how much is yet to be discovered.

2. Preparation of compounds of vanadium(II) from other oxidation states

The classical changes in colour observed as V^{V} is reduced sequentially to V^{II} in acidic aqueous solution suggests that reduction of vanadium in high oxidation states should be a reasonable route to compounds of vanadium(II). Nearly 30 years ago, Seifert and Auel [7] showed that the electrolytic reduction of VX_3 ($X=Cl$ or Br) in methanol containing HX produced "metastable" solutions containing V^{II}. They isolated a series of compounds $VX_2 \cdot nCH_3OH$ ($X=Cl$, $n=2$ or 4; $X=Br$, $n=2$, 4 or

6; and, by metathesis, X = I, $n = 4$ or 6). Basically the same halides, in the hydrated form $VX_2 \cdot nH_2O$, were prepared, independently, by electrolytic reduction of acidic solutions of vanadyl(IV) halides at a mercury cathode [8]. The compounds with $n = 4$ or 6 possessed "normal" spin-only magnetic moments, whereas those with $n = 2$ had low values and exhibited antiferromagnetic behaviour, presumably due to polymerization [7,8]. Various other V^{II} compounds were then obtained by direct exchange of water or alcohol molecules by other neutral ligands such as cyclic ethers, amines and nitriles [7,9].

Reduction of vanadyl(IV) sulphate in aqueous solution at a mercury electrode produces $VSO_4 \cdot 6H_2O$, presumably containing $[V(H_2O)_6]^{2+}$ [10]. Even as late as 1986 Cotton et al. [11] reported the structures of four vanadium(II) compounds, including highly air-stable saccharinates, prepared essentially by an electrolytic approach [12] first described 20 years earlier.

Other electrochemical routes to vanadium(II) include the reduction of an acidic solution of V_2O_5 and subsequent reaction with $MeCOCH_2COMe$ to give compounds containing $V^{II}(OCMeCHCOMe)_n$ ($n = 1$, 2 or 3) [13]; the production of methanolic vanadium(II) from $VOSO_4$ by direct electrolysis, and its use in situ to fix nitrogen in the presence of bidentate proligands[3] such as amines, thiols and catechols [14]; and the acid reduction of V_2O_5 to $VOSO_4$ followed by electrolysis to give $[V(H_2O)_6]^{2+}$, which was isolated in the form of the Tutton salt, $V(NH_4)_2(SO_4)_2 \cdot 6H_2O$[10,15]. None of these experimental pathways is particularly simple or versatile.

Two other routes would appear more amenable to general exploitation: reduction with chemical agents and reaction of vanadium metal with acids. For the latter, it had been reported previously that vanadium metal was unreactive towards non-oxidizing acids [16]. However, we have shown that vanadium(II) species can be reproducibly prepared from vanadium metal and aqueous HCl, HBr or CF_3SO_3H [17]. Even using acetic acid–HX mixtures (X = Cl or Br), one can isolate novel species such as $[VCl_2(CH_3COOH)_4]$ and $[V(CH_3COOH)_6]^{2+}$ [17,18]. These have enabled us to obtain further new materials, such as a number of $[VX_2(\text{diphosphine})_2]$ complexes, where diphosphine = $Et_2PCH_2CH_2PEt_2$ (depe) or $Me_2PCH_2CH_2PMe_2$ (dmpe) [19]. Nevertheless, much more discussion and interest seem to surround the reductive route.

Metals and low-oxidation-state compounds have variously been used to convert vanadium(III) into vanadium(II). Examples are as follows: VCl_3 and zinc, followed by treatment with KCN, yield $K_4[V(CN)_6]$ [20]; $[VCl_2\{OCMeCHCOMe\}(thf)_2]$ (thf = tetrahydrofuran) and zinc dust produce a compound formulated as $[V(\mu\text{-}OCMeCHCOMe)(\mu\text{-}Cl)ZnCl_2(thf)_3]$ [21]; V_2O_5 and Zn in aqueous HCl yield a "VCl_2 solution" [22]; and $[VBr_3(thf)_3]$ and magnesium in thf yield $[VBr_2({}^iPr_2PCH_2CH_2P^iPr_2)_2]$ in the presence of ${}^iPr_2PCH_2CH_2P^iPr_2$ [23]. An analogous reductive approach was used to prepare $[\{V(C_5H_5)Cl(PEt_3)\}_2]$ [24].

