CHEMICAL REVIEWS

THE CHEMISTRY OF OXOVANADIUM(IV)[1]

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CONTENTS

I. INTRODUCTION

Vanadium has a rich and varied chemistry which includes compounds in all oxidation states from −1 to +5. This review, however, will only be concerned with compounds of tetravalent vanadium. More specifically, it will cover those compounds in which there exists a strong vanadium–oxygen multiple covalent bond capable of persisting during chemical reactions involving the other ligands within the first coordination sphere of the vanadium ion. This restriction will delimit the review to an estimated 98% of the solid compounds and all of the aqueous solution species of tetravalent vanadium, that is, all of those which possess the oxovanadium(IV) entity, VO^{2+}. It will exclude consideration of the many pentavalent vanadium compounds which also possess that feature (the strong, persistent V–O bond) which makes the VO^{2+} chemistry so interesting, namely, those containing the dioxovanadium(V), VO_2^+, or the oxovanadium-(V), VO^{3+}, species. A recent review (71) dealing with the structure and reactivity of the oxyanions of the transition metals devotes some attention to the VO_4^{3-} species. But the voluminous literature dealing with solid vanadates(V), the compounds of VO^{3+} and VO_2^+, as well as the complicated solution chemistry, really deserves separate attention. A few compounds of trivalent vanadium presumably containing the oxovana-

dium(III) entity, VO^+, have been prepared. However, very little is known about the vanadium–oxygen bond in these compounds except that it does not appear to remain intact during chemical reactions in which no oxidation occurs. A summary of the preparation and some properties of VOCl (108, 315) has appeared recently (57, 325). The infrared spectra of the lower valent oxides VO and V_2O_3 are poorly defined and do not display the characteristic strong and narrow absorption bands in the metal–oxygen multiple bond stretching region shown by both V_2O_4 and V_2O_5, which indicates that the former compounds are considerably less covalent than the latter (120). Hence, further consideration of the chemistry of trivalent vanadium will not be given. Finally, the analytical chemistry papers dealing with oxovanadium(IV) will not be covered unless they contribute to the knowledge of basic properties. In analytical papers there is often lacking a knowledge (or even concern) of what the species involved actually are or might be.

Although there are nearly 60 oxometal entities known with the transition metals, of the type MO_x^{n+} (where x may be 1, 2, or 3, and n may be 1, 2, 3, 4, or 5), only two, UO_2^{2+} and VO^{2+}, have been prepared in a large number and variety of stable complexes, have been subjected to numerous and varied experimental studies, and have been discussed theoretically (330). The voluminous chemistry of dioxouranium(VI) (and the other dioxoactinyls) is in need of review because so much literature has appeared concerning this species since the

List of Abbreviations Used in This Review

1. 3-ASE, 3-aldehydosalicylic acid ethylenediamine
2. bigH, biguanide
3. 5-Br-sal-o-HA, 5-bromosalicylidene-o-hydroxyanil
4. BzQ, 5,6-benzoquinaldinate
5. $C_7H_6N_2O_4$, p-nitrobenzohydroxamic acid
6. $C_8H_8NO_2$, p-methylbenzohydroxamide
7. $C_8H_8NO_3$, p-methoxybenzohydroxamide
8. cat, catecholate dinegative ion
9. 5-Cl-sal-o-HA, 5-chlorosalicylidene-o-hydroxyanil
10. DCHT, 1,2-diaminocyclohexane-N,N,N',N'-tetraacetate
11. dipy, 2,2'-dipyridine
12. DMSO, dimethyl sulfoxide
13. DNS, 1,8-dihydroxynaphthalene-3,6-disulfonate ion
14. EDTA, ethylenediaminetetraacetate quadrinegative ion
15. en-bis-sal, ethylenediaminebissalicylaldehyde
16. Et, ethyl
17. GH, guanylalkyl- and guanylalkoxyalkylureas
18. HEDDA, N,N'-dihydroxyethylethylenediaminediacetate ion
19. HIMDA, N-hydroxyethyliminodiacetate ion
20. i-pr-NH₂, isopropylamine
21. mal, malonate dinegative ion
22. Me, methyl
23. 5-NO₂-Q, 5-nitroquinaldinate ion
24. o-HAPE, o-hydroxyacetophenoneethylenediamine
25. ophen, 1,10-phenanthroline
26. ox, oxalate dinegative ion
27. pc, phthalocyanine dinegative ion
28. PDS, pyrocatechol-3,5-disulfonate ion
29. Ph, phenyl
30. pn-bis-sal, propylenediaminebissalicylaldehyde
31. py, pyridine
32. QH, quinaldinic acid
33. RH₂, benzohydroxamic acid
34. sal, salicylaldehyde dinegative ion
35. sal-o-HA, salicylidene-o-hydroxyanil
36. sal-o-phend, salicylaldehyde-o-phenylenediamine
37. 5-SSA, 5-sulfosalicylate ion
38. t-bu-NH₂, t-butylamine
39. TH, 3-hydroxy-1,3-diphenyltriazene
40. T'H, substituted triazenes
41. THF, tetrahydrofuran

general review in 1960 by Comyns (79). However, the chemistry of the oxovanadium(IV) species is likewise very extensive and this appears to be the first review devoted to the total subject, although a few special phases of oxovanadium chemistry were briefly reviewed in 1951 by Ducret (94).

It is perhaps appropriate at the outset to give some justification to a review devoted entirely to so seemingly narrow a topic as the chemistry of a single chemical entity. (1) The oxovanadium(IV) ion is very likely the most stable biatomic ion known. (2) It forms many stable complexes, which may be anionic, cationic, or neutral, and they may be found in the solid, liquid, or even vapor phase. The VO^{2+} entity has a discrete existence in compounds in the solid state, in the fused state, in solution, and in the vapor state. (3) The ion is a d^1 system (tetravalent vanadium having the ground-state configuration $[Ar]3d^1$), giving it some important similarities (via the "hole" formalism) to the Cu^{2+} d^9 system. This property alone confers an unusual significance upon the VO^{2+} ion since the other known d^1 systems: (Ti, Zr, Hf, Th) (III), (Nb, Ta, Pa) (IV), (Cr, Mo, W, U) (V), (Mn, Tc, Re) (VI), and (Ru, Os) (VII), are all much less stable and less common species and, except for Ti(III) and Mo(V), form very few compounds amenable to detailed and facile investiga-

tion. The value from a theoretical standpoint of being able to study a species having but a single electron outside of a closed shell and available in such a variety of environments cannot be overstated. (4) The oxovanadium(IV) complexes have been investigated by: (a) a variety of methods, such as potentiometry and polarography, in solution; (b) magnetic susceptibility measurements; (c) X-ray diffraction studies; (d) visible and ultraviolet spectroscopy; (e) infrared and Raman spectroscopy; and (f) electron paramagnetic resonance spectroscopy. (5) Finally, there is the intriguing novelty with this species of making observations on the changes with environment in some of the properties of the metal–oxygen multiple bond, acting as a kind of internal molecular probe, in order to try to learn more about other metal–ligand bonds. It was this possibility which first interested the present author in oxocation chemistry in general and oxovanadium chemistry in particular. It is one purpose of this review to stimulate further research in this area.

A brief discussion of nomenclature is necessary. The term "vanadyl" by itself is ambiguous; it does not distinguish VO^{2+}, which should be termed oxovanadium, (IV) ion; VO^{3+}, which is then oxovanadium(V) ion; and VO_2^+, which then should be dioxovanadium(V) ion. "Vanadyl(IV)" is acceptable as there is only one mononuclear monoxo species of vanadium(IV) known. Obviously, however, vanadyl(V) and pervanadyl are both ambiguous terms. *Chemical Abstracts* indexes oxovanadium (IV) compounds under four headings. (1) The simple (or presumed simple) compounds appear under "Vanadyl"; for example, VOF_2 is listed as *Vanadyl fluoride*. (2) Anionic complexes are listed under "Vanadates(IV)" (these being the vanadites or hypovanadates of the early literature); for example, $VO(NCS)_5^{3-}$ would be found as *Vanadate(IV), oxopentaisothiocyanato-*. (3) The cationic complexes can be found under "Vanadium Compounds" with the oxo- prefix; for example, $VO(dipy)_2(ClO_4)_2$ is listed as *oxobis(2,2'-bipyridine)vanadium perchlorate*. (4) Finally the neutral complexes are found listed under "Vanadium"; for example, $[VO(ophen)Cl_2]$ is listed as *Vanadium, oxodichloro-(1,10-phenanthroline)-*.

II. THE COMPOUNDS OF OXOVANADIUM(IV)

An index to the literature of vanadium from its discovery data, 1801, to 1877, is given by Rockwell (301). Early reviews of vanadium chemistry are to be found just after the turn of the century (111, 249, 279) and, of course, there are those comprehensive, often nondiscriminatory, surveys by Mellor (228), Gmelin (145), and Sidgwick (342), as well as the more recent (1958) "Nouveau Traité de Chemie Minerale," Tome XII (265). The survey of oxovanadium(IV) compounds which follows represents an attempt to distil from a great mass of published literature that part which

appears to the present author to be correct and likely to be of value or at least interest to the chemists concerned today with vanadium and oxometal chemistry.

A. THE SIMPLE COMPOUNDS AND THE COMPLEXES WITH UNIDENTATE LIGANDS ONLY

1. Dioxide and Hydroxides

That the oxide V_2O_4 contains the VO^{2+} entity may be deduced from its structure (3, 166, 217), which reveals one particularly short V–O distance of 1.76 Å.; or from the structure (114) of the mineral duttonite, $V_2O_4 \cdot 2H_2O$, in which there is an even shorter V–O distance of 1.65 Å. Berzelius (32–34) was apparently the first to obtain the tetravalent oxide, which he obtained by heating equimolar parts of V_2O_3 and V_2O_5 in the absence of air (57). Since then it has been obtained by oxidation of trivalent vanadium, but more often by reduction of pentavalent vanadium using a great variety of reducing agents (67, 84, 106, 152–154, 160, 170, 203, 228, 324), including, most recently, sunlight (319). Since the first hydrate was prepared in 1906 (132), the hydrates have received intermittent study (31, 65, 143, 264). The pink compound $V_2O_4 \cdot 2H_2O$ can be dehydrated isothermally (31) to two distinct compounds of composition $V_2O_4 \cdot H_2O$. Magnetic susceptibility measurements have been carried out on the mono- and dihydrated oxide as well as the anhydrous oxide (6, 92, 300), and the values range from 1.62 to 1.73 B.M. for the hydrated compounds, whereas the latter is antiferromagnetic. Vanadates(IV) are generally quite unstable toward oxidation (vide infra), but they are nevertheless well known (84, 90, 204, 302). The most common ions which are formed are $V_2O_6^{4-}$, $V_2O_5^{2-}$, and $V_4O_9^{2-}$ (214). The solid compounds are not nearly so numerous as the more stable vanadates(V), to which they are usually readily oxidized (58).

The interesting compound $VO(OH)(SH)$, a black powder, has been obtained by H_2S reduction of NH_4VO_3 in solution (62). It begins to lose H_2S at 40°, and at 390° only VO_2 remains providing the heating is carried out in an inert atmosphere.

2. Halides

The anhydrous fluoride, VOF_2, is known (63, 160, 281, 317) as well as some hydrated forms, $VOF_2 \cdot xH_2O$ (63, 267, 270, 271, 332). Recent investigation (63) of the system VO_2–HF–H_2O by an isothermal method has established a pale blue $VOF_2(4H_2O)$ and a green $VOF_2(2H_2O)$, whereas at HF concentrations above 68.5% anhydrous VOF_2 is stable. A series of complexes $VOF_2 \cdot RF$ (where R = M(I) or M(II)/2) has been prepared (16, 27, 112, 275, 276, 372, 373), and they may all be formulated as either $R_2[VOF_4]$ or $R_2[VOF_5]$ (2, 16, 241). Fluoro and chloro complexes have been studied in aqueous solutions (2), and the former ligand

forms the more stable complexes. The fluoro complexes of VO^{2+} also have been found to be thermodynamically more stable than those of Cu^{2+}, Zn^{2+}, and Ni^{2+}, but not as stable as those of UO_2^{2+} (2). There are other indications, from both infrared and visible-ultraviolet spectral data (vide infra), that fluoride is perhaps the strongest ligand atom known for vanadyl (IV). Apparently the small fluoride ion with its high charge density can very easily relieve its compact charge situation by transferring charge onto the vanadium atom which has energetically available and empty orbitals. It would be very interesting to have e.s.r. and magnetic susceptibility data for the VOF_5^{3-} species, since these data could be utilized to verify and expand the foregoing suggestion. The author in collaboration with I. Bernal hopes to obtain such data very soon.

