Progress Report

DOE Grant ER 13702

**A Model Approach to Vanadium Involvement in
Crude Oils and their Refining**

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This section of the proposal will summarize results obtained during the last three years. Our efforts have been directed along several fronts; the unifying theme is that they have all been concerned with elucidating various aspects of vanadium chemistry that are relevant to the presence and involvement of this metal in crude oil refining. A detailed discussion of the occurrence of V in crude oils and its deleterious consequences on refining processes is presented in the main body of the proposal, and only a brief summary will be presented here. The reader may wish to read sections *A. (Introduction)* and *B. (Objectives and Their Significance)* of the main proposal before proceeding further with the Progress Report.

Briefly, heavy crude oils contain a large amount of metal impurities, primarily vanadium species (but also nickel and some others).^{1,2} These comprise both vanadyl porphyrins^{1,2} and vanadyl non-porphyrins,³⁻⁵ the latter with a variety of O, N and/or S ligation. During hydrotreating of crude oils (reaction with H₂ over a supported Mo/S catalyst at 350-450 °C) for upgrading to usable products (hydrodesulfurization (HDS), hydrodenitrification (HDN) and hydrodemetallization (HDM)), the V impurities are converted to insoluble V sulfides (primarily V₂S₃ and V₃S₄) which help poison the fixed-bed Mo catalyst.^{1,2,6-8} Very little is known about the chemistry occurring at a detailed level; basically, it is known that initial impurities are vanadyl (VO)²⁺, i.e., V^{IV} species, and that during the refining processes they are reduced and sulfided into polymers, i.e., the metal is reduced from V^{IV} to ~V^{III}, the oxo is lost, the organic ligation is lost, and the metal is sulfided. In what order and in precisely what manner this overall transformation is occurring is not known, but it is unlikely to be a single pathway given the variety of vanadyl compounds present with different ligand types. To guide our thinking and planning, in fact, we have long used a 'road-map' as in Figure 1. Such transformations can occur both at the heterogeneous catalyst surface or in the bulk "solution" leading to V₂S₃/V₃S₄ deposition both on the fixed-bed catalyst and on the reactor walls. The V impurities are almost all in the high boiling-point asphaltene and resin fractions of the oil, associated with high molecular weight species (thus, they become concentrated in the residues as the low boiling-point organics are removed from the oil by initial thermal distillation).⁹ Upgrading these literally "bottom-of-the-barrel" fractions

represents an important and tough challenge in heavy crude refining and in the total utilization of any crude.

The essence of our research efforts is to develop vanadium chemistry of relevance to this area and to thereby provide fundamental information on the transformations occurring and that might prove useful in catalyst design. On the basis of the above discussion and the "road-map" of Figure 1, our work has encompassed the study of the reactivity chemistry of $[\text{VO}]^{2+}$ species and the formation and characterization of V/S aggregates under conditions designed to mimic those present under hydrotreating conditions. Thus, we are applying an Inorganic Model Approach to provide insights into the chemistry occurring during the refining process. Our emphasis has been on definitive characterization of products using a variety of physical techniques, including X-ray crystallography since hard structural data are particularly lacking in this area. Our work can be sub-divided into several areas, each of which will be described in turn.

A. Studies in $[\text{VO}]^{2+}$ Chemistry. Although $[\text{VO}]^{2+}$ chemistry had been well-studied over several decades, such chemistry with S-based ligation was nevertheless poorly-explored. Our early work had established synthetic procedures to a number of vanadyl thiolate species, e.g., $[\text{VO}(\text{edt})_2]^{2-}$ (edtH_2 = ethane-1,2-dithiol) and we had developed a number of new reactivity characteristics for such species under reducing conditions.^{10,11} During the last three years, we have extended such studies.

For a long time, we had wondered whether a $[\text{VO}]$ complex could be 'sulfided' without loss of the O; previous work had established that $(\text{Me}_3\text{Si})_2\text{S}$ would convert $[\text{VO}]^{2+}$ to $[\text{VS}]^{2+}$, but what we now sought was a $[\text{VO}]$ attached to S groups (to model $[\text{VO}]$ adsorption onto a V/S surface; *vide infra*). Treatment of $[\text{VOCl}_4]^{2-}$ (a convenient source of $[\text{VO}]^{2+}$ groups) with sulfide sources led to intractable, black solids difficult to characterize, but the introduction of chelating 2,2'-bipyridine (bpy) to prevent polymerization gives the discrete new complex

$[\text{VO}(\text{S}_2)_2(\text{bpy})]^+$ (equation 1 and Figure 2)^{F7}; this is the first example of a $[\text{VO}]^+$ in an environment rich in 'inorganic' sulfur (i.e., not thiolate, thioether, etc.). We have characterized it by crystallography and ^{51}V NMR spectroscopy.