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[3] Because a ligand is only a ligand when bound to a metal ion, the term proligand is used to indicate a material with the potential to act as a ligand but which is actually unbound.

However, the most interesting reaction involves VCl_3 and Zn and related reducing agents.

It was reported in 1981 that $[VCl_3(thf)_3]$ is slowly reduced by zinc metal in thf to generate $VCl_2(thf)_2$, and that this can be used to prepare dinuclear complexes such as $[\{VCl_2(PEt_3)_2\}_2]$ [25]. In 1983, it was reported that the product is not $VCl_2(thf)_2$, but that X-ray analysis showed it to be $[V_2(\mu\text{-}Cl)_3(thf)_6]$ $[Zn_2(\mu\text{-}Cl)_2Cl_4]$, undoubtedly containing vandium(II), but dinuclear [26]. Independently, another group of workers came to the same conclusion [27]. Later, it was shown that $AlEt_2(OEt)$ is also a useful reducing agent [28]. It can be employed to form thf and 2-Me-thf adducts [29], and also bromo adducts [30], all containing the $[AlEt_2Cl_2]^-$ counter ion. From these compounds, other dinuclear complexes such as $[V_2(\mu\text{-}Cl)_3(PMe)_6]$ $[AlCl_2Et_2]$ were synthesized [28]. A further variant has been mentioned briefly, namely $[V_2(\mu\text{-}Cl)_3(thf)_6]$ $[ZnCl_3(thf)]$, which is formed if a restricted amount of zinc is used in the reduction [31]. Finally, a mixture of VCl_3, Al and $AlCl_3$ in toluene–thf can also yield the $[AlCl_4]^-$ salt of the dinuclear cation [32].

Other redox pathways have been successfully used in specific systems, but they are unlikely to become general routes to V^{II}. Thus, $[VCl_3(CN^tBu)_3]$ reacts with an excess of ^tBuNC in ethanol to generate $[V(CN^tBu)_6]^{2+}$ [33]. This cation can also be obtained by oxidation of $[V(CO)_6]^-$ and addition of *tert*-butyl isocyanide [34]. The oxidation and disproportionation of $[V(\eta^6\text{-arene})_2]^{n+}$ ($n=0$ or 1) again provide V^{II} species. For example, on heating in thf, $[V(\eta^6\text{-mesitylene})_2]I$ yields $VI_2(thf)_{0.7}$, while $[VI_2(dme)_2]$ is produced in dimethoxyethane (dme). Likewise, oxidation of $[V(\eta^6\text{-mesitylene})_2]$ with Ph_3CBr in dme affords $[VBr_2(dme)_2]$ [32]. Other workers have reported similar reactions [35].

Recently, the reduction of $[VCl_3(thf)_3)]$ with $Na[BHEt_3]$ in the presence of the lithium salt of *N*,*N*′-di-4-tolylformamide (Hdfm) was reported to yield the dinuclear V^{II} species $[V_2(dfm)_4]\cdot$toluene. This interesting diamagnetic complex contains a vanadium–vanadium triple bond and is stable in low-polarity solvents [36], but again it is not expected to be a common starting material for further research.