The anhydrous bright green chloride, $VOCl_2$, has been prepared (57, 123, 306, 308) (a) by passing a mixture of $VOCl_3$ vapor and hydrogen gas through a red-hot tube, and (b) by the action of zinc on $VOCl_3$ in a sealed tube at 400° (342). The product is extremely deliquescent. Its catalytic activity with Et_3Al in vinyl polymerization has been investigated (129), but the anhydrous material must still be considered a laboratory curiosity which is both difficult to handle and to study. The hydrated compound, now commercially available, is formed when V_2O_5 reacts with concentrated hydrochloric acid or when VCl_4 hydrolyzes (84, 215, 348, 388). It is a convenient alternative to the sulfate as a starting material for the preparation of many oxovanadium(IV) compounds. The following adducts of $VOCl_2$ (I) with monodentate ligands other than water are known: (I)3MeOH, (I)(2py)(MeOH), (I)(3py)(0.5EtOH), (I)2py, (I)3py (122, 124); (I)3-DMSO (169, 173, 332); (I)4Ph₃AsO, (I)2Ph₃PO (173); (I)(2H₂O)(2Et₂O) (280); (I)3THF (194); (I)(2Ph₃P)-(2H₂O) (218); and (I)(2PhN₂Cl)(H₂O), (I)(2p-MeO-C₆H₄N₂Cl)(H₂O) (74). An adduct with acrylonitrile, (I)(2 acryl)(0.42C₆H₆), is thought possibly to be a clathrate, trapping benzene (195). At least two adducts form with RHCl (R = pyridine or quinoline); $VOCl_2(4RHCl)(xH_2O)$ comes out of excess base with solvents such as absolute alcohol or glacial acetic acid, and $VOCl_2(2RHCL)(xH_2O)$ forms in alcohol–water solvents (205). Solid complexes $R_2[VOCl_4(H_2O)]$ (169) and $R_2[VOCl_4]$ (331) are known, but they decompose easily and rapidly in aqueous solutions. In general, it is observed that chloride is not a strong ligand and it is not strongly attached like fluoride; it is only when there are other ligands also attached to the vanadyl(IV) ion that the chloride seems to be bound with any firmness at all.

The bright yellow $VOBr_2$ can be obtained by the action of S_2Br_2 and Br_2 on V_2O_5 at elevated temperatures (308, 316), but it is not nearly so stable as its adducts with molecules such as water or DMSO (169, 332).

TABLE I

BOND LENGTHS AND V–O STRETCHING FREQUENCIES FOR SOME OXOVANADIUM COMPOUNDS[a]

Compound	V–O length, Å.	V–X length, Å.	Ref.	V–O stretch, infrared, cm.$^{-1}$	Ref.
VOCl$_3$	1.56	2.12	262	1035	229
[VO(acac)$_2$]	1.56	1.97(O)	91	996	334
V$_2$O$_5$	1.58	1.77, 1.88, 2.02, 2.81	12, 64	1020	24, 334
(NH$_4$)$_2$[VO(NCS)$_4$(H$_2$O)](4H$_2$O)	1.62	2.04(N) 2.22(O)	146	982, 963	146
V$_2$O$_4$(2H$_2$O)	1.65		114	968(955)	334(65)
VO(H$_2$O)$_5$SO$_4$	1.67	2.3, 2.4	216, 261	975, 1003	334
V$_2$O$_4$	1.76	1.86, 1.87, 2.01, 2.03, 2.05	3, 166	—	—

[a] Data for Li$_{1+x}$V$_3$O$_8$, Na$_{2-x}$V$_6$O$_{17}$, K$_{0.33}$V$_2$O$_5$, KVO$_3$(H$_2$O), and Ca(VO$_3$)$_2$(2H$_2$O) have been collected by Bachmann and Barnes (12), and the shortest V–O distances are 1.60, 1.56, 1.55, 1.65, 1.63, and 1.64 Å., respectively, for these compounds.

Reports of iodides of tetravalent vanadium are not firmly based, and, since iodide can reduce vanadium below this oxidation state, there is little chance that stable iodides will ever be prepared.

3. Thiocyanates and Cyanides

Complexes of the thiocyanate ion have been studied in aqueous solutions (83, 227), aqueous methanol, methanol, and acetone solutions (150), and in aqueous acetone (151). Vanadium can be determined spectro-photometrically as a VO^{2+}–NCS$^-$–pyridine complex (9). Although VO(NCS)$^+$ and VO(NCS)$_2$ are unstable complexes (151), VO(NCS)$_2$(2MNCS) (204) and R$_3$-[VO(NCS)$_6$] (169, 332) are all quite stable complexes. Recently the crystal structure of (NH$_4$)$_2$[VO(NCS)$_4$-(H$_2$O)](4H$_2$O) was elucidated by X-ray diffraction (165), demonstrating the following: (a) that the thiocyanate is coordinated through the nitrogen atom; (b) that the sixth coordination position, *trans* to the multiply bonded oxygen, is occupied by a water oxygen at a somewhat distant 2.22 Å., but interestingly not as distant as the water oxygens in VOSO$_4$(5H$_2$O), which are approximately 2.3 Å. from the vanadium (261) in the equatorial plane and 2.4 Å. away in the *trans* axial position[2]; and (c) that the vanadium atom, 1.62 Å. from the oxygen, is located slightly above the plane formed by the four nitrogen atoms. The crystalline products KVO(NCS)$_3$(1.5EtOH) and VO(NCS)$_2$(2dioxane) have recently been obtained (150), as well as [VO(NCS)$_2$py$_2$]-(py) (9).

Potentiometric studies show that no stable cyanato complexes with VO^{2+} exist in acid solution and that addition of KCN to a solution of VO^{2+} gives only the hydroxide (95). However, Selbin and Holmes (332) have succeeded in obtaining solid R$_3$[VO(CN)$_5$], where the large cation, R = Et$_4$N$^+$, Me$_4$N$^+$, or Cs$^+$, appar-

(2) It is interesting to speculate on this observation. The stronger ligand NCS$^-$ (*vide infra*) is expected to weaken the V–O bond more than the ligand H$_2$O. If this is the case, a ligand in the sixth, axial position can be more strongly attached. hence closer to the vanadium atom, which is what is observed here.

ently provides the necessary crystal stability to allow the complex cyanide to exist.

4. Sulfates (84, 251) and Sulfites

The hydrated sulfate is perhaps the most common starting material for the preparation of vanadium(IV) compounds, and it is available commercially in at least two forms which differ only in the extent of hydration. Of these two forms (203), the blue one is water-soluble (32–34) and the gray-green one insoluble (139, 140). Classically the sulfate is obtained by reducing pentavalent vanadium in sulfuric acid solution using SO$_2$ (57). The product will be VOSO$_4$(xH$_2$O) if less than 3 moles of H$_2$SO$_4$ per mole of V$_2$O$_5$ is present, but acid sulfates, e.g., VOSO$_4$(xH$_2$SO$_4$)(yH$_2$O), are obtained if the ratio is higher. Other reducing agents which can be used include NH$_2$OH(HCl), dextrose, HCHO, EtOH, and H$_2$S (203). Anhydrous VOSO$_4$ can be obtained (8, 57, 343), and, e.g., the thermal decomposition of VOSO$_4$(4–5H$_2$O) proceeds stepwise as: 4H$_2$O → 3H$_2$O → H$_2$O → anhydrous → V$_2$O$_5$, with increasing temperature (298). Although many different hydrates may apparently form depending upon the conditions, it appears that the most stable room temperature forms of the sulfate are VOSO$_4$, VOSO$_4$(3H$_2$O), and VOSO$_4$-(5H$_2$O) (304). It is the latter for which X-ray structural data have been obtained (216, 261) (see Table I for some of the pertinent data).

A solid adduct VOSO$_4$(3DMSO) has been prepared, which is a nonelectrolyte in nitrobenzene, suggesting that the sulfate may be bidentate (332). Dark blue complexes, M$_2$[VO(SO$_4$)$_3$], and pale blue ones, M$_2$-[(VO)$_2$(SO$_4$)$_3$], are fairly stable and presumably also contain bidentate sulfate (21, 68, 132, 311). Many reactions involving the sulfate salt as reactant have been studied, for example, with KBrO$_3$ (379), KIO$_3$ + KOH (283), KMnO$_4$ (221, 222), NH$_4$OH (204), and NaCN + hexmethylenetetramine (23). The synthesis and decomposition of the sulfate between 360 and 630° have also been investigated (374).

A few sulfites are known (21, 68, 203, 304) including, for example, $3VO_2(2SO_2)(4.5H_2O)$, and some complex sulfites with the formulas $M_2[VO(SO_3)_2](aq)$, green, $M_2O(2VO_2)(2SO_2)(aq)$, blue, and $Zn[VO(SO_3)_2](aq)$ (203). At least two selenites have been reported, $VO(SeO_3)(xH_2O)$, $x = 2$ (131–133) and 3 (347).

5. Other Oxyanions and Miscellaneous Compounds

Aqueous solutions of the perchlorate salt have been obtained by many workers (54, 95, 185, 350, 382), but a solid perchlorate can be prepared providing heat is avoided in its preparation (150, 169, 332). For example, very hygroscopic blue crystals having approximately 5 moles of water per mole of VO^{2+} can be obtained. However, it is easier to get solid compounds when ligands other than water are used. Thus crystalline $[VO(DMSO)_5](ClO_4)_2$ can be prepared by cautious treatment of the hydrate with DMSO (169, 332), and solid adducts of $VO(ClO_4)_2$ with $4Ph_3PO$, or 5(pyridine N-oxide), or $4Ph_3AsO$ are known (173).

A formate of vanadium(IV) has been prepared and characterized recently in two different laboratories (82, 321). An interesting method of preparation involves exposing a solution–suspension of V_2O_5 in aqueous formic acid to sunlight (321). The resulting deep blue solution can be evaporated slowly to yield bright blue crystals of $VO(HCOO)_2(1.5H_2O)$. This can be thermally decomposed at 300° *in vacuo* to yield a pure sample of VO_2. Other monobasic organic acids from which vanadyl(IV) complexes have been prepared include stearic, oleic, benzoic, o-toluic (282), and cinnamic (339). The molecular weights, densities, and dielectric constants for a benzoate and cinnamate have been recorded (339).

There are many old reports of vanadyl phosphates (33–35), going all the way back to Berzelius in 1831, but the compounds have not been recently reinvestigated and most of the old compounds appear to require modern study before meaningful formulas can be written. Ignoring the possible presence of water, Zolotavin and Kuznetsova (390a) formulated a phosphate precipitate as $(VO)_3(PO_4)_2$, and they polarographically determined its k_{sp} value at 25° as 8×10^{-25}, but this work should be repeated with greater regard for the composition of the precipitate. However, there is a recent report of the preparation of blue-green crystals of formula $(VO)_2(H_2PO_2)_4(2H_2O)$, which resulted from the reaction between hypophosphorous and vanadic acids (220).

A carbonate has been reported (205), but its formula is uncertain. It is not expected that this basic anion should form a complex, at least not in aqueous systems. However, since a cyanide complex has been realized (*vide supra*), it is perhaps just a matter of time before an analogous procedure or one involving non-aqueous solvents yields a carbonato complex. No solid nitrate salt or nitrato complexes have yet been reported owing undoubtedly to the ease with which oxidation of vanadium(IV) by nitrate ion occurs. However, it does appear that a dilute solution of the nitrate may be realized (161, 367).