The new reagent we introduced with Dr. J. G. Reynolds (Lawrence Livermore) for deoxygenation of $[\text{VO}]^{2+}$ groups under mild conditions, *viz* carboxylic acid halides (RCOCl), has been under further study. Together with John Reynolds, we have shown that a variety of $[\text{VO}]^{2+}$ species may be so treated (eq. 2),^{F2,F6} including those containing S-based ligands (L)

for which other deoxygenation reagents are ineffective. Only for $\text{VO}(\text{PTC})$ (PTC = phthalocyanine) which is very insoluble, is there no deoxygenation observed.

The ligand pyridine-2-thiol (pytH) has been employed as a model for some of the functional groups potentially binding V in crude oils (pyridine N; thiolate S). We have shown that a range of V species in different oxidation states $\text{V}^{\text{II}}\text{-V}^{\text{IV}}$ may be prepared with this ligand *viz* $[\text{VO}(\text{pyt})_2]_2$, $\text{Na}[\text{V}(\text{pyt})_4] \cdot 2\text{thf}$ and $\text{V}(\text{pyt})_2(\text{tmeda})$ (Figures 3-5, respectively).^{F3} In addition to useful X-ray structural and EPR information provided by these complexes, our interest has been in their EI mass spectral behavior: gas-phase fragmentation characteristics, including C-S bond cleavage, can serve to provide insights into high-energy reactions occurring during the harsh conditions of HDS/HDM. We have now finished and published our detailed analysis of the MS behavior of $\text{V}(\text{SBu}^t)_4$ and seen all possible $[\text{VS}_x(\text{SBu}^t)_{4-x}]$ product fragments; interestingly, we see only C-S bond cleavage, not V-S cleavage.^{F1} Similar studies with the pyt complexes have probed similar C-S bond cleavage for the aryl thiolate bond, which is a stronger C-S bond. As for $[\text{V}(\text{SBu}^t)_4]$, binding of pyt to a V^{2+} center facilitates C-S bond cleavage and a number of products are observed in abundance; $[\text{VO}(\text{pyt})_2]_2$, for example, gives a $[\text{VO}(\text{pyt})_2]^+$ parent ion, and $[\text{VO}(\text{pyt})(\text{C}_5\text{H}_5\text{N})]^+$, $[\text{VO}(\text{C}_5\text{H}_5\text{N})_2]^+$ and $[\text{VO}(\text{S})(\text{pyt})]^+$ fragmentation products, among others.

The possibility that some of the V non-porphyrin impurities in crude oils are non-mononuclear is consistent with their molecular weight behavior in size exclusion chromatography,^{3,12,13} and is also consistent with the known ability of, e.g., amines, thiolates, thioethers, carboxylates (and other functional groups found in crude oils) to bridge more than

one metal center. Non-mononuclear $[\text{VO}]^{2+}$ complexes to serve as model complexes are rare, and we have therefore characterized in detail the few that we have obtained in our work. $[\text{VO}(\text{pyt})_2]_2$ described above is one example. The V..V distance ($\sim 4\text{\AA}$) is too large to allow significant inter-metal interactions, but for the related complexes $[\text{V}_2\text{O}_2(\text{edt})_3]^{2-}$, $[\text{V}_2\text{O}_2(\text{het})_3]^{2-}$ (het = 2-hydroxyethanethiolate) and $[\text{V}_2\text{O}_2\text{Cl}_2(\text{het})_2]^{2-}$ (Figures 6-8), the two metals are monoatomically bridged and significantly interacting.^{F13} Magnetochemical studies (variable-temperature magnetic susceptibility measurements and fitting to appropriate equations) show the magnetic exchange interactions are $J = -63.1$, -42.4 and -36.4 cm^{-1} , respectively, i.e., the complexes are antiferromagnetically coupled. We have correlated the variation of J as a function of the extent of overlap of the five-coordinate metal's magnetic orbitals (d_{xy}) in the various geometries adopted, and compared them with other complexes in the literature where six-coordination means that J is not a function of the geometry (*syn* or *anti*). In essence, we can rationalize the weaker coupling in our five-coordinate species ($J = -36$ to -63 cm^{-1}) vs the six-coordinate values ($J = -150$ to -191 cm^{-1}) as due to poorer overlap of magnetic orbitals in the former. This is summarized in Figure 9.^{F13} It is interesting to note that Silbernagel's spectroscopic study of partially-spent catalysts has detected a diamagnetic deposit using ^{51}V NMR, prior to formation of $\text{V}_2\text{S}_3/\text{V}_3\text{S}_4$.^{14,15} This suggests polynuclear species (since mononuclear V^{IV} and V^{III} are both paramagnetic) where strong inter-metal magnetic interactions serve to pair up unpaired electrons. Clearly, bridged $[\text{VO}]^{2+}$ units could not be the origin of the diamagnetic V signature since the calculated J values (strength of electron pairing) are too weak to give a diamagnetic response at ambient temperatures. Candidate models for the diamagnetic species must await developments elsewhere (*vide infra*). It is emphasized at this point that it is work such as that cited from Silbernagel that has convinced us of the need to characterize the magnetic properties of our V_x ($x \geq 2$) products at every opportunity and to record ^{51}V NMR spectra for our diamagnetic products.

