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RECENT DEVELOPMENTS IN VANADIUM SULPHUR AND OXYGEN CHEMISTRY

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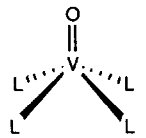
Abstract—We survey recent results from our efforts in vanadium sulphur and oxygen chemistry. A unifying theme for most of the discussion is the reactivity characteristics of vanadyl (VO^{2+}) complexes, and it is shown how such complexes are capable of a variety of transformations leading to products with oxidation states in the range III–V and nuclearities in the range 1–5. Also described are mononuclear non-oxo vanadium sulphur complexes, including the structural characterization of both $V(SBu^t)_4$ and $V(SBu^t)_4^-$. The relevance of this work to our understanding of the fate of crude oil vanadyl impurities during hydrotreating processes is discussed.

This paper will survey some of our recent results in vanadium chemistry and will concentrate primarily on the reactivity characteristics of vanadyl ($V{=}O^{2+}$)-containing materials. Our interest in this area stems from the presence of large amounts of vanadium impurities in crude oils (as both vanadyl porphyrins and non-porphyrins) and their conversion via currently unknown mechanisms into vanadium(III) sulphides under reducing and sulphide-rich hydrotreating conditions.[1–4] These sulphides contribute to the deactivation of hydrotreating catalysts and thus represent a serious problem in processing the heavy crudes characteristic of the western hemisphere. Our programme is directed towards achieving a greater understanding of the various pathways by which vanadyl impurities are reduced/aggregated/sulphided to vanadium sulphides, an objective which entails the systematic exploration of the reactivity characteristics of model vanadyl complexes. Although such complexes have been prepared in great numbers over many decades, the reactivity chemistry of these very stable materials has been poorly investigated.[5–7] We herein describe the products from the reaction of vanadyl complexes under a variety of conditions.



(1) PRODUCTS CONTAINING ONLY VANADIUM(IV)

A variety of procedures have now been developed that lead to products involving no change in metal oxidation state. These involve both attack at the terminal oxide and attack at the basal ligands. Treatment of $VO(edt)_2^{2-}$ (**1**; edt = ethane-1,2-dithiolate) with $(Me_3Si)_2S$ in MeCN, leads to clean conversion to $VS(edt)_2^{2-}$ (**2**).[8] By rapid addition of a large excess of Et_2O, an intermediate in this transformation can be isolated, viz $V(OSiMe_3)(edt)_2^-$ (**3**),[9] indicating the probable mechanism to be as shown in eq. (1):

$$\begin{aligned} VO(edt)_2^{2-} + (Me_3Si)_2S &\rightarrow V(OSiMe_3)(edt)_2^- \\ + Me_3SiS^- &\leftrightarrows V(SSiMe_3)(edt)_2^- + Me_3SiO^- \\ &\rightarrow VS(edt)_2^{2-} + (Me_3Si)_2O. \quad (1) \end{aligned}$$

Complex **2** may more conveniently be prepared[10] in large quantities by the direct reaction of VCl_3, S and Na_2edt [eq. (2)]:

$$\begin{aligned} VCL_3 + E + 2.5Na_2edt &\rightarrow [VE(edt)_2]^{2-} \\ + 3NaCl + 2Na^+ &+ \tfrac{1}{2}\text{“}(edt)_2\text{”}. \quad (2) \\ (E = S, Se)& \end{aligned}$$

Advantage of this direct synthesis procedure was subsequently taken to prepare an extremely rare

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example of a selenovanadyl (VSe^{2-}) unit in the complex $VSe(edt)_2^{2-}$ (**4**), which allowed the first structural characterization of this moiety.[10]

In contrast to $(Me_3Si)_2S$, treatment of **1** with equimolar Me_3SiCl leads to attack at the basal edt^{2-} ligands and the formation of dinuclear $V_2O_2(edt)_3^{2-}$ (**5**), shown in Fig. 1.[11] Its formation is rationalized in eq. (3), the aggregation triggered by lowering of the edt–V ratio:

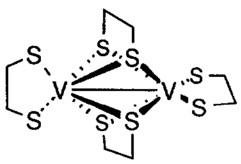
$$2VO(edt)_2^{2-} + 2Me_3SiCl \rightarrow V_2O_2(edt)_3^{2-} + 2Cl^- + Me_3SiSCH_2CH_2SSiMe_3. \quad (3)$$

The VO^{2+} units adopt a *syn*-arrangement. Interestingly, although complex **1** exhibits only irreversible electrochemical processes, the cyclic voltammogram of **5** exhibits a *reversible* one-electron oxidation at −0.83 V vs ferrocene in MeCN; coulometry confirmed the one-electron nature of this process. Reactions employing higher Me_3SiCl–V ratios could lead to a greater degree of aggregation, and such reactions have been under investigation.[11,12]