The reaction of VO^{2+} with phosphotungstic acid (PW), studied spectrophotometrically, gives a pK of 5.49 for the 1:1 complex (351), and a pK of 4.27 for the equilibrium

$$VO(PW) + 2ox^{2-} = VO(ox)_2^{2-} + 2PW^{2-} \quad (359)$$

The acetate $VO(CH_3COO)_2$ is easily produced in solution, for example, by reducing V(V) in acetic acid solution with $N_2H_4(H_2O)$. Whereas solutions of it have been employed for various purposes, such as titrations using VO^{2+} (371), it does not appear that the solid has been properly characterized.

A solid formulated as $(VO)_2[Fe(CN)_6]$ can be obtained (42, 290), and more recently (144) it has been shown that this is the only product formed when $Na_4[Fe(CN)_6]$ is added to an excess of VO^{2+}. Equimolar amounts of $VOSO_4$ and $K_3[Fe(CN)_6]$ appear to produce only $KVO[Fe(CN)_6]$ (144). It is interesting that a compound with the latter composition has been prepared from $K_4[Fe(CN)_6]$ and acidified vanadate(V) solutions (37).

The least stable of the metal oxodiamides (*cf.* the U and Ti compounds) is $VO(NH_2)_2$ (326). It is prepared by reaction of $K_2[VO(NCS)_4]$ with KNH_2 in liquid ammonia, and from it by reaction with excess KNH_2 may be obtained $K_3[(VO)_2N(NH)_2]$. Slowly at room temperature and rapidly upon heating to 100°, $VO(NH_2)_2$ loses NH_3 to give $VO(NH)$, undoubtedly polymeric, and at 150° $(VO)_3N_2$ is obtained (326).

B. THE COMPLEXES WITH MULTIDENTATE LIGANDS

Very stable chelate complexes are expected and found. The ion VO^{2+} has been placed (355) in the Irving–Williams metal ion series on the basis of the stability of its complexes with acetylacetone, salicylaldehyde, and oxalate: $VO^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+}$.

1. At Least One Ligand Atom Is Oxygen

Photolysis of an aqueous suspension of V_2O_5 in oxalic acid (1:3) for 5–6 hr. yielded quantitatively $VO(ox)(3H_2O)$ upon evaporation of the solution (322). An analogous dihydrate was obtained by fusing V_2O_5 and oxalic acid (1:3) at 100–110°. The thermal decomposition of these oxalates *in vacuo* yields V_2O_3 as final product (322). Oxalato complexes form very readily and have been prepared and studied many times (94, 163, 204, 221, 310, 322, 332, 357, 384, 387, 390). They are mainly of two types: $M_2[VO(ox)_2](xH_2O)$ and $M_2[(VO)_2(ox)_3](xH_2O)$. The pK value for the equilibrium

$$VO^{2+} + ox^{2-} = VO(ox)_2^{2-}$$
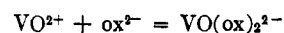
is 9.76 (360). The electronic spectrum of this latter ion has been recorded several times (146, 163, 185), and there is some support (390) for the two species $VO(Hox)_2$ and $VO(Hox)^+$. A compound with the unusual empirical formula $VO(ox)(H_2ox)(3H_2O)$ has been prepared (332), but nothing is known of its structure. The mixed ligand complexes [VO(ox)(ophen)] and [VO(ox)(dipy)], both nonelectrolytes in benzene, have been prepared also (332).

Malonato complexes (327), generally $M_2[VO(mal)_2]$-(xH_2O), can be dehydrated in stages, producing several different colored species. The reaction of VO^{2+} with malonic acid produces a 1:1 complex (39) with $pK = 3.8$ at 20°. There is also some spectral support claimed for the ion $[(VO)_2mal]^{2+}$ (358). Salicylaldehyde (20, 51, 118, 311, 368) and catechol (44, 310, 311, 340, 356) complexes have received much attention. Stable complexes of salicylaldehyde, $M_2[VO(sal)_2](aq)$, which may be recrystallized from water, are, curiously, white or pale yellow solids which produce green solutions in water. The Tl^+ salt is anhydrous. That these are indeed chelates is supported by the inability of the m- and p-hydroxybenzoic acids to give such compounds. A complex with p-aminosalicylaldehyde has also been synthesized (80), and reactions of vanadyl(IV) with other hydroxyaldehydes (4-phenyl-, 5-chloro-, 5-bromo-, 3,5-dichloro-, and 3,5-dibromosalicylaldehyde, and β-hydroxynaphthaldehyde) and their imines have been recently reported (268). Compounds with the formulas $M_2[VO(cat)_2](H_2cat)(xH_2O)$ can be obtained from alkaline solutions. They all seem to contain "catechol of crystallization" as well as water. Recently (44) a continuous variation study of $VOSO_4$ with catechol revealed a violet 1:2 complex and a violet-black 1:3 complex. In another study (356) of VO^{2+} + $3OH^-$ + excess catechol, the pK_1 and pK_2 values were determined to be 15.05 and 13.66, respectively.

The complex with the tartrate ion, a potential quadridentate ligand, is of great interest because in ammonia solution (185, 240) and in the solid $(NH_4)_2[VO(tart)]$-(H_2O) (240) the complex ion possesses, at room temperature, four distinct absorption bands in the ligand-field region (1000–380 mμ) which, with the possible exception of the lactic acid complex (240), is the only VO^{2+} complex known to this author to display so many room temperature bands (vide infra). Interestingly, the acidified solution, presumed to contain the ion $VO(Htart)^-$, gives only three standardly placed bands at room temperature like most other complexes of VO^{2+}. Further work on this and related hydroxycarboxylic acid complexes in the author's laboratory is in progress. At this time the suggestion of Jørgensen (185), that the complex in alkaline solution has all four oxygens of the tartrate ion coordinated, appears to be supported by additional work performed thus far (240). Many papers have appeared on the tartrate complexes

(19, 22, 46, 80, 94, 185, 189, 190, 311, 386, 391–393, 396), but in spite of this many questions remain to be answered before we can claim we understand them. An interesting report has appeared of the use of the purple crystals of the salt $(NH_4)_2[VO(tart)](H_2O)$ for the inhibition of cholesterol synthesis by brain tumors (80).

Oxovanadium(IV) complexes of other polybasic organic acids have been prepared and these include: citric (94, 167, 282, 380, 386, 389), ascorbic (345), trihydroxyglutaric (157), picolinic (263), salicylic (10, 40, 370), sebacic, succinic, and phthalic (282), all of which were allowed to react by heating a suspension of the acid in CCl_4 with $VOCl_3$ in CCl_4 under anhydrous conditions to 10–15° higher than the melting point of the acid.

Still other organic acid complexes have been prepared recently, a particularly unusual and large group coming from the laboratory of Dutta and Lahiry. Benzehydroxamic acid (BH) forms a rose-colored paramagnetic complex $[VO(B)_2]$ (99). Quinaldinic acid (QH) is reported (97, 98) to give a cream-colored hydrate $[VO(Q)_2](H_2O)$ and an isomeric olive-green aquo complex $[VO(Q)_2(H_2O)]$, both of which yield the anhydrous complex on heating and yield bluish green adducts $[VO(Q)_2X]$ (with X = aromatic amine or heterocyclic base). Complexes have also been prepared from 11 different substituted aromatic hydroxamic acids (RH) (101). The same laboratory has reported com-

BH   QH

TH   GH
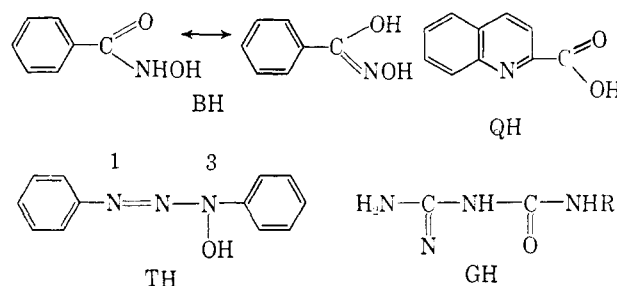
plexes of 3-hydroxy-1,3-diphenyltriazene (TH) (102), of formula $[VO(T)_2]$, as well as its adducts with organic amines (X), $[VO(T)_2X]$. Complexes, $[VO(T')_2]$, where $T'H$ is one of 15 different substituted hydroxytriazines (substituted on the 1- and 3-nitrogens), have also been synthesized (103) and they display a surprisingly wide susceptibility range, $\mu_{eff} = 1.6$–2.1 B.M. Finally, several guanylalkyl- and guanylalkoxyalkylureas (GH) have been complexed to VO^{2+} (104) to form $[VO(G)_2]$ complexes. Magnetic and spectral studies of many of the foregoing complexes are reported along with the preparative procedures.

With polyhydroxybenzenes (PH$_2$), [VO(P)] complexes in the pH range 4–5 are formed, whereas at higher pH values $[VO(P)_2]^{2-}$ result; the ligands include pyrocatechol, pyrogallol, gallic acid (341), as well as some more exotic ones (311, 340). In general, it

appears that phenolic hydrogens are rather easily displaced by vanadium(IV), and the same can be said with almost the same certainly about aliphatic alcoholic hydrogens providing the oxygen becomes a member of a chelate ring.

Complexes have also been prepared with diphenylcarbazone (55) and with salicylidene o-hydroxyanil and its 5-chloro and 5-bromo analogs (383), as well as other substituted derivatives (384). The lower than spin-only (1.73 B.M.) moments observed with these complexes are believed (383) to be caused by partial metal-metal bonding arising from overlapping of d-orbitals on neighboring vanadium atoms. However, this is by no means firmly established and further work on these complexes is surely in order.

Stability constants (given in parentheses), as well as some other properties have been determined for the following multidentate ligands: EDTA (18.77) (323, 328, 329); the solids BaVO(EDTA)(5H$_2$O) and Na$_2$VO-(EDTA)(3H$_2$O) have been isolated (329); HEDDA (5.5) (73); HIMDA (5.7) (73); PDS (17.2) (73, 328); DNS (17.4) (73, 287, 328); 5-SSA (14.8) (73, 328); DCHT (19.40) (328); glycolic acid (3.90) (1); and ethanolamine (288).

Complexes formed from β-diketones are numerous and have received much more extensive study recently than any others. This is particularly the case with the very stable, commercially available, crystalline blue-green bis(acetylacetonate)oxovanadium(IV). This easily synthesized (61, 313) complex was apparently first prepared in 1876 by Guyard (161); again about 1900 (130, 366), and then in 1914, by Morgan and Moss (238, 239), who formulated it as [VO(acac)$_2$]. It was next reported in 1925 by Rosenheim and Mong (311), who believed it to be a monohydrate, [VO(acac)$_2$-(H$_2$O)]. The latter workers assumed that when the complex reacted with another ligand, B (e.g., py or NH$_3$), the water molecule was simply replaced by a molecule of B. Again, in 1954, Jones (182) investigated this complex and in particular its addition compounds with the bases, B = piperidine, isoquinoline, γ-picoline, and methylamine. He concluded that the original formulation without the water is correct, and he found the neutral complex to be monomeric in benzene. Graddon (155) has since made the curious observations that it is dimeric in triphenylmethane, biphenyl, and diphenylaniline, although monomeric in camphor. In 1957, Jones (183) concluded (correctly) from the chemical and physical properties of [VO-(acac)$_2$] that the structure must be tetragonal pyramidal. The verification of this came with the determination of its X-ray crystal structure (91), which revealed discrete molecules of [VO(C$_5$H$_7$O$_2$)$_2$], with the vanadium atom in the approximate center of gravity of the five oxygen atoms arranged in a rectangular (nearly square) pyramid. The V–O distances are

1.56 Å. to the axial oxygen and 1.97 ± 0.01 Å. to the other four.