In earlier work, we have shown that reaction of $[\text{VOCl}_4]^{2-}$ with three equiv. of VCl_3 in the presence of edt^{2-} and a reducing agent lead to the unusual product $[\text{V}_4\text{OCl}_8(\text{edt})_2]^{2-}$ (eq. 3

and Figure 10).¹¹ This is a type of reaction that we believe represents the initial fate of crude oil $[\text{VO}]^{2+}$ species during reduction, i.e., the terminal $[\text{V}\equiv\text{O}]$ triple bond becomes unstable on

reduction of V^{IV} to V^{III} and the oxo becomes bridging. We have probed this important transformation further. Is the $[VO]^{2+}$ unit really not affected until the e^- is added? Or does a mixed-valence (V^{III}/V^{IV}) oxo-bridged species form that is then merely reduced to a totally- V^{III} oxo-bridged species? To answer this, we have investigated the reactions between $[VOCl_4]^{2-}$ and $VCl_3(thf)_3$ in various ratios but in absence of a reducing agent. In all cases, we have found that the only reaction observed is Cl^- transfer, with no involvement of the $[VO]^{2+}$ group.^{F9} For example, for the 1:1 reaction in MeCN, the products are $[VCl_4(MeCN)_2]^-$ and "[VOCl₃]" (the latter we believe to be dinuclear, viz $[V_2O_2(\mu-Cl)_2Cl_4]^{2-}$) (eq. 4). In CH_2Cl_2 ,

again only Cl^- transfer occurs, this time to give $[V_2Cl_7(thf)_2]^-$ (eq. 5 and Figure 11), no matter what the reaction ratio (which affects only the yield).

Magnetic studies on V^{III} dimers are rare, and although its structure did not suggest that inter-V interactions in $[V_2Cl_7(thf)_2]^-$ would be strong, we thought it appropriate to confirm this. Indeed, variable-temperature studies show $J = -42 \text{ cm}^{-1}$. The antiferromagnetic coupling is again too weak to give a diamagnetic system (except at very low temperatures where only the spin singlet ($S = 0$) ground state is thermally populated).

Because in the very earliest stages of deposition of V onto the Mo catalyst there must be V/Mo heterometal units produced, we have sought to prepare mixed Mo/V systems. No such species are currently known. Our attempts to-date have proven unsuccessful, but one reaction gave an interesting product. Treatment of $VCl_2(dtc)_2$ ($dtc = \text{diethyl-dithiocarbamate}$) with MoS_4^{2-} unfortunately gave a messy reaction with multiple products; one of these was isolated in very small amounts and identified as $[Mo(S_2O)(dtc)_3]$ (Figure 12), a very rare example of a bound S_2O , the O arising presumably from adventitious O_2 .^{F10} The

corresponding S₂ complex Mo(S₂)(dtc)₃ is known and generally accepted as a Mo^V species. Intrigued by our unusual product and recognizing the ambiguity in the literature over the precise redox description of a bound S₂O (is it formally S₂O, S₂O[•] or S₂O²⁻?), we sought and developed a high-yield and rational synthetic route (eq. 6) using *meta*-Cl-perbenzoic acid and

have studied the complex in detail, including crystallography, electrochemistry and EPR.^{F10} Further, we have carried out Extended Hückel calculations on the model complexes MoX(S₂CNH₂)₃ (X = S₂, S₂O, SO₂) to compare their electronic structures and address the redox ambiguity. The MO diagram for the S₂O complex is shown in Figure 13. To cut a long story short, the S₂ and S₂O complexes are both concluded to best be described as Mo^V species containing bound X²⁻ ligands, a picture which we believe to be valid for all S₂O complexes in the literature. At least for this system, and perhaps for others, the bound SO₂ is also best described as SO₂²⁻.

B. V^{III}/O Chemistry. One of the initial transformations of crude oil [VO]²⁺ impurities under hydrotreating conditions is reduction of the metal to V^{III}. As stated above, this necessarily destabilizes the [VO]²⁺ multiple bond and triggers conversion of the oxygen into a bridging mode, as in the formation of [V₄OCl₈(edt)₂]²⁻.¹¹ Well-characterized oxide-bridged V^{III} systems in the literature number only in single figures and we have chosen to prepare and characterize some in detail. Earlier examples from our laboratory included V₂O(Me₂-aet)₄ (Me₂-aet = 2-(dimethylamino)ethanethiolate)¹⁰ and V₂OCl₄(py)₆,¹⁶ both containing the linear [V-O-V]⁴⁺ unit. Recently, we have prepared two additional ones of particular interest. Our objective was to incorporate sulfur-based and aromatic N-based ligands, common crude oil functionalities. To do so, we first developed mononuclear complexes that would be good stepping-stones to these (and other) objectives. The complexes are (NR₄)[V(SPh)₄(bpy)] and [V(SPh)₂(bpy)₂](PF₆), the bpy to prevent polymeric and insoluble [V(SPh)₃]_n.¹⁷ Treatment of [V(SPh)₂(bpy)₂]⁺ with 0.5 equiv. of H₂O leads to clean formation of [V₂O(SPh)₂(bpy)₂]²⁺ (eq. 7

and Figure 14). This is only the second linear $[V-O-V]^{2+}$ complex with thiolate ligation. The complex is paramagnetic with a temperature-independent magnetic moment corresponding to four unpaired electrons.