(2) REACTIONS INVOLVING OXIDATION STATE CHANGES

(a) *Reduction*

To model the reducing conditions that the crude oil vanadyl impurities experience during hydroprocessing, we have treated several model vanadyl complexes with an electron source in the presence of protons; this combination is designed as a low-temperature substitute for hydrogen gas employed at high temperature, and also allows homogeneous single-phase reactions. The electron source chosen is the organic radical anion acenaphthylenide (ACN^-). Treatment of **1** with NaACN in the presence of $HNEt_3Cl$, leads to formation of the V^{III} anion, $V_2(edt)_4^{2-}$ (**6**).[13] In contrast, a similar reaction employing $VO(aet)_2$ (aet = 2-aminoethanethiolate) leads to $V_2O(aet)_4$ (**7**) containing the linear $[V{-}O{-}V]^{4+}$ unit.[13] Both **6** and **7** are also available by direct synthesis from VCl_3 and have been structurally characterized.[14,15] In both these transformations, initial reduction of V^{IV} to V^{III} destabilizes the VO multiply-bonded terminal unit and leads to aggregation with either partial or complete loss of the oxide ions, the latter facilitated by H^+. The basic reaction is summarized in eqs (4) and (5):



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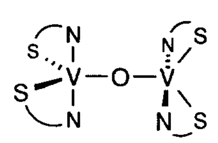

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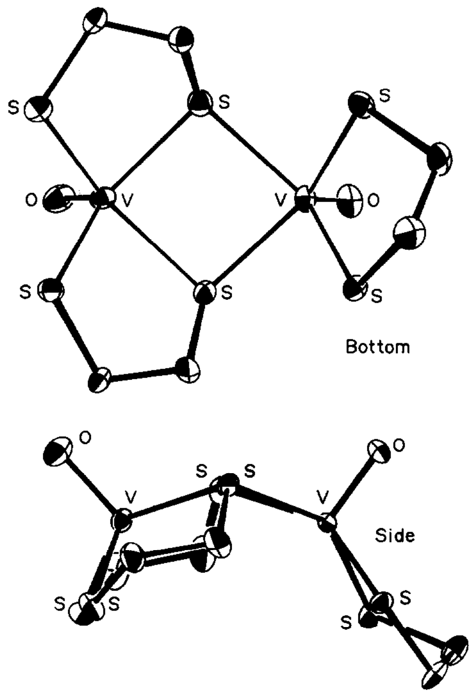

Fig. 1. Two views of the structure of complex **5**, $V_2O_2(edt)_3^{2-}$.

$$2VO(edt)_2^{2-} + 2e^- + 4H^+ \rightarrow V_2(edt)_4^{2-} + 2H_2O \quad (4)$$

$$2VO(aet)_2 + 2e^- + 4H^+ \rightarrow V_2O(aet)_4 + H_2O + 2H^+. \quad (5)$$

The actual identity of the product (i.e. remaining content of O^{2-}) must be governed by the identity of the basal ligands, since in both reactions sufficient protons were available for complete loss of oxygen as H_2O. That complex **7** is indeed the thermodynamically-preferred product with this ligand is supported by its direct synthesis from VCl_3, Na(aet) and advantitious oxygen (probably H_2O), with no evidence for a non-oxo product.[13]

More recently, we have extended use of this "reductive activation" of the VO^{2+} unit to access additional V^{III} species from simple VO^{2+} complexes. Using $VOCl_4^{2-}$, a convenient source of the VO^{2+} unit, we have investigated reactions with just NaACN or with NaACN/VCl_3; the latter have been investigated in greater detail to date and one example is described here. Reaction of $VOCl_4^{2-}$ with VCl_3 and NaACN in CH_2Cl_2 in the presence of excess pyridine leads to reductive coupling of the VO^{2+} unit with the V^{3+} centre and the formation