In 1956, Trujillo and Brito (352) obtained evidence, using Bjerrum's method, for the existence in aqueous solutions of both VO(acac)$^+$ and [VO(acac)$_2$], having the successive equilibrium constants at 25° of pK_1 = 8.68 and pK_2 = 7.11. In 1961, Claunch, Martin, and Jones (78) used vapor pressure measurements to obtain enthalpies, entropies, and free energies of coordination to the sixth, unsolvated position in the acac complex. The coordination of NH$_3$, MeNH$_2$, i-Pr-NH$_2$, or t-bu-NH$_2$ was found to be accompanied by an enthalpy change of approximately 15 kcal./mole, but the free energy change in each case is relatively small. These workers noted a number of interesting similarities in the thermodynamic data to that found with addition compounds of trimethyl boron, indicating the general similarities of the act of coordination in both cases. Extending this work to still other amines by evaluating association constants (K) with the acac complex in homogeneous benzene solution, Carlin and Walker (69) found also that the general order of K values agrees qualitatively with the complex stability order found for trialkylboron adducts with the same series of amines in the gas phase. In a later study from the laboratory of Jones (184) the heat of combustion of [VO(acac)$_2$], −1276 kcal./mole, was measured and then used in a thermochemical cycle to obtain a value for the V–O (i.e., the acac-O) bond energy. The value so obtained, 77.2 kcal./mole, is larger (by 7–28 kcal./mole) than every other M–O (where M = UO$_2$$^{2+}$, Cu^{2+}, Mg^{2+}, Co^{3+}, Cr^{3+}, Fe^{3+}) bond energy evaluated except for M = Th^{4+}, for which case it is roughly equivalent. This high V–O bond energy may be taken as an indication of either a very strong σ-bond or, what is much more likely in light of the data for the later transition metals, substantial π-bonding of the ligand-to-metal variety.

In many solvents and particularly water and alcoholic solutions the acac complex is very slowly oxidized to some, as yet unknown, pentavalent species by atmospheric oxygen (240, 254). This oxidation proceeds very rapidly with hydrogen peroxide, and it appears to be at least partially reversible. Other recent studies involving this complex (to be discussed later) have included: infrared spectra (24, 213, 245, 333–335, 364), visible–ultraviolet spectra (30, 85, 164, 185, 336, 337), and electron paramagnetic resonance spectra (4, 30, 142).

Other β-diketones which have formed complexes with VO^{2+} include: 3-cyanoacetylacetone (117); 2-chloro- and 2-bromoacetylacetone (200); acetylmethylacetone (238, 239); benzoylacetone (118, 238, 239) and its 1:1 adducts with the bases pyridine, methylamine, isoquinoline, and γ-picoline (182); 2-furoyltrifluoroacetone (monohydrated) (182); 2-furoylperfluorobutyrylacetone (monohydrated) (182); and dibenzoylmethane

(118, 174, 175, 182, 183, 273), for which a dipole moment of 3.61 D. was obtained in benzene solution (174) and for which stable adducts with both benzene (175) and chloroform (273) have been obtained.

Schiff bases derived from β-diketones have also yielded stable complexes, such as bis(benzoylacetone-propylenediimino)oxovanadium(IV) (and its benzene adduct) (175), for which a dipole moment of 6.05 D. has been measured. Of very great interest is the complex bis(acetylacetonepropylenediimino)oxovanadium(IV), which has the distinction of being the first compound of V(IV) to have been successfully resolved into optical isomers (282a), accomplished through the use of an adsorption column of D-lactose followed by elution with toluene.

The Schiff base formed from ethylenediamine and salicylaldehyde likewise complexes oxovanadium(IV) (7, 27, 47, 118, 273, 274, 335, 365). Whereas this complex has a normal spin-only moment of 1.72 B.M. (27), the Schiff base derived from 3-aldehydosalicylic acid and ethylenediamine gives an orange-yellow complex with an unexpectedly high magnetic moment of 1.96 B.M. (277). A curious observation by the authors who reported the latter complex is that if the amine used with the 3-aldehydosalicylic acid is aniline, sulfanilamide, anthranilic acid, or o-phenylenediamine, the product obtained from refluxing the Schiff base with VOCl₂ always contains vanadium(V). Apparently in all of these cases air oxidation takes place during refluxing. Nevertheless, the propylenediamine (47) and o-phenylenediamine (7) analogs with salicylaldehyde are known. The Schiff base formed from o-hydroxyacetophenone and ethylenediamine also yields a complex with an unusually high magnetic moment of 2.50 B.M. Magnetic measurements have also been made on the complexes formed from the Schiff bases of salicylaldehyde and the amino acids glycine, alanine, and anthranilic acid (242). Perhaps the largest number of Schiff base complexes were prepared in the laboratory of Pfeiffer (273, 274). Some were shown to be monomeric by molecular weight determination and many were obtained with smaller molecules (S) adduced. This series of compounds, VO(Schiff base)(S), includes the following Schiff bases (273): (1) salicylaldehyde-ethylenediimine, monomeric, S = CHCl₃ or py; (2) salicylaldehydepropylenediimine, free or S = py or MeOH; (3) salicylaldehydetrimethylenediimine; (4) salicylaldehydediphenylethylenediamine; (5) salicyl-aldehyde-o-phenylenediimine, monomeric, free or S = py or MeOH or acetic acid; (6) resorcylaldehydeethylenediimine, free or S = py; (7) 2-oxy-1-naphthalde-hydediphenylenediimine, free and S = toluene; (8) 2-oxy-1-naphthaldehydeethylenediimine; (9) 2-oxy-1-naphthaldehyde-o-phenylenediimine; (10) o-oxyacetophenoneethylenediimine; (11) o-oxyacetophenonedi-phenylethylenediimine.

The stability constants for the 8-hydroxyquinoline complexes VO(oxine)⁺ and VO(oxine)₂ have been recorded (354), but these may not be reliable owing to the unexpected ease with which the vanadium(IV) complex with oxine undergoes oxidation, even by atmospheric oxygen (331). The complexes of oxine and substituted oxines with pentavalent vanadium, and many of the reactions which these undergo, have received a great deal of attention (10, 27, 47–50, 53, 236, 349) and have even stirred up some healthy controversy concerning the structure and composition of the complexes. However, the vanadium(IV) complex appears to be [VO(oxine)₂] (48, 169) in the solid state, its magnetic moment is a near-normal 1.75 B.M. (27), and it forms a pyridine adduct (27, 48) which appears to be more stable toward air oxidation.

Finally in this section complexes which form from hydroxy- and aminoazo dyes, which have considerable stability (93), may be mentioned. Salicylhydroxamic acid forms complexes with VO²⁺ which allow a spectrophotometric determination of this ion (36). Conductance and spectral measurements were used to establish a 1:1 vanadyl leucinate complex (41).

2. The Ligand Atoms Are Nitrogen or Some Other Atom

A claim is made (45) for the existence in aqueous solution of the ion [VO(en)₂]²⁺, presumably formed from vanadyl(IV) sulfate and ethylenediamine hydrochloride. Its composition was established spectrophotometrically and conductometrically by Job's method, and its dissociation constant was calculated to be 2×10^{-6} at 20°. This appears to be the sole claim of a complex of VO²⁺ in which an aliphatic amine is the only ligand. Further investigation in this area is clearly indicated.

Complexes containing 1,10-phenanthroline (ophen) and 2,2'-bipyridyl (dipy) are of at least two types. Those containing one ligand molecule (AA) per VO²⁺ are: [VO(AA)F₂], [VO(AA)(ox)], [VO(AA)(SO₄)] (169, 332, 334), and [VO(AA)Cl₂] (77). Those containing two ligand molecules per unit are: [VO(AA)₂](ClO₄)₂, [VO(AA)₂Cl]Cl, [VO(AA)₂Br]Br(H₂O), and VO(ophen)₂SO₄ (169, 332, 334). Two complexes with the unusual empirical formulas VO(AA)₁.₅(NCS)₂ have been formulated on the basis of their mode of formation, conductivity data, and infrared spectra (332) as [VO(AA)₂NCS][VO(AA)(NCS)₃]. All of these complexes have been studied by infrared and visible–ultraviolet spectroscopy.

Complexes of biguanide and six different substituted biguanides have been reported (285), and they are formulated as [VO(big)₂(H₂O)]. They have magnetic moments near the spin-only value.

The large organic four-nitrogen bases yield very stable complexes. Chelates of tetraphenylporphine (52, 171, 364) and its p-methyl- (364), p-methoxy- (364),

and *p*-chloro- (149, 364) substituted derivatives have been synthesized and their infrared and visible spectra recorded. The red-violet tetraphenylporphyrin compound does not melt below 460°, and it is reported to sublime *in vacuo* at 880° (52). A phthalocyanine complex has been prepared (22, 138) and its infrared V–O stretch frequency recorded (334), as well as other of its properties (29, 177, 338).

A Belgium patent (76) reports the preparation of complexes with hydrazinophthalazines as ligands. Finally, it is believed (224) that oxidation of dicyclopentadienylvanadium(II) gives $(C_5H_5)_2VO$, with a $\langle g \rangle$ value of 1.99.

C. OXOVANADIUM(IV) IN AQUEOUS SOLUTIONS

Early evidence (162) obtained from oxidation–reduction potential studies on the system V(IV)–V(V), which indicated that the VO^{2+} entity exists in acidic solutions, has been reinforced with much more convincing evidence from both electronic spectral and paramagnetic resonance data (18). Thus electronic absorption bands and paramagnetic resonance g factors vary little from solids to aqueous solutions (see Tables III and V). For example, if the more symmetrical ion $V(OH)_2^{2+}$ were to be formed in aqueous solution, not only would electronic bands be expected to shift markedly, but also a smaller g value should be found, as is the case for V(IV) in the TiO_2 lattice where a $\langle g \rangle$ value of 1.938 is observed. To this may be added the still more recent and equally significant evidence presented by Evans (115) from his infrared and Raman spectral studies of some vanadyl(IV) salts in aqueous solutions of Cl^-, F^-, SO_4^{2-}, and ClO_4^- (see Table II and below). The re-

TABLE II

INFRARED AND RAMAN V–O STRETCHING FREQUENCIES (CM.$^{-1}$) FOR SOME OXOVANADIUM(IV) SALTS DISSOLVED IN H_2O OR D_2O (115) AND AS SOLIDS IN NUJOL MULLS (334)

	Infrared			Raman		
Salt	Solid	H_2O	D_2O	H_2O	D_2O	V–O[a]
$VOCl_2(xH_2O)$	990	1000	992	1001	992	280 (275)[b]
$VOF_2(xH_2O)$	984	984	...	986	...	280
$VO(ClO_4)_2(xH_2O)$	995	1000	...	1001	...	277
$VOSO_4(5H_2O)$	1003	997	992	996	...	282
	975	982	976	984		

[a] Single bond, in H_2O solution.   [b] In D_2O solution.

sistence of the VO^{2+} species to protonation can be explained by the MO bonding scheme (18) (*vide infra*). Since the oxygen 2p-orbitals are used for π-bonding, only an sp_σ hybrid remains for proton attachment, but as this orbital has considerable 2s character it is energetically unsuited for bonding purposes. Nevertheless, Rivkind (296) has recently concluded from relaxation of the proton magnetic resonance and the e.s.r. of VO^{2+} solutions that H (or D) bonding to the ion occurs. He finds also that the 3d-electron is partly transferred to the solvent molecules.

Rossotti and Rossotti (312) have used spectrophotometric and potentiometric measurements to study the hydrolysis of VO^{2+} in the acidity (perchloric acid) range: $3 M > H^+ > 0.002 M$. They summarize earlier work (58, 59, 181, 226) which is not definitive and report their results and conclusions obtained with vanadium concentrations in the range 0.05–0.005 M. Only two complexes, in addition to VO^{2+}(aq), are assumed to form, and these may be written as $VO(OH)^+$(aq) and $(VO)_2(OH)_2^{2+}$(aq). The equilibrium constants which were obtained are
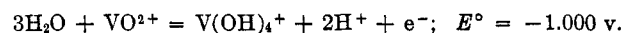
$$[VO(OH)^+][H^+]/[VO^{2+}] = 10^{-6.0}$$

and

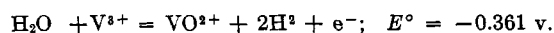$$[(VO)_2(OH)_2^{2+}][H^+]^2/[VO^{2+}]^2 = 10^{-6.88}$$

Precipitation ensues when approximately 10% of the oxovanadium(IV) ions are further hydrolyzed.