The same hydrolysis reaction with $[V(SPh)_4(bpy)]^-$ or its $VCl_3/NaSPh/bpy$ reaction mixture leads to a novel complex, $[V_2O(SPh)_4(bpy)_2]$ (eq. 8 and Figure 15).^{F11} The triply-

bridged $[V(\mu-O)(\mu-SR)_2V]^{2+}$ core is unique for V and extremely rare for any metal; two unsymmetrical forms are known for Mo^{VI} dimers. Interestingly, the V..V separation ($\sim 2.6 \text{ \AA}$) is characteristic of a V-V single bond; metal-metal bonding at the V^{III} level is quite rare (but not unknown) and all singly-bonded species have a $\sim 2.6 \text{ \AA}$ V..V separation. Since this is a d^2/d^2 dimer, two electrons remain and account for the observed paramagnetism. Variable-temperature magnetic studies (Figure 15a) indicate the V^{III} centers are antiferromagnetically-coupled ($J = -355 \text{ cm}^{-1}$). Thus, this molecule is another very rare example in which both a metal-metal bond and weaker magnetic coupling of unpaired electrons coexist. The complex behaves magnetically like a d^1/d^1 dimer with a $S = 0$ ground state and $S = 1$ excited state. Since only the latter is responsible for the observed paramagnetism (via thermal population), the variable-temperature solution 1H NMR spectra were recorded and used to provide an alternate determination of J ; the value obtained (-280 cm^{-1}) is satisfactorily close to the solid-state value given the inherent inaccuracies of the two methods.^{F11} Final confirmation of the deduced electronic structure was provided by an Extended Hückel calculation on $V_2O(SH)_4(NH_3)_4$ (Figure 15b) which shows an occupied V-V σ -bonding MO, and a HOMO and LUMO consisting of d-orbitals with δ and δ^* symmetry, respectively, and a HOMO/LUMO gap of only $\sim 0.15 \text{ eV}$; this compares favorably with the singlet-triplet gap determined from the magnetic studies of $\sim 0.10 \text{ eV}$.^{F11} Note again that these V_2O complexes do not provide an example of a diamagnetic V species as detected on partially-spent catalyst surfaces.

C. V/S Complexes. After the V impurities have been reduced and sulfided, it is likely that a variety of V/S species of various nuclearity are present, both on the Mo catalyst surface and in the main body of the oil, which build up in nuclearity and ultimately lead to the V/S

polymers that totally plug the catalyst pores as well as depositing on the reactor walls. These intermediate V/S species likely include the species responsible for the diamagnetic V signatures. We have therefore been preparing and studying discrete V/S aggregates to gain insights into the nature of these intermediates to V_2S_3/V_3S_4 polymers.

Treatment of the V^V species $[VS(S_2)_2(SPh)]^{2-}$ with CS_2 leads to the V^{IV} dimer $[V_2(S_2)_2(CS_3)_4]^{4-}$ (eq. 9 and Figure 16).^{F4} We believe the CS_2 groups undergo a (2 + 2)

cycloaddition reaction with the VS groups, a belief for which there is precedence in the literature.^{F4} The $[V_2(S_2)_2]^{4+}$ core has been seen previously, but not with CS_3^{2-} (perthiocarbonate) ligands. Interestingly, the V..V distance ($\sim 2.87\text{\AA}$) suggests a V-V bond and the complex is diamagnetic giving a clean ^{51}V NMR spectrum. We have studied this system with an Extended Hückel calculation, which supports a V-V bonding interaction and shows a large HOMO/LUMO gap (~ 1.2 eV) rationalizing the diamagnetism. Our feeling is that these metal-metal bonded systems are not likely to be responsible for the diamagnetic species detected on catalyst surfaces since under hydrotreating (reducing) conditions, the catalyst species are likely to be at the V^{III} oxidation state.