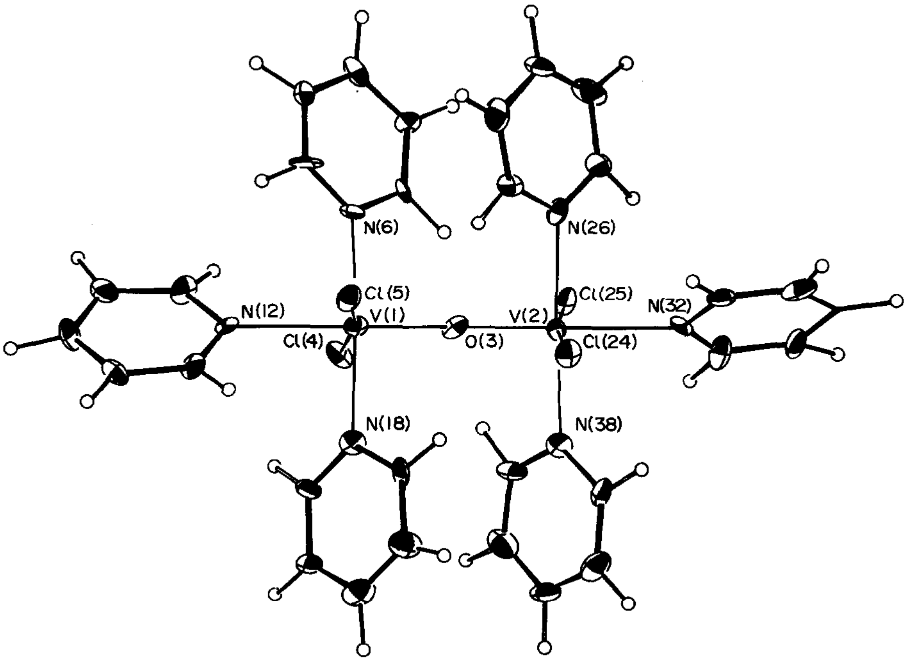

Fig. 2. The structure of complex **8**, $V_2OCl_4(py)_6$.

of $V_2OCl_4(py)_6$ (**8**) (Fig. 2),[12] as summarized in eq. (6):

$$VOCl_4^{2-} + VCl_3 + e^- \xrightarrow{py} V_2OCl_4(py)_6 + 3Cl^-. \qquad (6)$$

The complex possesses the same linear $[V—O—V]^{4+}$ unit as **7** but the metals are now six- rather than five-coordinate.

(b) *Oxidation*

An additional ligand type we have been employing is carboxylates, since they have been detected in crude oils and may therefore be involved in metal binding.[1,2,4] Treatment of $VOCl_4^{2-}$ with sodium thiophene-2-carboxylate (Natca) under aerobic conditions leads to formation of deep green $V_5O_9(\mu_4\text{-}Cl)(\mu\text{-}tca)_4^{2-}$ (**9**), containing 4 V^{IV}, V^{V}; its structure is shown in Fig. 3.[16] If the reaction is carried out in the presence of $AgNO_3$ to sequester all available Cl^-, the resulting product is $V_4O_8(tca)_4(NO_3)^{2-}$ (**10**), possessing V^{IV}, 3 V^{V}. The structure is similar to complex **9** except that the apical VO is absent, leaving a square of four vanadium atoms. In addition, the μ_4-Cl^- is now replaced by a η^1-μ_4-NO_3^-, a single NO_3^- oxygen bridging all four metals. There is no evidence for OH^- instead of O^{2-} in any position of either **9** or **10**. The oxidation state assignments are being confirmed as part of a detailed magnetochemical investigation; results

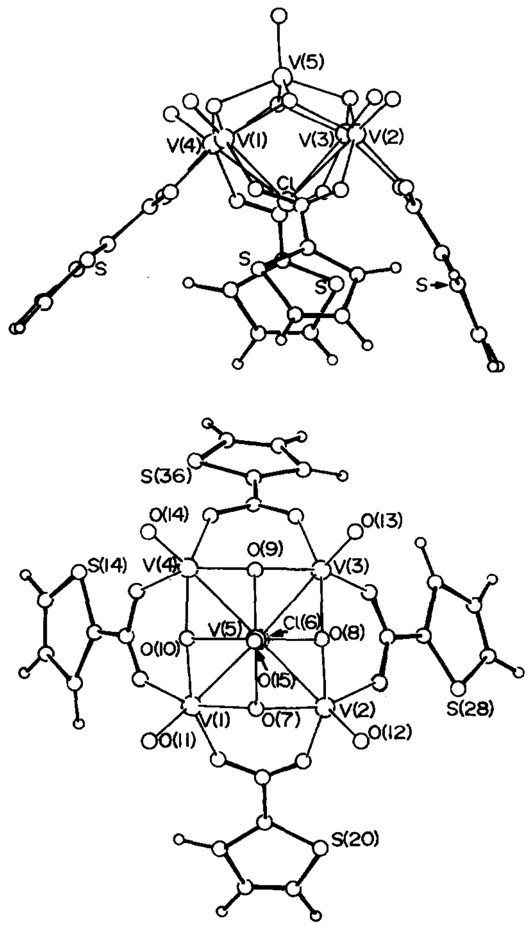

Fig. 3. Two views of the structure of complex **9**, $V_5O_9Cl(tca)_4^{2-}$.

available at the time of writing conclusively establish the V^{IV}, 3 V^{V} nature of **10**, a temperature-independent magnetic moment corresponding to a single unpaired electron per V_4 being observed.