There remains a further path to vanadium(II) which is worthy of mention in this respect, namely the smooth reaction of Me_3SiI in MeCN with $[VCl_3(MeCN)_3]$, which yields $[V(MeCN)_6]^{2+}$ [37]. This unexpectedly facile reduction should prove a useful entry into V^{II} chemistry from a readily accessible V^{III} species, provided that interference from the $(I_4)^{2-}$ ion generated at the same time can be avoided. The cation, which can also be formed from $VOCl_3$ and Me_3SiI in acetonitrile [38], and from mixtures of $[VI_2(thf)_4]$ and MeCN [37], was obtained originally by disproportionation of $[V(CO)_6]$ in acetonitrile–benzene [39] and by reduction of VCl_3 by $ZnEt_2$ in MeCN. In the last case, a reaction mechanism was suggested [40].

Among the methods described so far, the reduction of commercially available VCl_3 by zinc, yielding the dinuclear cation **1** (Fig. 1) [28], is apparently the most widely used and simplest way into the chemistry of vanadium(II). Salts of **1** are actually key starting materials that can be employed, both in protic and non-protic media, for the synthesis of other useful vanadium(II) complexes such as $[VCl_2(MeOH)_4]$ and $[V(MeOH)_6]Cl_2$ [28] (also accessible by other pathways described here) and, more recently $[VCl_2(tmeda)_2]$ [41] (tmeda = *N*,*N*,*N*′*N*′-

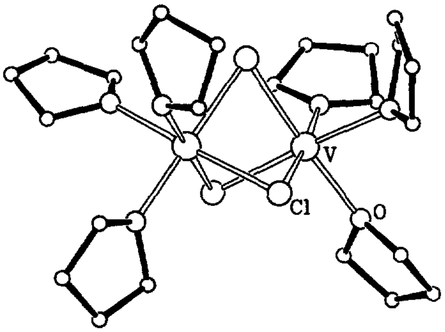

Fig. 1. Structure of the triply-halide-bridged species $[V_2Cl_3(thf)_6]^+$ (1) generated by chemical reduction of V^{III} at room temperature [26–29,32].

tetramethylethylenediamine) and $[VI_2(thf)_4]$ [37]. These transformations have the advantage of preventing contamination of subsequent reactions by the metal contained in the counter ion of **1**.

The reaction of salts of **1** with amines such as pyridine, pyrrolidine (L), tmeda and trimethylethylenediamine (L_2) generates the remarkably stable compounds $[VCl_2L_4]$ and $[VCl_2(L_2)_2]$ [41]. The latter is soluble in organic solvents. In fact, $[VCl_2(tmeda)_2]$, $[VBr_2(tmeda)_2]$ [42] and $[VI_2(tmeda)_2]$ [37] are now all fully characterized, and we have, in addition, prepared some complexes of *N*,*N'*-dimethylethylenediamine (dmeda) such as $[VCl_2(dmeda)_2]$ and $[VBr_2(dmeda)_2]$ [42]. They are all simple, mononuclear, octahedral complexes of vanadium(II), with easily replaceable ligands and, as such, constitute a good selection of reasonable starting materials.

$[VI_2(thf)_4]$ is easily prepared from the $[AlCl_2Et_2]^-$ salt of **1** in thf upon addition of Me_3SiI. The reaction is carried out at 0 °C. If the reaction mixture is heated under reflux, the known product of metathetical anion exchange, $[V_2Cl_3(thf)_6]I$, is generated [32,37]. The complex $[VI_2(thf)_4]$ has proved to be a versatile starting material for the synthesis of many other V^{II} iodides [37].

In summary, unlike in Chatt's chemistry, where phosphines were employed as "all-purpose" ligands, in the chemistry of vanadium(II) O- and N-donors seem to be the most appropriate, although phosphine derivatives are indeed accessible, and apparently no single class of ligand can be exploited above all others. The advantages of ligands such as tmeda and thf are that they confer solubility in organic solvents upon their complexes, and that they are relatively poor, easily replaceable, ligands [43,44] when used in subsequent reactions. However, V^{II}–tmeda adducts are not as simple or stable as they might appear to be. The complications and the challenge will be discussed below.