We have studied the reactivity characteristics of $[V_2(S_2)_2(CS_3)_4]^{4-}$. Reaction with MeI methylates a S and leads to $[V_2(S_2)(S_2CSMe)_4]$ (eq. 10), which reacts with R_2NH to give the dtc complexes (eq. 11). Such chemistry has been seen before for CS_3^{2-} ligands, but only for mononuclear organometallic complexes.^{F4}

We had several years ago reported,¹⁸ as had others,^{19,20} a complex containing the $[V_2(edt)_4]^{2-}$ ion, but had not studied it in detail. Its V..V separation ($\sim 2.6\text{\AA}$) indicated a V-V single-bond, and Holm²⁰ had briefly suggested that metal-metal bonding and antiferromagnetic coupling were both present. After we characterized $V_2O(SPh)_4(bpy)_2$, as described above, we

returned to $[V_2(edt)_4]^{2-}$ with renewed interest. An Extended Hückel calculation on $[V_2(SH)_8]^{2-}$ showed a V-V σ -bonding orbital and a HOMO and LUMO composed of weakly overlapping d orbitals of δ and δ^* symmetry.^{F14} The HOMO-LUMO gap is small (~ 0.12 eV, ~ 960 cm^{-1}) supporting thermal population of the triplet ($S = 1$) excited state. Since this description reminded us of the $[V_2O(SPh)_4(bpy)_2]$ complex, we carried out a variable-temperature magnetic susceptibility study and found J to be -418 cm^{-1} ; this gave a singlet-triplet gap ($|2J|$) of 936 cm^{-1} , satisfying close to the Extended Hückel prediction.^{F14} $[V_2(edt)_4]^{2-}$ and $[V_2O(SPh)_4(bpy)_2]$ are thus two electronically very similar and unusual molecules.

Since $[V_2(edt)_4]^{2-}$ has a reversible one-electron oxidation in the cyclic voltammetry, at $-0.48V$ vs Ag/AgCl, we tried and succeeded in generating and isolating in pure form the oxidized material $(NEt_4)[V_2(edt)_4]$ using the thianthrene radical cation as the oxidizing agent. Its magnetic study showed a temperature-independent moment corresponding to one unpaired electron, confirming our previous conclusions on $[V_2(edt)_4]^{2-}$. Further, the EPR signal at 260K looks almost like that of a mononuclear V^{IV} (i.e., $S = 1/2$) complex, showing the unpaired electron is essentially localized on one V. At higher temperatures, the signal becomes more complex, indicating greater electron delocalization between the two metal centers.^{F14}

Although $[V_2(edt)_4]^{2-}$ has a metal-metal bond, it is not expected to be strong (because V is a 3d metal) and reaction with $VCl_3(thf)_3$ indeed cleaves it to give the new ion $[V_3(edt)_3Cl_6]^{3+}$ (eq. 12 and Figure 17). The species has long ($\sim 3.1\text{\AA}$) V..V separations, i.e., no

V-V bonds, and is paramagnetic, but we have not yet had the opportunity to carry out a variable-temperature magnetic susceptibility study.

Reaction of $[V(SPh)_2(bpy)_2]^+$ with four equivalents of elemental S leads to clean formation of $[V_3S(S_2)_3(bpy)_3]^+$ (Figure 18).^{F5,F12} No change to the oxidation state (V^{III}) occurs the PhS^- being the electron donors for reduction of S to S^{2-} and S_2^{2-} . We have studied this material in great detail because we have discovered that it is diamagnetic even at room temperature, i.e., an $S = 0$ ground state and no thermally-accessible $S \neq 0$ excited states. $[V_3S(S_2)_3(bpy)_3]^+$ is the first diamagnetic V^{III}/S aggregate and thus an interesting development in our work.

Some additional description of Silbernagel's work is called for here. In his ^{51}V NMR and EPR study of the V deposits on used, alumina-supported Mo/S hydrotreating catalysts, he observed that at low V loadings ($< \text{wt } \%$), the characteristic EPR spectra of $[\text{VO}]^{2+}$ species was detected, but different from those of the $[\text{VO}]^{2+}$ impurities in the untreated crude oil.^{14,15} These "altered- $[\text{VO}]^{2+}$ " species could have the $[\text{VO}]^{2+}$ group adsorbed on the Mo/S surface (*vide infra*). At greater V loading ($\sim 5 \text{ wt } \%$), the diamagnetic V phase is observed, and at still greater V loadings ($\geq 10 \text{ wt } \%$), the dominant V phase is V_2S_3 (and variations thereof, such as V_3S_4) (Figure 19). The diamagnetic phase has always been intriguing from an inorganic viewpoint because of the large paramagnetism normally associated with V^{III} systems which make detection of ^{51}V signals difficult. Further, as we have carefully emphasized above, even known dinuclear metal-metal bonded $\text{V}^{\text{III}}/\text{S}$ systems only contain a single-bond and still display significant paramagnetic properties from remaining unpaired electrons. We have thus for a long time sought diamagnetic $\text{V}^{\text{III}}/\text{S}$ systems to act as potential models for the diamagnetic species on the catalyst surface and provide insights into its/their identity. Note that the V^{IV} species, $[\text{V}_2(\text{S}_2)_2(\text{S}_2\text{CSR})_4]^{2-}$, described earlier are also diamagnetic, although, as stated already, it appears more likely that the V/S species are in the V^{III} state on the catalyst surface.