The oxidation–reduction potential for the couple V(VI)–V(V) has been studied as a function of acidity (126, 162, 179, 377), and more recently in the presence of different acids (H_2SO_4, HCl, HNO_3, $HClO_4$, and H_3PO_4) at various pH values (284). This latter study indicated that the formal potentials increase with increasing acid concentration and are a maximum in sulfuric acid medium. The data obtained at high acidities indicate the presence of the VO^{2+} ion (but do not rule out $V(OH)_2^{2+}$). At higher pH values the measurements are difficult to interpret because of the presence of hydrolysis products of both oxidation states. Indeed, the complexities which arise at pH values above about 2.5, because of the formation of isopolyvanadates and vanadylvanadates, have been recently investigated (231a–233, 255), but the results are complicated and by no means conclusive. Lattimer (212) reports, from the work of others (70, 80)

$$3H_2O + VO^{2+} = V(OH)_4^+ + 2H^+ + e^-; \quad E^\circ = -1.000 \text{ v.}$$

which demonstrates that at 1 M hydrogen ion concentration, vanadic acid is a fairly powerful oxidizing agent. The values for E° in 1 and 3 M NaOH are -0.74 and -0.85 v., respectively (377). Nuclear resonance line broadening due to ^{51}V has been used (159) to study the V(IV)–V(V) electron exchange in acid–chloride solution. The rate of electron transfer is first order in V(IV) and second order in V(V), and for 6.5 N acid solutions the rate constant for the exchange reaction is 1.5×10^6 l.^{2}/mole^2 sec. Oxidation of V(IV) at the Pt electrode has also been studied (87).

For the V^{3+}/VO^{2+} couple we have (119, 180)

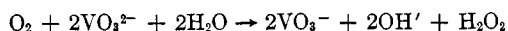$$H_2O + V^{3+} = VO^{2+} + 2H^+ + e^-; \quad E^\circ = -0.361 \text{ v.}$$

Recently the influence of organic complexing agents on this oxidation–reduction potential has been investigated (361), and the results indicate that V^{3+} forms more stable complexes than VO^{2+}.
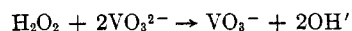
Polarography of tetravalent vanadium in 1 M OH^-

in the presence of other anions, SO_3^{2-}, NCS^-, Cl^-, and F^-, has revealed (214) the existence of only two important ions under these conditions, $V_2O_5^{2-}$ and $V_4O_9^{2-}$. The half-wave oxidation potential is found, expectedly, to be pH dependent. $E_{1/2}$ (vs. satd. calomel) for the reduction of 0.0007 N VOSO$_4$ in 0.1 N H$_2$SO$_4$ at $25°$ is -0.89 v. (393). The irreversible reduction gives a value of -1.2 v. at $13°$, illustrating the very large temperature dependence. Polarographic investigation has also been carried out at Pt microelectrodes (232), in buffered (pH 9.1–13.7) and aged solutions (202), on the EDTA complex (266), and on VO^{2+} in aqueous perchloric acid in the presence of ascorbic acid at different pH values (231). The reduction wave is always irreversible.

Solutions of VO^{2+} in concentrated and moderately concentrated strong acids are stable for 6 months or more (58, 126, 346), and, as a specific example, below pH 2.45 oxidation by air at $14°$ was found negligible for 1 week (179). However, above this pH the rate of oxidation increases rapidly. Dean and Herringshaw (88) have investigated the air oxidation of vanadium-(IV) in alkaline solutions (0.006–3.8 N NaOH) and found that the oxidation proceeds rapidly at $15°$ and via the reduction of oxygen to peroxide, which was formulated as

$$O_2 + 2VO_3^{2-} + 2H_2O \rightarrow 2VO_3^- + 2OH' + H_2O_2$$

followed by

$$H_2O_2 + 2VO_3^{2-} \rightarrow VO_3^- + 2OH'$$

The initial oxidation rate is proportional to the hydroxide concentration and Fe(III) catalyzes the reaction while Cr(III) inhibits it. With vanadium concentrations greater than 0.002 N, the rate of oxidation is controlled by the rate of diffusion of aerial oxygen. The authors propose the use of O_2 in alkaline solution to obtain quantitative oxidation of V(IV) to V(V) prior to vanadium determination by titration with iron(II) sulfate. Not only is the oxidation quantitative but the oxidant is inactivated upon acidification, overcoming difficulties encountered with various other oxidants, which have included nitric acid (193), permanganate, persulfate (192), perborate (375), bromate (201), perchloric acid (344, 376), and ozone (378). Investigation of ClO_2^-, ClO_3^-, BrO_3^-, and IO_4^- as oxidants for V(IV) in alkaline solutions has shown ClO_2^- to be the best (289). The importance of acidity (160) and temperature (243, 244) on the oxidation of tetravalent vanadium has long been known.
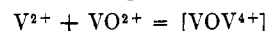
Thermodynamic data on the aqueous ion, VO^{2+}, includes (48) $\Delta H_f° = -113$ kcal./mole, $\Delta G_f° = -109$ kcal./mole, and $\Delta S_f° = -13.4$ e.u. Adsorption of VO^{2+} ions by sulfocarbon and other agents has been studied (394, 395). The ion has recently been investigated (148) as a back titrant for indirect amperometric titrations with EDTA. Any cation with an EDTA sta-

bility constant of 10^{16} or greater can be determined in this way. Other analytical determinations involving EDTA have recently appeared (38, 186) as well as some determinations involving other chelating "indicator" ligands (89, 255).

A recent study has been reported (247, 248) of the kinetics and probable mechanism of the reaction between VO^{2+} and V^{2+} in acid perchlorate solutions from 0.2–2.0 M in HClO$_4$ over a temperature range from 0.4 to $34.5°$ at an ionic strength of 2.0 M. The over-all reaction

$$V^{2+} + VO^{2+} + 2H^+ = 2V^{3+} + H_2O$$

which goes to completion (196, 207, 250) is believed to involve a net activation step

$$V^{2+} + VO^{2+} = [VOV^{4+}]$$

with the two hydrogen ions being acquired after this rate-determining process. Chloride ion increased the rate only slightly, while sulfate ion increased it markedly, leading to speculation of an alternative intermediate $[VOV(SO_4)^{2+}]^*$. Finally it might be appropriate to note that there has been a very recent study also made of the kinetics of the reaction between V(III) and V(V), of interest here because of the product of the reaction (85a).

III. INFRARED SPECTRAL STUDIES

As has been already mentioned, one of the more significant pieces of evidence for the existence of the multiple V–O bond is the observation of a relatively pure and energetic metal–oxygen stretching vibration, which persists with some variation in frequency in all compounds of vanadyl(IV). Indeed, this narrow, strong absorption may be considered diagnostic of the presence of the V–O multiple bond. The variation of the frequency of this characteristic vibration with changes in the environment of the VO^{2+} entity has been studied for a large number and variety of complexes (119, 169, 333–335). The frequency spread for over 50 oxovanadium compounds was summarized by $\bar{\nu} = 985 \pm 50$ cm.$^{-1}$, which corresponds approximately to a force constant spread, $k = 7.0 \pm 0.7$ mdynes/Å. (334). These data include the high values for three oxovanadium(V) compounds: VOCl$_3$ (1035 cm.$^{-1}$), VOBr$_3$ (1025 cm.$^{-1}$), and V$_2$O$_5$ (1020 cm.$^{-1}$).

It is interesting that the total spread of $\sim$100 cm.$^{-1}$ in the stretch frequency is approximately the frequency difference between the metal–oxygen antisymmetric stretch of MO_2^{2+} and MO_2^+ (M = Np and Am). With these latter ions the shift to lower frequencies (of about 110 cm.$^{-1}$) from MO_2^{2+} to MO_2^+ is probably due mainly to the extra electronic charge present in the univalent species. Thus it is tempting to suggest tentatively that the shift to lower frequencies of the V–O stretch is due to the transfer of increasing amounts of charge onto the vanadium by ligands of increasing donor strength. In this connection it would be of

great interest to gain insight into this suggestion by investigating the e.s.r. spectrum of a vanadyl complex such as $R_3[VOF_5]$, which has the same symmetry as the sulfate pentahydrate, but which has the much stronger donor ligand fluoride ion in place of the water molecule. This work is now in progress by the author in collaboration with I. Bernal. The V–O stretch frequency lies over 50 cm.$^{-1}$ apart for these two compounds (334).

In Table I, the V–O stretch frequencies are recorded for the compounds whose V–O distances have been independently measured. It is seen that there is a rough correlation, as there should be, between decreasing frequency and increasing bond length.

It has been suggested (334) that the V–O frequency shifts may serve to establish certain ligand series, not unlike the spectrochemical series. For example, for the complex type $[VO(a)_5]^{n\pm}$, such a series, in order of decreasing V–O stretch frequency (334), is: $H_2O > NCS^- > CN^- > DMSO \sim F^-$. For the complex type $[VO(AA)_2a]$, the series observed is: ophen $>$ mal^{2-} $\sim$ ox^{2-} $>$ dipy. With the type $[VO(AA)_2]$, the series is: DBM $>$ acac $>$ ophen $>$ dipy. It may be noted that these ligand series do not exactly parallel the spectrochemical series and, in fact, there is little reason to believe they should. The latter series has been established by ranking ligands according to the value of the octahedral ligand field splitting parameter Δ_0 or 10·Dq, which is determined from the electronic spectra of complexes of the d^5–d^{10} transition metal ions in their common oxidation states. Metal-to-ligand π-bonding is expected to play a significant role in many such complexes. On the other hand, the ligand series derived from vibration spectra arises primarily as a result of variations in σ-bonding by the ligands and secondarily as a result of ligand-to-metal π-bonding. This is the most likely reason for CN$^-$ (a strong metal-to-ligand π-bond former) being displaced from its normal extreme spectrochemical position. The extreme position of the F$^-$ ion then reflects, perhaps, its strong tendency to delocalize its high charge density by forming a ligand-to-metal type of π-bond.

It has been suggested also that the V–O frequency changes are directly related to decreased $2p\pi \rightarrow 3d\pi$ donation (i.e., from oxygen to vanadium), which results from the transfer of charge onto the vanadium by the equatorial ligands. This effect has been written (334)

$$\Delta\bar{\nu} = -\sigma(L \rightarrow M) - \pi_{\parallel}(L \rightarrow M) - \pi_{\perp}(L \rightarrow M)$$

where the relative importance of the three right-side terms was estimated to be 8:2:1. (Note that metal-to-ligand contributions are probably safely assumed negligible for a d^1-system.)

Although most infrared studies have been carried out using solid compounds, there is appearing a growing amount of solution work. Evans (115) has obtained

infrared and Raman spectra of H_2O and D_2O solutions of $VOCl_2$, $VOSO_4$, VOF_2, and $VO(ClO_4)_2$. These results (Table II) clearly preclude the existence (at least in large amounts) of the symmetrical ion [HO–VO–OH]$^{2+}$ in acid solution, and the evidence seems straightforward for a species $[VO(H_2O)_n]^{2+}$, although n is not determined.