3. Dinitrogen chemistry of vanadium(II)

Vanadium(II) has taken a central place in non-biological nitrogen fixation chemistry, primarily owing to the extensive researches of Shilov's group [5,45]. Their most efficient dinitrogen-reducing systems include gels of $V(OH)_2$ and $Mg(OH)_2$ at very alkaline pH, and a mixture of V^{II} and catechol in methanol within a very restricted "pH" range (9–11) [45]. These studies suggested that O-donor ligands could have a central role in supporting N_2 reduction by V^{II} centres.

In spite of many years of heated arguments in the literature between Shilov's and Schrauzer's groups on the kinetics of these redox reactions, there are no hard data available which clarify the mechanism of nitrogen fixation in such systems. Shilov is very much of the opinion that polynuclear intermediates containing V^{II} ions bridged by dinitrogen molecules are involved, whereas for Schrauzer a side-on bonded dinitrogen is the key intermediate [46].

No vanadium(II) dinitrogen complexes were isolated until 1989, when Gambarotta and co-workers [44] used $[VCl_2(tmeda)_2]$ as a starting material to synthesize $[\{V(C_6H_4CH_2NMe_2)_2(py)\}_2(\mu\text{-}N_2)]$ (**2**) (Fig. 2). Subsequently we showed that this complex reacts with HCl to generate ammonia and vanadium(III) species [47]. We have also developed several other systems with C,N-donors, directly analogous to Gambarotta's, but they are not yet completely evaluated. The uptake of N_2 by these systems is very fast and limited to one dinitrogen molecule to two V^{II} ions, suggesting the formation of bridging-N_2 complexes [48].

It was demonstrated later that compound **2** invariably loses the coordinated N_2 on addition of a number of phenols [49]. When compared with the observations of Shilov's group that catechols and vanadium(II) can fix nitrogen, this is perhaps surprising. However, simple phenols do not appear to replace catechols in the Shilov system, and rather specific polynuclear species seem to be efficient in the fixation process [14,45].

Other dinitrogen complexes of vanadium(II) or vanadium(III) are known (and all contain bridging N_2 molecules), e.g. $[Na(diglyme)_2]$ $[\{V(mesityl)_3\}_2(\mu\text{-}N_2)Na]$ [50], $[\{V(CH_2{}^tBu)_3\}_2(\mu\text{-}N_2)]$ [51], $[\{({}^iPr_2N)_3V\}_2(\mu\text{-}N_2)]$ [52] and $[(\{Me_3Si)NC(Ph)N(SiMe_3)\}_2V)_2(\mu\text{-}N_2)]$ [43]. Apparently V^{II} must be present before protonation can generate ammonia, since V^{III} complexes do not yield any [53]. Interesting as this work is, it sheds little light on Shilov's systems. Some idea of the species which

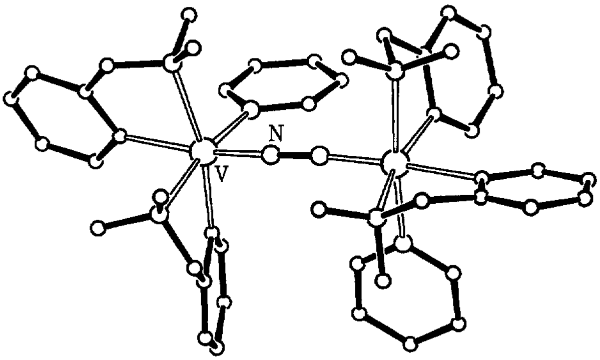

Fig. 2. Structure of the first stable V^{II}–dinitrogen complex, **2**, obtained from $[VCl_2(tmeda)_2]$ by substitution of chlorides by the C,N-chelating ligand $1,2\text{-}C_6H_4CH_2NMe_2$ [44].