Complexes **9** and **10** can be considered to possess V_xO_y units representing fragments of known iso- or heteropolyvanadates, examples of which include $PV_{14}O_{42}^{9-}$ and $V_{18}O_{42}^{12-}$. The function of the carboxylates is thus to stabilize these "fragments", preventing higher aggregation; it can readily be seen how the RCO_2^- moiety can substitute for an $O_2VO_2^{3-}$ group and terminate higher oligomer formation.

(3) NON-OXO VANADIUM THIOLATE COMPLEXES

We conclude with some recent results in vanadium chemistry not derived from vanadyl starting materials and not possessing any oxygen. Treatment of VCl_3 with 2 $NaSBu^t$ and Bu^tSSBu^t leads to formation of $V(SBu^t)_4$ (**11**), whose structure is shown in Fig. 4.[16] This molecule joins the few other known examples of neutral tetrahedral $M(SR)_4$ species, including $Ti(SBu^t)_4$,[17] $W(SBu^t)_4$[19] and $Mo(SBu^t)_4$.[20] The synthetic procedure is summarized in eq. (7):

$$2\,VCl_3 + 6\,NaSBu^t + Bu^tSSBu^t \rightarrow 2\,V(SBu^t)_4 + 6\,NaCl. \quad (7)$$

In the absence of an oxidizing agent, a black intractable solid is obtained, which we believe to be $NaV(SBu^t)_4$ or polymeric $[V(SBu^t)_3]_n$. In a subsequent reaction carried out in the presence of bipy, we hoped to form soluble $V(SBu^t)_3(bipy)$, and analytical data on the resulting product certainly supported this formulation:

$$2\,VCl_3 + 6\,NaSBu^t + 2\,bipy \rightarrow [V(SBu^t)_2(bipy)_2][V(SBu^t)_4]. \quad (8)$$

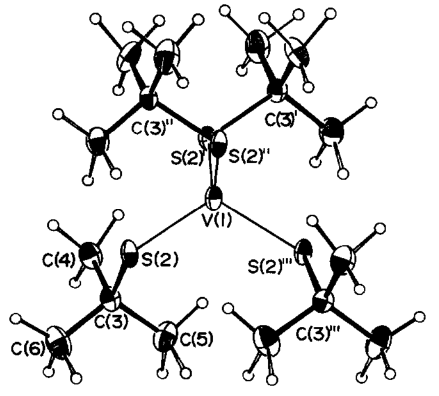

Fig. 4. The structure of complex **11**, $V(SBu^t)_4$.

However, a crystal structure determination showed a ligand redistribution had occurred, for the product was in reality $[V(SBu^t)_2(bipy)_2]^+[V(SBu^t)_4]^-$ (**12**); this would of course yield the analytical formulation "$V(SBu^t)_3(bipy)$". The cation of **12** has an octahedrally-coordinated vanadium and *cis*-Bu^tS^- groups, while the anion is essentially identical to the V^{IV} complex, **11**, in Fig. 4, except for the expected slight lenghthening of V—S bond distances.[16]

CONCLUDING COMMENTS

In an attempt to ascertain the possible fate of crude oil vanadyl impurities under reducing and sulphur-rich conditions, we have investigated a variety of reactivity characteristics of model VO^{2+} complexes. Conversion to VS^{2+}, aggregation to $[VO^{2+}]_2$ and reductive coupling to oxo or non-oxo V^{III} aggregates have all been shown to be possible in the initial stages of hydroprocessing, and probably all occur. Interestingly, the complexity of the observed vanadyl carboxylates suggests not all vanadium impurities may be mononuclear if bound to such functionalities; the behaviour of these synthetic clusters under reducing conditions will be interesting to determine.

Continued reaction under reducing and sulphur-rich conditions is known to yield vanadium products with only sulphur ligation which aggregate and deposit on the molybdenum catalyst. To model these species, we have synthesized a variety of V/S species including $V(SBu^t)_4^{0,+}$, $V_2(edt)_4^{2-}$, $V_3S_4(edt)_3^{3-}$ and $V_4S_2(edt)_6^{2-}$ (the latter two from work not described here[15,20]). This kind of progressive build-up of V/S nuclearity may correspond to that occurring for the crude oil vanadium that ultimately leads to $(V/S)_\infty$ polymer formation. The interaction of such synthetic V/S species with synthetic Mo/S species now provides a model system for the initial stages of V/S deposition on the MoS_2 catalyst, which initiates the contribution by the former to the deactivation of the latter. Such investigations are currently in progress.

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