The infrared solution studies of $[VO(acac)_2]$ have been reported (335) in which the shift in the V–O multiple bond frequency was examined as a function of (a) solvent, (b) neutral ligand, and (c) anionic ligand. The $\bar{\nu}_{V–O}$ for the solvents acetonitrile, chloroform, carbon disulfide, acetone, nitromethane, and benzene may be written as 1006 $\pm$ 2 cm.$^{-1}$, which is close to the value for the solid complex in Nujol mull, 997 cm.$^{-1}$. In dimethylformamide, a solvent with appreciable coordinating capacity in contrast with the others, the value is significantly shifted to 972 cm.$^{-1}$. Neutral and anionic ligands investigated fall readily into one of three groups. Those producing shifts of 48 $\pm$ 3 cm.$^{-1}$, when in chloroform solution in a 1:1 mole ratio with the complex, include pyridine, ammonia, isobutylamine, piperidine, ethylamine, diethylamine, ethylenediamine, thiocyanate ion, and acetate ion. Those producing no shift, even at 25:1 mole ratios, include thiourea, diethyl ether, diphenyl sulfide, diphenyl selenide, triphenylphosphine, triphenylarsine, chloride ion, perchlorate ion, and nitrate ion. Some ligands, such as aniline, phenol, tetrahydrofuran, and p-dioxane, produced shifts of 23 $\pm$ 1 cm.$^{-1}$ with the original (unperturbed) V–O band still present, but with reduced intensity. No explanation of these results has been offered, but it may be pointed out that all ligands producing shifts are at least moderately strong protonic bases and/or they coordinate well with transition metal ions. Weak field ligands and/or those with very weak σ-donor capacity produce little or no shift. Steric effects may also play an important role when the ligand becomes bulky, since the sixth position on the vanadium is not as accessible as it would be if the four acac oxygens were coplanar with it instead of lying in a plane below the vanadium, with reference to the lone oxygen. Unfortunately, no strong field ligands, such as F$^-$, CN$^-$, or OH$^-$, have been tried, owing to the difficulty of finding salts of these ions which will dissolve in the necessary inert solvent. Perhaps the most obvious point to come from infrared studies is that the metal-oxygen stretching vibration is not as sensitive to the environment of the metal ion as was hoped by the author and his co-workers. In fact, looking beyond vanadyl(IV) to other oxocations we find the same is true of all of them for which we have sufficient data. More generally we may state that not only is the stretching frequency relatively insensitive, but so also are stretching force constants and bond lengths, both of which are of course closely related to the stretching frequency.

TABLE III

PARAMAGNETIC RESONANCE g FACTORS FOR VO^{2+} IN VARIOUS ENVIRONMENTS

Complex	Conditions	$g_{\parallel}$	$g_{\perp}$	$\langle g \rangle$	Ref.
$VOSO_4(5H_2O)$	Powder, 4–300°K.	—	—	1.99	261
$VOSO_4(2H_2O)$	Powder	—	—	1.96	176
VO^{2+}	Aq. soln.	—	—	1.962	134, 206, 303
	Alc. or glycerol soln., 90°K.	—	—	1.96	206
	Adsorbed on				116
	a. IR-100	1.93	1.983	1.97	
	b. Dowex-50	1.88	1.979	1.95	
	c. Charcoal	—	1.983	—	
	d. IR-4B	1.93	1.989	1.97	
	In single crystals of $Zn(NH_4)_2(SO_4)_2(6H_2O)$	1.94	1.983	1.969	52a
VO(etioporphyrin I)	Petroleum oil soln.	1.948	1.987	1.974	252
VO(etioporphyrin II)	Castor oil soln.	1.947	1.988	1.974	297
VO(pc)		—	—	2.02	177
$VOCl_2$	Powder	—	—	2.0	210
$VO(C_5H_5)_2$	Solid	—	—	1.99	224
$K_2[VO(ox)_2]$	In crystal of $K_2[TiO(ox)_2]$	1.940	1.972	1.961	146, 147
VO(tetraphenylporphine)	1:1 DMF-CHCl$_3$	1.95	1.99	—	29a
V(IV)	Aq. H_2SO_4	—	—	1.962	234
	In TiO_2	1.957	1.914	1.938	141
$VO(acac)_2$	MeOH	—	—	1.968	30
	py	—	—	1.971	
	Acetone	—	—	1.968	
	Acetonitrile	—	—	1.969	
	Nitrobenzene	—	—	1.972	
	Benzene	—	—	1.970	
	60:40 CHCl$_3$-toluene	1.944	1.996	—	142

IV. ELECTRON PARAMAGNETIC RESONANCE AND MAGNETIC SUSCEPTIBILITY STUDIES

The factors of (a) a single d-electron outside of a closed (argon) shell, (b) isotopic purity of the naturally occurring vanadium-51, and (c) the high nuclear spin $(I = 7/2)$, combine to make the oxovanadium(IV) species attractive for experimental studies and theory testing in electron spin resonance (e.s.r.) spectroscopy. Approximately 40 papers dealing with e.s.r. experiments or theory attest to the interest in this system. For example, the following e.s.r. measurements have been reported: $VOSO_4$ in aqueous solutions (208, 259, 295, 369), the dihydrate (176), the trihydrate (369), and the pentahydrate (260, 261); $VOCl_2$ in aqueous solutions (107, 208, 294, 295, 363), in powder form (210), and in LiCl-KCl fused mixtures (60); VO^{2+}(aq) adsorbed on cationic and anion exchangers (116), in alcohol or glycerol solutions at 90°K. (206), and in variously constituted aqueous solutions (134, 135, 137, 199, 206, 208, 223, 258, 259, 295, 296, 303, 320a); $VO(acac)_2$ (4, 142) and the same dissolved in several solvents (30); VO-(etioporphyrin I) (252); VO(etioporphyrin II) (297); VO(pc) (178); $K_2VO(ox)_2$ in dilute single crystals of $K_2TiO(ox)_2(2H_2O)$(146, 147), and in solutions (134, 161, 224, 259); V(IV) in α-Al_2O_3 (208); $VO(C_5H_5)_2$ (224); V(IV) in SnO_2 at 77°K. (191), and in TiO_2 (141); and VO^{2+} in single crystals of $Zn(NH_4)_2(SO_4)_2(6H_2O)$ (52a). Nuclear relaxation measurements on solutions of vanadyl(IV) salts have been extensive (208, 257, 291–293, 296, 368). In Table III are given some of the

paramagnetic resonance g-factors which have been obtained experimentally in different laboratories. It is worth noting that (a) the average g values, $\langle g \rangle$, are close to the free electron value; (b) the anisotropy of the g-values is relatively small, for example, when compared with those for analogous Cu^{2+} or V^{3+} complexes; and (c) the $\langle g \rangle$ values are relatively independent of the environment of the VO^{2+} species. Although it would appear that a great deal of work has already been done in this area, it is expected that further e.s.r. investigations will be necessary and forthcoming before the many interesting possibilities for understanding this unique d¹-system are exhausted.

The normal magnetic moment expected for the vanadyl(IV) complexes when the orbital contribution is completely quenched, as it is expected to be by the low symmetry fields, is, of course, 1.73 B.M. As is seen in Table IV, most of the measured values fall on or close to this ideal value, but there are a few notably high and low values which are not easily explained. It would appear that for laboratories well equipped to carry out thorough magnetic susceptibility studies, this ion presents obvious possibilities for further fruitful investigation.

V. VISIBLE–ULTRAVIOLET SPECTRAL STUDIES AND THEORETICAL INTERPRETATIONS

Perhaps the phase of oxovanadium(IV) complex ion chemistry which is being most actively investigated and discussed at the present time is that dealing with visible-

TABLE IV

MAGNETIC SUSCEPTIBILITY DATA ON VANADYL(IV) COMPLEXES

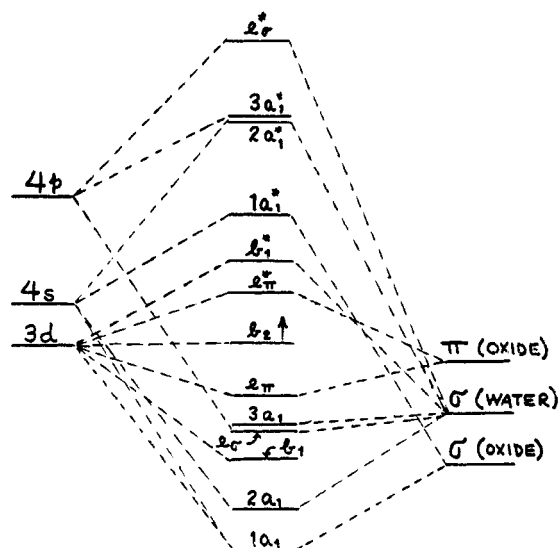| Compound	Value, B.M.	Ref.
VOSO₄(5H₂O)	1.73	17
[VOSO₄(3H₂O)]	1.73	267
[VO(acac)₂]	1.73	17
[VO(ophen)Cl₂]	1.73	77
[VO(dipy)Cl₂]	1.74	77
[VOCl₂(2Ph₃PO)]	1.74	173
[VO(Q)₂(Me₂NCHO)]	1.74	105
[VO(Q)₂(thiophene)]	1.74	105
[VO(C₇H₅N₂O₄)₂], green	1.74	101
[VO(T)₂], form II	1.74	102
[VO(RH)₂]	1.72	99, 105
VO²⁺ (aq. HClO₄)	1.72	121
[VO(acac)₂(H₂O)]	1.72	7
[VO(en-bis-sal)]	1.72 (1.68)	27 (7)
[VO(oxine)₂py]	1.75	27
[VO(big)₂(H₂O)]	1.75	285
[VO(Q)₂(H₂O)]	1.75	100, 105
VO(ClO₄)₂(5C₅H₅NO)	1.75	173
VOCl₂(4Ph₃AsO)	1.76	173
[VOCl₂(3DMSO)]	1.76	173
(NH₄)₂[VO(mal)₂](3H₂O)	1.70	7
[VO(T)₂], form I	1.77	102
[VO(Q)₂(THF)]	1.695	105
[VO(C₇H₅N₂O₄)₂], violet	1.78	101
[VO(sal-o-phend)]	1.68	7
[VO(G)₂]	1.67-1.69	104
[VO(Q)₂(dioxane)]	1.66	105
[VO(Q)₂(PhNH₂)]	1.805	105
[VO(Q)₂(Me-py)]	1.81	105
[VO(C₈H₈NO₃)₂]	1.64	101
[VO(BzQ)₂(H₂O)]	1.84	105
[VO(C₈H₈NO₂)₂]	1.63	101
[VO(Q)₂(py)]	1.86	105
[VO(5-NO₂-Q)₂(H₂O)]	1.61	105
[VO(C₇H₅N₂O₄)₂]	1.61	101
VOCl₂(2Ph₃P)(2H₂O)	1.61	218
VO(ClO₄)₂(4Ph₃AsO)	1.88	173
[VO(Q)₂(Ph₂NH)]	1.93	105
[VO(Q)₂ o-C₆H₄(NH₂)(COOCH₃)]	1.96	105
[VO(3-ASE)]	1.96	277
[VO(pc)]	1.60	338
[VO(T)₂]	1.6-2.1	103
[VO(5-Br-sal-o-HA)]	1.47	383, 384
[VO(5-Cl-sal-o-HA)]	1.33	383, 384
[VO(sal-o-HA)]	1.24	383, 384
[VO(o-HAPE)]	2.50	278

Figure 1.—Energy level diagram for VO(H₂O)₅²⁺, according to Ballhausen and Gray (17). Vanadium orbitals are to the left, oxygen orbitals are to the right, and the molecular orbitals are in the center. The single unpaired electron is shown in the nonbonding b_2 level.

ultraviolet spectral studies (17, 18, 26, 30, 169, 240, 253, 254, 336, 337). In the past dozen years there have appeared at least 30 publications containing results of electronic spectral studies, but only a few of these deal with the interesting by-product of such studies, viz., theoretical interpretation of the spectra in terms of an electronic structural model (17, 118, 125, 169, 185, 253, 254, 336, 337). The spectral data are summarized in Table V.