might be involved arise from the work of Shilov's group itself. From the nitrogen-fixing system VCl_2/3,5-$^tBu_2C_6H_2(OH)_2$-1,2/$NaOCH_3$ in methanol, they recently isolated, after completion of any fixation reaction, the polynuclear V^{II}/V^{III} complex $[Na_2V_4(OMe)_2\{O_2C_6H_2(^tBu)_2\}_4\{O(OH)C_6H_2{}^tBu_2\}_2(MeOH)_8]$ (**3**) [54]. In **3** (Fig. 3), the vanadium atoms are chelated by catecholate(2−) and bridged by catecholate(1−). OMe^- is terminal and bridging. The relevance of this material to the nitrogen-fixation process is not clear, but it suggests that vanadium(II) species, under N_2-fixing conditions, undergo polymerization and redox chemistry. This at least implies that we may have to look further than simple species to solve the nitrogen-fixation riddle of V^{II} in such systems.

4. The deceptively simple starting material $[VCl_2(tmeda)_2]$

This complex (**4**) (Fig. 4), has a simple trans octahedral structure [41]. It dissolves in thf at room temperature to give a blue solution, from which blue crystals can be obtained. On addition of trimethylsilyl iodide or sodium tetraphenylborate to this solution, there is an immediate change from blue to green, at room temperature. Green crystalline material can be isolated from such systems. When redissolved in thf, the solutions of the green material remain green, at both high and low temperatures. However, if both tmeda and tetraalkylammonium chloride are added, then blue $[VCl_2(tmeda)_2]$ separates on cooling.

These observations were all readily rationalized when we determined that the green colour is due to the trinuclear ion *triangulo*-$[V_3(\mu\text{-}Cl)_3(\mu_3\text{-}Cl)_2(tmeda)_3]^+$ (**5**) (Fig. 5), which is generated reversibly from $[VCl_2(tmeda)_2]$ through loss of both

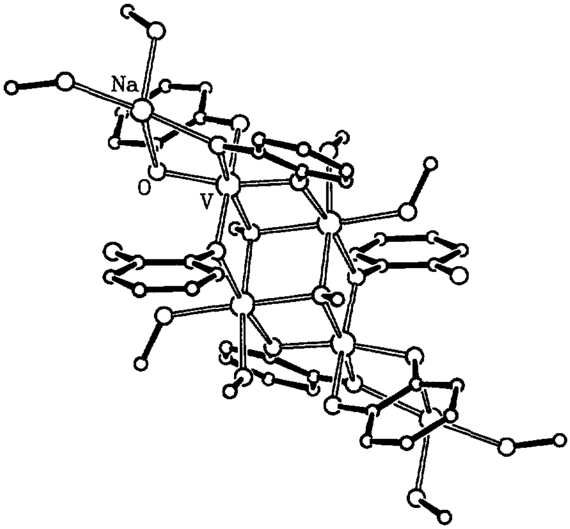

Fig. 3. The tetranuclear mixed-valence V^{II}/V^{III}/*tert*-butylcatechol/OMe^- complex 3. Non-coordinated MeOH molecules omitted for clarity [54].

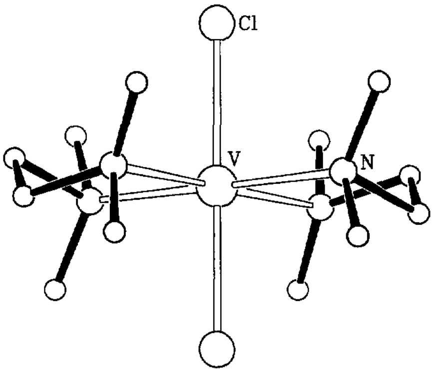

Fig. 4. Structure of *trans*-$[VCl_2(tmeda)_2]$ (**4**) [41].