An Extended Hückel MO calculation has been carried out on the model system $[\text{V}_3\text{S}(\text{S}_2)_3(\text{NH}_3)_6]^+$ to document the electronic structure of this unusual diamagnetic species.^{F5,F12} The highest occupied orbitals are metal-metal bonding in character and composed primarily ($\approx 70\%$) of metal d orbitals. There is a large HOMO/LUMO gap (1.3 eV) rationalizing the diamagnetism as a result of the six metal d orbitals becoming paired in three metal-metal bonds between the V^{III} ions to give an $S = 0$ ground state, with the large HOMO/LUMO gap preventing thermal population of $S \neq 0$ excited states. Solid-state magnetic studies, together with solution NMR studies confirm $[\text{V}_3\text{S}(\text{S}_2)_3(\text{bpy})_3]^+$ is diamagnetic. Electrochemical studies show the complex undergoes a reversible one-electron oxidation at -0.47 V vs ferrocene; we have generated the oxidized form, $[\text{V}_3\text{S}(\text{S}_2)_3(\text{bpy})_3]^{2+}$, *in situ* and observed on EPR signal at 5K in the $g \approx 2$ region, consistent with the expected $S = \frac{1}{2}$ spin state.

Thus, we have finally obtained $\text{V}^{\text{III}}/\text{S}$ species that are diamagnetic and that could be related to the species forming on the Mo/S catalyst during early stages of V deposition. If the possibility is entertained that these might be V^{IV} species, then complexes such as

$[\text{V}_2(\text{S}_2)_2(\text{CS}_3)_4]^{4+}$ and others in the literature are also potential models; if, however, the more likely possibility that they are V^{III} species is considered solely, then our work to date suggests that trinuclear species similar to $[\text{V}_3\text{S}(\text{S}_2)_3(\text{bpy})_3]^+$ may be forming on the surface which then polymerize to the V sulfide polymer. Note that bpy is itself an acceptable mimic of heteroaromatic N organics in crude oils, such as may be bound to V in the non-porphyrin impurities. Of course, a number of different organic groups could also be bound in the peripheral positions.

D. Adsorption of $[\text{VO}]^{2+}$ Groups on Catalyst Surfaces. To model the adsorption on $[\text{VO}]^{2+}$ groups onto the surface of the growing V sulfide phase during HDM catalysis, we have sought complexes containing a $[\text{VO}]^{2+}$ group bound to four S atoms. The $[\text{VO}(\text{S}_2)_2(\text{bpy})]^-$ complex (Figure 2) was such a species, but its relationship to a surface-bound $[\text{VO}]^{2+}$ is admittedly tenuous. Nevertheless, together with $[\text{VO}(\text{edt})_2]^{2-}$, they did establish the stability of a $[\text{VO}]$ group bound to a S-rich ligand set. More interesting were the complexes obtained in a reaction between $\text{VCl}_3(\text{thf})_3$, bpy, and edt^{2-} ; isolated from this mixture and structurally characterized was a mixture of $[\text{V}_3\text{O}_2\text{Cl}_2(\text{edt})_2(\text{bpy})_2]$ (Figure 20) and $[\text{V}_3\text{OCl}_3(\text{edt})_2(\text{bpy})_2]$ (Figure 21).²² These cocrystallized, the former we believe forming from reaction of the latter with adventitious O_2 during the long crystallization times employed; attempts to obtain these materials in pure form for detailed study are an important objective for future work. The structures were very surprising, particularly that of $[\text{V}_3\text{O}_2\text{Cl}_2(\text{edt})_2(\text{bpy})_2]$; here is a $[\text{VO}(\text{edt})_2]^{2-}$ unit, exactly the same as seen in the mononuclear $[\text{VO}(\text{edt})]^{2-}$ ion, acting as a 'bridging group' across a linear $[\text{V}-\text{O}-\text{V}]^{4+}$ unit (also seen by itself in discrete complexes). Apart from the novelty of the structure, the latter also suggests how the initial interaction between a non-porphyrin $[\text{VO}]^{2+}$ impurity in crude oils and a catalyst surface (here modelled by the V-O-V unit) may be occurring. Vanadyl porphyrins are already believed to be interacting with the catalyst in exactly this way if with a surface donor site (or upside-down at an acceptor site) (Figure 22),^{23,24} followed by reductive loss of the porphyrin ring and attachment of the liberated $[\text{VO}]^{2+}$ group to the surface (*vide infra*). The identification of $\text{V}_3\text{O}_2\text{Cl}_2(\text{edt})_2(\text{bpy})_2$ suggests many future studies along related lines (see Research Plan).