In general, three low intensity absorption bands are found at room temperature in the spectral region 1200–350 mμ (8300-28,600 cm.⁻¹). These are often called d–d or ligand-field bands, but for convenience we shall refer to these as bands I (between 11,000 and 16,000

cm.⁻¹), II (between 14,500 and 19,000 cm.⁻¹), and III (between 21,000 and 30,000 cm.⁻¹). The intensities fall in the ranges 10-10, 5-50, and 5-100, respectively. From Table V the following pertinent observations may be made. (a) The third band, III, is not always observed, being often buried beneath a high intensity charge-transfer band (or more accurately the low energy tail of that band), and when it is observed it is generally a shoulder so that its maximum position is known with the least accuracy among the three bands. (b) The wide range of energies for the three bands reflects the sensitivity of the electronic transitions to the environment (first coordination sphere members) of the VO²⁺ species. (c) In at least two (and perhaps more) cases, VO(tart)²⁻ and VO(lact)²⁻, four bands are observed in this spectral region at room temperature. (d) It is not yet possible to make meaningful assignments of the high intensity charge-transfer-type bands which have (occasionally) been reported in the ultraviolet region. As with many other transition metal complexes, these are generally more difficult to interpret and this becomes particularly the case when the central species itself is a molecule ion rather than an atomic ion. Now let us consider what theoretical interpretations can be or have been made to account for the low intensity bands.

Early (1957) crystal field models of the vanadyl(IV) ion, proposed by Furlani (125), Feltham (118), and Jørgensen (185), were later (1962) shown by Ballhausen and Gray (17) to be quantitatively inadequate. (It should be mentioned here, however, that Jørgensen did suggest that two of the orbitals of the partly filled 3d-shell become strongly π-antibonding to the oxygen.) Using a modified self-consistent Wolfsberg-Helmholtz

TABLE V

Visible and Ultraviolet Band Maxima (in kK. = 1000 cm.$^{-1}$ Units) for Various Complex Species

Complex	Conditions	I	II	III	Other	Ref.
VO^{2+}	0.5–2 M HClO$_4$	13.1	16.0	—	41.7	165
	3 M HClO$_4$	13.06	(14.9)	—		278
	10 M HClO$_4$	13.6	15.8	—		165
	12 M HCl	13.7	—	—		5, 165
	2 M H$_2$SO$_4$	13.3	16.3	—		73a
	Aq. H$_2$SO$_4$	13.23	16.2	—		211
	8 M H$_2$SO$_4$	13.3	—	—		165
	65% oleum	12.5	14.9	—		211
	100% H$_2$SO$_4$	12.8	14.5	—		211
VOSO$_4$(5H$_2$O)	0.1–0.01 M H$_2$SO$_4$	13.06	16.0	—		14
	Crystal	13.0	16.0	—	41.7	14
	Powder	12.9	16.1	—	41.7	14
	Powder	13.0	16.2	—		73a
VO–NCS$^+$	Aq. soln.	13.9	17.2	—		161
(Me$_4$N)$_3$[VO(NCS)$_5$]	CH$_3$CN	13.5	17.2	23.9	31.8, 37.9	169
(Et$_4$N)$_3$[VO(NCS)$_5$]	CH$_3$CN	13.6	17.2	23.7	3.18, 38.5	169
Cs$_3$[VO(CN)$_5$]	H$_2$O	14.7	—	24.3		169
(Me$_4$N)$_3$[VO(CN)$_5$]	MeOH	14.6	20.4	—		331
	1:1 propylene glycol–water	14.7	19.4	24.6		337
(NH$_4$)$_3$[VOF$_5$]	Aq. HF		15.8	—	43.0	169
	H$_2$O	10.97	14.97	—		337
[VO(DMSO)$_5$](ClO$_4$)$_2$	CH$_3$CN	12.8	14.8	—	39.2, 40.2	169
VO(DMSO)$_5$Br$_2$	CH$_3$CN	12.9	15.5	25.7	39.4, 40.3	169
[VO(ox)$_2$]$^{2-}$	H$_2$O	12.6	16.5	29.4		185
	H$_2$O	12.6	16.2	(30.3)	(38.5)	163
	H$_2$O	12.6	16.7	29.0		146
[VO(DMSO)$_3$Cl$_2$]	CH$_3$CN	14.4	—	25.3	34.0, 39.2, 40.2	169
	CH$_2$Cl$_2$	14.0	—	(25.3)	(26.7)	173
VO(ClO$_4$)$_2$(5C$_5$H$_5$NO)	CH$_2$Cl$_2$	—	16.0(18.0)	27.8		173
VOCl$_2$(4Ph$_3$AsO)	CH$_2$Cl$_2$	13.4	(15.4)	(25.3)		173
VOCl$_2$(2Ph$_3$PO)	CH$_2$Cl$_2$	13.5	—	(25.0)		173
[VO(ophen)](ClO$_4$)$_2$	CH$_3$CN	—	15.4	28.9	30.6, 33.8	169
[VO(dipy)$_2$](ClO$_4$)$_2$	CH$_3$CN	—	15.4		31.6, 32.8, 33.3	169
VO(ophen)$_2$Cl$_2$	CH$_3$CN	14.5	17.9	25.3	28.8, 30.8, 34.3	169
VO(dipy)$_2$Cl$_2$	CH$_3$CN	14.6	—	26.8	32.0, 32.5	169
VO(ophen)$_2$Br$_2$(H$_2$O)	CH$_3$CN	14.6	—	25.3	28.8, 34.3	169
VO(dipy)$_2$Br$_2$(H$_2$O)	CH$_3$CN	14.3	16.0	27.0	31.9, 33.4	169
VO(ophen)$_2$SO$_4$	CH$_3$CN	—	16.0	23.6	28.9, 30.8, 35.0	169
VO(ophen)$_{1.5}$(NCS)$_2$	CH$_3$CN	13.7	19.0	23.8	29.2, 30.5, (34.7)	169
VO(dipy)$_{1.5}$(NCS)$_2$	CH$_3$CN	13.7	18.3	—	32.0, 32.5, 33.9	169
[VO(ophen)Cl$_2$]	EtOH	13.2	16.0	23.0		77
	Refl.	11.0, 12.0	15.15	23.2		77
[VO(dipy)Cl$_2$]	EtOH	13.3	16.0	26.8		77
	Refl.	11.06	15.5	23.5		77
[VO(py)$_2$(NCS)$_2$]	CHCl$_3$	13.5	17.1	29.9		9, 14
[VO(oxine)$_2$]	CH$_3$CN	—	—	21.3	26.7 30.0, 31.4	169
	py	—	—	24.4		48
[VO(acac-F$_6$)$_2$]		13.0	16.0	21.0	33.0	253
(Me$_4$N)$_2$[VOCl$_4$(EtOH)]	CH$_3$CN	13.9	—	25.25	34.2	169
[VO(edta)]$^{2-}$	H$_2$O	12.8	17.2	29.8		185
VO(cit)$^{x-}$	2 M NH$_4$OH	11.8	18.8	24.0		185
VO(tart)$^{2-}$	Aq. NH$_3$	11.0	17.1, 18.8	25.3		185, 240
VO(tartH)$^-$	H$_2$O	13.0	17.7	28.8		185
	pH 3.5	12.9				73
(NH$_4$)$_2$[VO(tart)](H$_2$O)	Refl.	11.8	17.0, 19.3	25.3		240
VO(lact)$_y$$^{x-}$	Aq. NH$_3$	12.3	16.6, 18.9	24.4		240
[VO{o-C$_6$H$_4$(O)(CO$_2$)}$_2$]$^{2-}$	H$_2$O	13.15	17.25	31.25	40.8	10
[VO(tetraphenylporphines)]	CHCl$_3$	—	—	23.5		364
[VO(en-bis-sal)]	MeOH	—	17.5	27.7	36.1, 42.0	47
	CHCl$_3$	—	16.8	27.0	35.1, 40.5	47
[VO(pn-bis-sal)]	MeOH	—	17.65	27.8	36.1, 41.7	47

(318) molecular-orbital method, Ballhausen and Gray (17) treated the molecule ion $VO(H_2O)_5^{2+}$. In a sophisticated and detailed calculation, necessarily with many approximations, they arrived at the energy level scheme shown in Figure 1. They used their model to interpret optical, e.s.r., and magnetic properties of VO^{2+} complexes in general and others followed them using the same model to interpret results for many more VO^{2+} complexes. In fact, essentially the same model was proposed for CrO^{3+} and MoO^{3+} (both d^1-systems also) by Gray and Hare (156)

The Ballhausen–Gray orbital transformation scheme for the C_{4v} species $VO(H_2O)_5^{2+}$ defines: (a) a strong σ-bond of a_1 symmetry between the $(3d_{z^2} + 4s)$ hybrid on vanadium and the sp_σ oxygen hybrid; (b) two π-bonds of symmetry e between the d_{xz} vanadium orbitals and the $2p_x$ and $2p_y$ oxygen orbitals; (c) four σ-bonds formed between the sp_σ hybrids (on the equivalent water oxygens) and the vanadium $(4s-3d_{z^2})$ (a_1 symmetry), $4p_x$ and $4p_y$ (e symmetry), and $3d_{x^2-y^2}$ (b_1 symmetry) orbitals; (d) the sixth ligand forming a σ-bond with the $4p_z$ vanadium orbital; and (e) the non-bonding $3d_{xy}$ vanadium orbital of symmetry b_2.

The resulting energy level diagram is that shown in Figure 1.

An entirely analogous, but independent, ligand field approach has been applied by McGlynn (334) to a general species VOL_4^{n+}. He first elaborated the electronic structure of the $C_{\infty v}$ entity, VO^{2+}, and then he coupled the equatorial ligands to this molecule ion in C_{4v} symmetry by inclusion of $\pi_\parallel$- and $\pi_\perp$-bonding, as well as σ-bonding. This added feature (the inclusion of π-bonding from the equatorial ligands, which we feel must be quite important) is the primary source of the only major difference in the two energy schemes, which is the relative ordering of the two antibonding levels b_1^* and e_π^*. The matter of this divergence of prediction has not been unambiguously settled experimentally yet, but it may not be of very great importance because it appears now that energy levels in question are so close together that inversion of their order may occur from complex to complex.

Ballhausen and Gray assign the first optical band, I, to the electron transition $b_2 \rightarrow e_\pi^*$ or $^2B_2 \rightarrow {}^2E(I)$; the second, II, to $b_2 \rightarrow b_1^*$ or $^2B_2 \rightarrow {}^2B_1$; and the third, III, to $b_2 \rightarrow Ia_1^*$ or $^2B_2 \rightarrow {}^2A_1$. All higher energy bands that are observed out to 50,000 cm.$^{-1}$ are assumed to be charge transfer in origin. Thus three optical transitions are predicted by the symmetry C_{4v} of the $VO(H_2O)_5^{2+}$, and it would appear that these are generally the bands designed as I, II, and III. Note that the lower symmetry C_{2v} complexes, e.g., [VO-(acac)$_2$], also show only three bands, and it has been assumed that the splitting of the e_π^* level caused by the lower symmetry is simply too small to be observed experimentally.
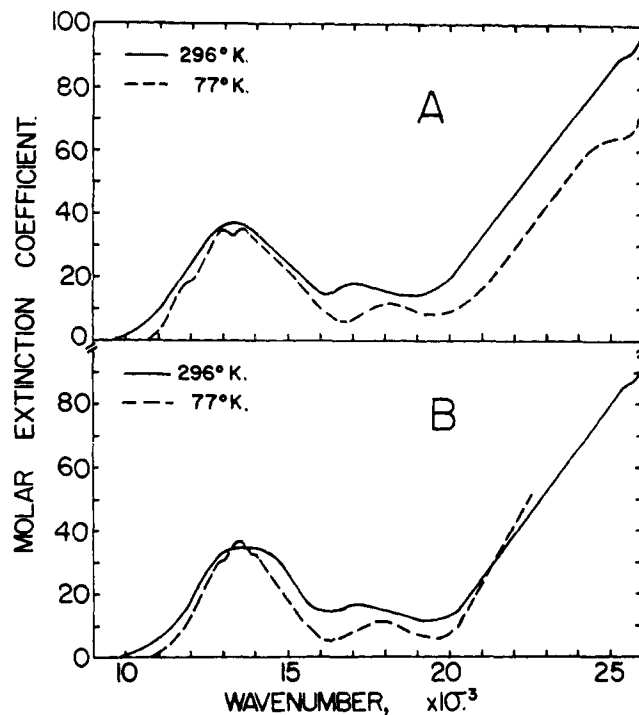

Figure 2.—The optical absorption spectra of VO(acac)$_2$ dissolved in: A, 3:7 isopropyl alcohol–isopentane; B, 2:5:5 ethanol–isopentane–ether; at 296 and at 77°K. (337).