Cl^- and tmeda, according to Eq. (1) [55]. This ion has already been reported to be formed in the reactions of $[VCl_2(tmeda)_2]$ with $NaNPh_2$, $[VCl_3(thf)_3]$, $[TiCl_3(thf)_3]$ or $[YCl_3(thf)_3]$ [56], though how it arises was not precisely described.

$$3[VCl_2(tmeda)_2] \leftrightharpoons [V_3Cl_5(tmeda)_3]^+ + 3tmeda + Cl^- \qquad (1)$$

We now have persuasive evidence that the *triangulo*-$\{V_3(\mu\text{-}Cl)_3\}$ motif is easily formed by vanadium(II). For example, reaction of $VCl_2(EtOH)_2$ [9] with KI and tmeda in thf–methanol, in an attempt to produce $[VI_2(tmeda)_2]$, actually yielded crystalline material containing both $[V_3(\mu\text{-}Cl)_3(\mu_3\text{-}OMe)_2(tmeda)_3]^+$ and $[V_3(\mu\text{-}Cl)_3(\mu_3\text{-}Cl)(\mu_3\text{-}OMe)(tmeda)_3]^+$ [55]. It is not clear how this happens, but it does raise the question of whether the trinuclear moiety is present in $VCl_2(EtOH)_2$ (cf. other VX_2L_2), perhaps better formulated as $[V_3(\mu\text{-}Cl)_3(\mu_3\text{-}Cl)_2(EtOH)_6]Cl$. In addition, $[V(MeOH)_6]Cl_2$ [9,28] on the thermal balance (or heated under vacuum) loses weight smoothly to leave $VCl_2(MeOH)_2$ [55], which is supposed to be polynuclear [8] and could again be formulated as $[V_3Cl_5(MeOH)_6]Cl$. Finally, the tetra-

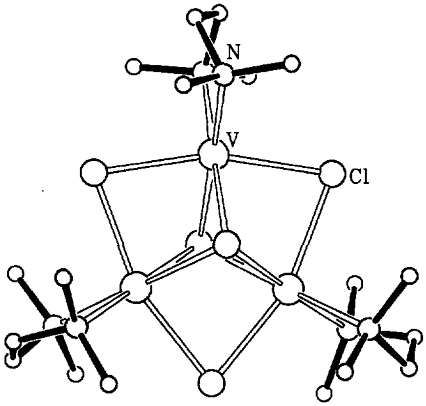

Fig. 5. The highly symmetrical trivanadium(II) cation $[V_3Cl_5(tmeda)_3]^+$ (**5**) [55,56].

phenylborate salt of $[V_3Cl_5(tmeda)_3]^+$ (**5**) reacts with depe in methanol to yield $[V_3(\mu\text{-}Cl)_3(\mu_3\text{-}OMe)_2(depe)_3]^+$ as determined by X-ray structural analysis [42,55]. This drives the attention to the stability of the planar $\{V_3Cl_3\}$ core, which remains intact after substitution of all the axial chlorides and neutral tmeda ligands. These transformations occur under very mild conditions, and similar changes would seem very likely under Shilov's nitrogen fixation conditions, and also in reactions of $[VCl_2(tmeda)_2]$ with any reagent capable of abstracting or replacing a halide ion. We are currently exploring this chemistry, and in particular determining whether we can synthesize heteronuclear species containing the moiety $\{V_2M(\mu\text{-}Cl)_3\}$ where $M = Fe^{II}$, Cr^{II}, Mn^{II}, etc.

5. Conclusions

There are several sources of vanadium(II), mononuclear and polynuclear, available to date, and a rich vanadium chemistry in this oxidation state is being developed worldwide. There seems to be no single class of ligand, such as the phosphines, which stabilizes the majority of these materials. There is a great deal of O-donor, N-donor and halide chemistry to unravel, and phosphines also have their place. However, the formation of polynuclear compounds appears to be much more facile than in platinum chemistry, where Chatt started his work with the ambitious aim of understanding the coordinate bond.

Chatt's research has undoubtedly been a decisive influence in determining the shape of modern inorganic and organometallic chemistry. Had he started at the other end of the Transition Series, the chemical knowledge accumulated so far would have been different. It has been a privilege to have worked with Chatt in one kind of chemistry and also to have been involved in the development of another.

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