Although an interesting and important development, the above still did not provide what we had long sought *viz* $[\text{VO}]^{2+}$ groups attached to a $[\text{V}_x\text{S}_y]$ cluster that could be thought

of as a piece of a V sulfide surface. Takeuchi *et al.*²⁵ had proposed that $[\text{VO}]^{2+}$ groups liberated from vanadyl porphyrins or non-porphyrins would be adsorbed onto the surface where they would then be sulfided, building up another layer of the growing V_2S_3 or V_3S_4 phase (Figure 23). But how to model such a surface process? We were fortunate to find that hydrolysis of the extremely moisture-sensitive ion $[\text{VS}(\text{edt})_2]^{2-}$, available from previous work, gave $[\text{V}_6\text{O}_2\text{S}_4(\text{edt})_6]^{3-}$ (Figure 24).^{F8} Here can be seen $[\text{VO}]^{2+}$ groups attached to a $[\text{V}_4\text{S}_4]$ core that can be thought of as a 'piece' of a V sulfide. The $[\text{VOS}_4]$ coordination environment agrees with EPR and EXAFS studies that have concluded that surface-adsorbed $[\text{VO}]^{2+}$ units are also in a $[\text{VOS}_4]$ environment.²⁵⁻²⁷ Interestingly, in much earlier work, the complex $[\text{V}_4\text{S}_2(\text{edt})_6]^{2-}$ had been characterized by us; this is structurally very related to $[\text{V}_6\text{O}_2\text{S}_4(\text{edt})_6]^{3-}$, as emphasized in Figure 25. Basically, the V_4 complex can be thought of as a piece of a V sulfide surface and the V_6 complex as a model for adsorption of $[\text{VO}]^{2+}$ units on the latter. Particularly interesting was the observation that the complexes undergo related redox processes (centered in their V_4 cores) and that the presence of the $[\text{VO}]^{2+}$ groups on the V_6 cluster serves to make reductions easier (less negative potentials; Figure 26). This suggests that binding of $[\text{VO}]^{2+}$ groups to the surface of the growing V sulfide phase during HDM may in fact assist in the reduction of the V ions to the $\leq \text{V}^{\text{III}}$ level in the products, V_2S_3 and V_3S_4 , i.e., the adsorbed species are affecting the intrinsic properties of the surface. This is an interesting observation that needs to be extended to other model systems.

E. Conclusions. We are pleased that we have been fortunate to achieve progress in all the directions that we have been pursuing, from reactivity studies of simple $[\text{VO}]^{2+}$ complexes, to preparation and study of V/S aggregates, and even in our search for models of chemistry occurring at catalyst surfaces. Clearly, our concentration on preparing pure, crystalline, soluble and discrete molecular and ionic products that can be crystallized and studied by a variety of techniques, including definitive structural characterization by crystallography, has paid dividends in providing a wealth of hard data and complexes that can provide insights into this extremely complex industrial process. In addition, our work complements the EPR, EXAFS and other studies on the crude oil impurities themselves and the nature of deposits on catalysts by providing well-characterized model complexes to act as benchmarks to aid data

interpretation. Our work is merely one component of the multi-disciplinary effort required to tackle this difficult problem in detail.

F. Publications.

- F1. Preparation and Properties of Mononuclear Vanadium Thiolates: Structural Characterization of the $[\text{V}(\text{SBU})_4]^{0-}$ Pair and C-S Bond Cleavage in $\text{V}(\text{SBU})_4$ in the Gas Phase. D. D. Heinrich, K. Folting, J. C. Huffman, J. G. Reynolds, and G. Christou, *Inorg. Chem.* **1991**, *30*, 300-305.
- F2. Deoxygenation of Oxovanadium(IV) Complexes Under Mild Conditions: Synthesis and Structural Characterization of *Cis*-dihalobis(dialkyldithiocarbamate)-vanadium(IV). Edward L. Jones, John G. Reynolds, John C. Huffman, and George Christou, *Polyhedron* **1991**, *10*, 1817-1825.
- F3. Pyridine-2-thiolato Complexes of Vanadium in Oxidation States II, III, IV with Unusual Structural Features. J. G. Reynolds, S. C. Sendlinger, A. M. Murray, J. C. Huffman, and G. Christou, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 253-255.
- F4. Reactivity Studies of Mononuclear and Dinuclear Vanadium-Sulfide-Thiolate Compounds. Shawn C. Sendlinger, John R. Nicholson, Emil B. Lobkovsky, John C. Huffman, Dieter Rehder, and George Christou, *Inorg. Chem.*, **1993**, *32*, 204.
- F5. New Structural Types in Vanadium Chemistry; Vanadium(III) Complexes Containing the $[\text{V}_3(\mu_3\text{-S})(\mu\text{-S}_2)_3]^+$ and $[\text{V}_2(\mu\text{-O})(\mu\text{-SPh})_2]^{2+}$ Cores. Norman S. Dean, Kirsten Folting, Emil B. Lobkovsky, and George Christou, *J. Am. Chem. Soc.* **1993**, *32*, 594..
- F6. Deoxygenation of Oxovanadium(IV) Complexes Under Mild Conditions: Conversion of Vanadyl Species to the Corresponding Dihalides with Carboxylic Acid Halides. John G. Reynolds, Edward L. Jones, John C. Huffman, and George Christou, *Polyhedron* **1993**, *12*, 407.
- F7. A New Vanadium(V) Persulfide Complex: $(\text{NEt}_4)[\text{VO}(\text{S}_2)_2(\text{bpy})]$. S. L. Castro, J. D. Martin, and G. Christou, *Inorg. Chem.* **1993**, *32*, 2978.
- F8. $(\text{NEt}_4)_2[\text{V}_6\text{O}_2\text{S}_4(\text{edt})_6]$: a Model for the Adsorption of Naked $[\text{VO}]^{2+}$ Units on Vanadium Sulphide Surfaces. K. A. York, K. Folting, and G. Christou, *J. Chem. Soc., Chem. Commun.* **1993**, 1563.