However, there is a growing amount of experimental data which suggest that there may be cause for questioning the universality, if not the specific validity, of the Ballhausen–Gray scheme (vide infra). But before that most recent spectral work is considered, a brief discussion will be given of another spectral study carried out in the author's laboratory at a time when the Ballhausen–Gray scheme was accepted as generally valid for all vanadyl(IV) complexes. It will be seen that the empirical value of this study is not vitiated by the alterations in the theory which are to be suggested later.

The blue-green complex [VO(acac)$_2$] was dissolved in a number of pure solvents, and the shifts produced in the optical bands were recorded (336). It was expected that a solvent molecule would add more or less strongly to the sixth spatial position and thereby alter the magnitude of the strong axial perturbation due to the oxygen in the trans position to the solvent molecule. The effect was found to be most sensitively recorded in a new parameter, $D_{II,I}$, the difference between the first and second d-d bands. These are displaced in opposite directions upon solvent changes. The value for $10Dq$ (or Δ), determined according to the Ballhausen–Gray scheme as the second band maximum, changes by ~ 1200 cm.$^{-1}$ through a solvent series, whereas $D_{II,I}$ shows a spread nearly four times that large in the same series. The values of $D_{II,I}$ (given in units of kK. = 1000 cm.$^{-1}$) for a series of solvents is given in Table VI. It is seen that this totally empirical parameter is a

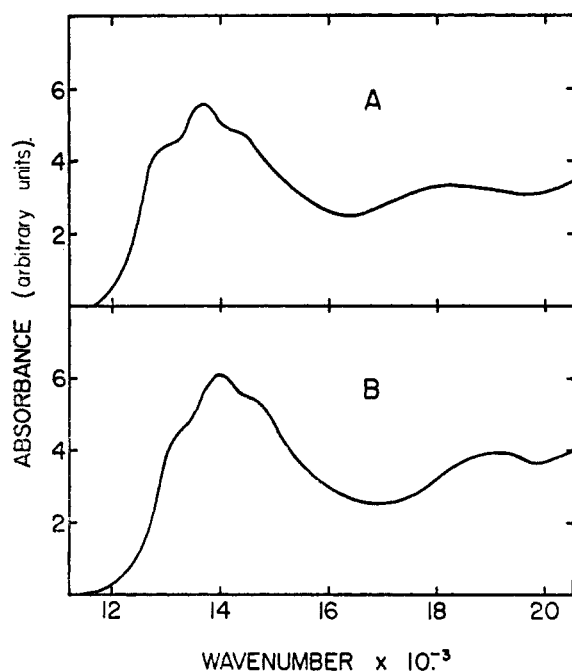Figure 3.—Optical absorption spectra of: A, $(NH_4)_3[VOF_5]$ and, B, $(Et_4N)_3[VO(NCS)_5]$ in KBr pellets at 77°K. (254).

moderately sensitive one for ranking solvents. It appears that what may be termed a "secondary" solvent effect, caused by the orientation of solvent molecules in the second coordination sphere, is not nearly so important as the "primary" effect, which is the addition of a single solvent molecule to the first coordination sphere. This may be seen in the closeness of the $D_{II,I}$ values for solid and solution samples where the same solvent molecule is involved.

Meaningful theoretical interpretations of the foregoing results are complicated by factors such as relative σ- and π-donor capacities of the ligands and their steric requirements, but also now by the recent low temperature spectral studies which have revealed more complex visible spectra than were found in the room temperature investigations. Examination of the visible spectrum at 77°K. of $VO(acac)_2$, dissolved in a number of different solvent mixtures which yield glass matrices at low temperatures, has revealed that the room temperature band, I, is actually an envelope containing at least three bands (253, 254, 337). Some of the pertinent data are collected in Table VII, where it is seen that low temperature KBr pellet spectra have also been obtained and they support the solution findings. Some of the low temperature spectra are shown in Figures 2 and 3.

Since the molecule has a C_{2v} symmetry, which predicts complete removal of d-orbital degeneracy (i.e., the twofold degeneracy of the e_π^* level is removed), four d–d transitions are possible, although not all are allowed by formal symmetry rules. Therefore it is

TABLE VI
EXPERIMENTAL BAND MAXIMA AND $D_{II,I}$, THE DIFFERENCE BETWEEN BANDS I AND II, ALL IN kK. UNITS, FOR $[VO(ACAC)_2]$ WITH VARIOUS SIXTH POSITION LIGANDS[a]

Sixth ligand (ref.)	I	II	III	$D_{II,I}$
Water	12.33	17.82	(2610)	5.49
Formamide (145)	—[b]	—	—	5.15
Ethylamine (145)	—[b]	—	—	4.73
Ammonia (145)	—[b]	—	—	4.62
Methanol	13.03	17.45	25.63	4.42
Methanol (103)	13.22	17.38	25.00	4.16
Methanol (24)	12.82	17.24	25.64	4.42
Methanol (73a)	13.0	17.6	25.4	4.6
Pyridine	13.00	17.39	—	4.39
Pyridine (103)	12.99	17.22	23.80	4.21
Pyridine (24)	13.02	17.24	—	4.22
Pyridine (145)	13.00	17.40	25.00	4.40
Pyridine (73a)	13.3	17.4	24.0	4.11
n-Propylamine	13.17	17.48	—	4.31
n-Propylamine (145)	12.94	17.30	24.69	4.36
Ethanol	12.98	17.24	(25.70)	4.26
Ethanol (165)	12.80	17.30	—	4.50
Ethanol (73a)	13.0	17.3	25.3	4.3
Quinoline (145)	—[b]	—	—	4.21
Dimethyl sulfoxide	12.85	17.03	24.99	4.18
n-Butyl alcohol (73a)	13.2	17.3	25.4	4.1
Dioxane	13.83	17.85	—	4.02
Piperidine[c]	13.28	17.30	—	4.02
Piperidine[c] (145)	—[b]	—	—	3.99
Dimethylformamide	13.03	16.97	25.12	3.94
n-Amyl alcohol (73a)	13.3	17.1	25.2	3.8
TEA-IP-E (3:1:3) (254)	13.50	17.25	—	3.75
Acetic acid[c]	13.79	17.48	—	3.69
IPA-IP (3:7) (304)	13.38	16.94	25.70	3.56
E-T-E (2:1:1) (254)	13.58	16.88	—	3.30
Formic acid[c]	13.28	16.52	—	3.25
E-IP-E (2:5:5) (304)	13.79	17.00	25.97	3.21
Tetrahydrofuran	13.66	16.80	—	3.14
Acetonitrile	14.20	16.80	25.80	2.60
Acetonitrile (24)	14.28	16.66	25.57	2.38
Nitromethane	14.57	16.83	(25.37)	2.26
Nitrobenzene (24)	14.71	16.66	—	1.95
Chloroform	14.92	16.86	25.97	1.94
Chloroform (103)	14.82	16.80	25.00	1.98
Chloroform (73a)	15.0	16.8	25.6	1.8
Benzene	15.31	16.89	25.70	1.58
Benzene (24)	15.15	16.78	25.32	1.63
Benzene (73a)	15.3	17.0	25.5	1.7
Carbon disulfide	15.08	16.66	—	1.58
Toluene	15.31	16.86	—	1.55
m-Xylene	15.22	16.72	25.31	1.50
Reflectance (296)	14.80	16.0	25.0	1.2
Reflectance (73a)	14.5	16.7	24.5	2.2
Carbon tetrachloride	15.79	16.86	25.97	1.07

[a] The $[VO(acac)_2]$ is dissolved in the solvent listed as the sixth ligand, except for those examples taken from ref. 145, which represent reflectance measurements on solid compounds [VO-(acac)_2L] in which the ligand L is presumed attached to the sixth position. All data not otherwise referenced come from ref. 302. [b] These data were not supplied to the author, only the values in the last column. [c] Precipitates form in a short time on standing.

tempting to assign all of the four bands observed between 11,000 and 19,000 cm.$^{-1}$ to this origin. This assignment would then prescribe a charge-transfer origin to the band III at about 25,000 cm.$^{-1}$, for which

TABLE VII

EXPERIMENTAL BAND MAXIMA FOR SOME VANADYL(IV) COMPLEXES AT LOW TEMPERATURE (254)

Compound	Symmetry	Medium[a]	$\bar{\nu}_{max}$, cm.$^{-1}$ T, 296°K.	$\bar{\nu}_{max}$, cm.$^{-1}$ T, 77°K.	Separations T, 77°K.
[VO(acac)₂]	C_{2v}	Soln. (2:5:5 ethanol–isopentane–ether)	13,790	12,980[b]	600
				13,580	600
				14,180[b]	
			17,000	17,920	3740
[VO(acac)₂]	C_{2v}	Soln. (3:7 isopropyl alcohol–isopentane)	13,380	12,040[b]	
				12,980	940
				13,000	620
			16,940	18,050	4450
[VO(acac)₂]	C_{2v}	Soln. (3:1:3 triethylamine–isopentane–ether)	13,500	11,440[b]	
				12,550[b]	1100
				13,000	450
			17,250	17,500	4500
[VO(acac)₂]	C_{2v}	Soln. (2:1:1 ether–toluene–ethanol)	13,580	13,000[b]	
				13,520	520
				14,070[b]	550
			16,880	17,790	3720
[VO(acac)₂]	C_{2v}	KBr pellet	14,800	13,950[b]	
				14,500	550
				15,100[b]	600
			16,000	17,330	2230
(NH₄)₃[VOF₅]	C_{4v}	KBr pellet		13,160[b]	
				13,660	500
				14,100[b]	440
				18,200	4100
(Et₄N)₃[VO(NCS)₅]	C_{4v}	KBr pellet		13,430[b]	
				14,000	500
				14,500[b]	500
				19,230	4730

[a] All solvent component ratios are by volume.   [b] These values represent shoulder estimates (± 100 cm.$^{-1}$).

evidence has been cited (254, 337). Although the origin of the splitting of band I into three would appear at first to be obviously vibronic, there are several good reasons (none, unfortunately, sufficiently unequivocal at the present time) for ruling out this explanation (254).

The complexes (Et₄N)₃[VO(NCS)₅] and (NH₄)₃[VOF₅], in which the vanadium(IV) is in a C_{4v} symmetry site, were expected to show three d–d transitions, but, as is seen from the data (Table VII) and Figures 2 and 3, even in these cases band I is resolved into three at low temperature. The explanation for the complete removal of d-orbital degeneracy in these examples is tentatively suggested (254) to be the operation of spin-orbit coupling, although Jahn-Teller splitting in the excited level might also be offered as causing this splitting

Low temperature (liquid air) studies from another laboratory (26), carried out on single crystals of VO(acac)₂, have subsequently revealed the same structure (three peaks) in band I, and a symmetrical band II; but additional features not uncovered before were observed at higher energies. Firstly, two sharp bands were found at about 23,000 cm.$^{-1}$, split by about 350 cm.$^{-1}$. Secondly, the 25,000-cm.$^{-1}$ band was found split into at

least six components spaced approximately 700 cm.$^{-1}$ apart. The authors of this work feel that the latter splitting as well as that occurring in band I is vibrational in origin, whereas the sharp, split bands near 23,000-cm.$^{-1}$ arise from doublet → quartet transitions. This author, however, still favors the electronic origin for all observed bands, including the six components in the 25,000 cm.$^{-1}$ region, all of which are predictable from the revised energy level scheme proposed by Ortolano, Selbin, and McGlynn (254).

However, it should be concluded that in spite of all of the new spectral evidence pointing to the necessity for modification of the attractive Ballhausen–Gray scheme for vanadyl complexes the picture has only become more cloudy, and it can only be hoped that further work now in progress in several laboratories will allow unambiguous assignment of bands.

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