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- F9. Preparation, Crystal Structure and Magnetochemistry of $[\text{NEt}_4][\text{V}_2\text{Cl}_7(\text{thf})_2] \cdot \text{CH}_2\text{Cl}_2$. J. R. Rambo, S. L. Bartley, W. E. Streib, and G. Christou, *J. Chem. Soc., Dalton Trans.*, submitted for publication.
- F10. Synthesis, Characterization and Molecular Structure of the S_2O Complex $\text{Mo}(\text{S}_2\text{O})(\text{S}_2\text{CNEt}_2)_3 \cdot \frac{1}{2}\text{Et}_2\text{O}$. M. A. Halcrow, J. G. Reynolds, J. C. Huffman, and G. Christou, *Inorg. Chem.*, submitted for publication.
- F11. A Combination of Metal-Metal Bonding and an Antiferromagnetic Exchange Interaction in the d^2-d^2 Complex $[\text{V}_2\text{O}(\text{SPh})_4(\text{Me}_2\text{-bpy})_2] \cdot \text{thf}$. N. S. Dean, S. L. Bartley, W. E. Streib, E. B. Lobkovsky, and G. Christou, *Inorg. Chem.*, manuscript in preparation.
- F12. Structural, Spectroscopic and Physicochemical Characterization of $[\text{V}_3(\text{S}_2)_3(\text{bpy})_3](\text{PF}_6)_3$, a Diamagnetic Vanadium(III) Aggregate. N. S. Dean, K. Folting, and G. Christou, *Inorg. Chem.*, manuscript in preparation.
- F13. Dinuclear Vanadyl Thiolate Complexes: Structural, Spectroscopic and Magnetochemical Characterization of $[\text{VO}(\text{L-L})_3]^{2+}$ Complexes ($\text{L-L} = \text{SCH}_2\text{CH}_2\text{S}$ or $\text{OCH}_2\text{CH}_2\text{S}$). J. R. Rambo, J. K. Money, J. C. Huffman, K. Folting and G. Christou, *Inorg. Chem.*, manuscript in preparation.
- F14. Magnetochemical Investigation of $(\text{NEt}_4)_2[\text{V}_2(\text{edt})_4]$, a Complex with a V-V Single Bond and an Antiferromagnetic Exchange Interaction: Isolation and Characterization of the Oxidized Form $[\text{NEt}_4][\text{V}_2(\text{edt})_4]$. J. R. Rambo, S. R. Bartley, and G. Christou, *Inorg. Chem.*, manuscript in preparation.
- F15. Vanadium(II,III,IV) Complexes with pyridine-2-thiolate Ligation: a Structural and Mass Spectral Investigation. J. G. Reynolds, S. C. Sendlinger, A. M. Murray, J. C. Huffman, and G. Christou, *Inorg. Chem.*, manuscript in preparation.

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Possible Routes From VO^{2+} to V_xS_y

$L = N, O, S$

Fig. 1

Fig. 2

Fig. 5

Fig. 3

Fig. 4

Fig. 7

Fig. 6

Fig. 8

Fig. 9

Fig. 12

Fig. 13

Fig. 10

Fig. 11

Fig. 14

Fig. 15

Fig. 15b

Fig. 15a

Fig. 16

Fig. 17

Fig. 18

Vanadium Distribution and Chemical Forms at Different Positions in a Reactor Used to Treat a Heavy Feed.

Fig. 19

Fig. 20

Fig. 21

Fig. 22

Fig. 24

Fig. 23

Model of HDM on Vanadium Sulfide.

Fig. 25

Fig. 26

* = isolated levels

[2] ⁻	$\xrightarrow{0.00 \text{ V}}$	[2] ²⁻	$\xrightarrow{-0.42 \text{ V}}$	*[2] ³⁻	$\xrightarrow{-0.97 \text{ V}}$	[2] ⁴⁻
[3] ⁻	$\xrightarrow{-0.56 \text{ V}}$	*[3] ²⁻	$\xrightarrow{-1.01 \text{ V}}$	[3] ³⁻	$\xrightarrow{-1.82 \text{ V}}$	[3] ⁴⁻
V ^{III} , 3V ^{IV}		2V ^{III} , 2V ^{IV}		3V ^{III} , V ^{IV}		4V ^{III}

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