OXOVANADIUM(IV) COMPLEXES

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A. INTRODUCTION

Interest in the chemistry of the oxovanadium(IV) species, VO^{2+}, has been increasing recently, as reflected in the seventy or so papers published or in press since this author's 1965 review article[1], which covered all previous literature (400 references) through the first few months of 1964. It is perhaps more pertinent that the papers which have appeared since that review have, in sum, advanced our knowledge of this interesting cationic entity at least as much if not more than all of the previous papers taken together.

Whence derives all the flurry of interest? Coordination chemists may see VO^{2+} as perhaps the most stable and persistent diatomic cation available for varied complex ion research. It forms hundreds of stable anionic, cationic, or neutral complexes, capable of existing in the solid, liquid, or even vapor phase, with the VO^{2+} entity maintaining a discrete discernable existence in each complex and in each phase. Since it is a central *molecule*-ion the compounds of this species may be investigated by means not possible with compounds of central *atom*-ions. Furthermore, the groundstate configuration, $[Ar]3d^1$, of the tetravalent vanadium gives this species added attraction because of the expected similarities, *via* the "hole" formalism, to the Cu^{2+}-d^9 system. Thus, of 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 $(Ru, Os)^{VII}$; *all* are much less stable and less common species and, except for Ti^{III} and Mo^{V}, form relatively few compounds amenable to detailed and facile investigation. Finally, the chemists concerned with ESR find this oxidation state of vanadium of great experimental and theoretical interest because of the isotopic purity of the naturally occurring vanadium-51 isotope, its high nuclear spin ($I = 7/2$), and the single, hence unpaired, *d*-electron outside of a closed shell. Since all of the aqueous chemistry and probably 98% of the solid state chemistry of tetravalent vanadium involves VO^{2+}, it is clear that almost all ESR work deals with compounds of this species.

TABLE I

SOME EXAMPLES[a] OF VO^{2+} COMPLEXES CATEGORIZED BY GENERALIZED FORMULA[b]

1. [VOa$_{4\text{ or }5}$ and [VOa$_4$b]
   a = H_2O, F^-, Cl^-, NCS^-, CN^-, DMSO, Ph_3PO, Ph_3AsO, pyNO, 4-substituted-pyNO[28]
   b = usually H_2O, ROH, or X^-
2. [VOa$_3$b] and [VOa$_2$b$_2$]
   a = py, DMSO, THF, Ph_3PO, ROH, H_2O b = Cl^-, F^-, SO_4^{2-}, Br^-, etc.
3. [VOa$_{2\text{ or }3}$(AA)]
   AA =[2] ox^-, *o*-phen, dipy, SO_4^{2-}, diphos[55]   a = F^-, Cl^-, Br^-, NCS^-, H_2O, etc.
4. [VO(AA)$_2$] and [VO(AA)$_2$a]
   AA = $acac^-$, F_6acac^-, *o*-phen, ox^{2-}, MNT^-, dipy[53]
   a = H_2O, X^-, NCS^-, py, substituted-py, Ph_3PO, Ph_3AsO, pyNO, DMSO[29], series of aromatic and aliphatic N-bases[32], MeOH[32], etc.
5. [VO(AB)$_2$] and [VO(AB)$_2$a]
   AB = $oxine^-$, unsym. β-diketones, cat^{2-}, sal^-, $benzohydroxamate^-$, quinaldinate, 3-hydroxy-1,3-diphenyltriazene, (and other N-1- or N-3-substituted hydroxytriazenes), big^- (and substituted-big), pyc[38,44]   a = solvent molecule, aromatic amine, heterocyclic base
6. [VO(AA) (BB)] (none known) and [VO(AB) (CD)]
   AB = X-salen-N(R)(R')$^-$ [28]   CD = X-sal^-
7. [VO(AA)a$_{1\text{ or }2}$] (none known) and [VO(ABA)a$_{1\text{ or }2}$]
   ABA = lut^{2-} [44,57] $coll^{2-}$ [57], iminodiacetate[57]
   a = H_2O, aromatic amine, heterocyclic base[57]
8. [VO(ABC)a$_{1\text{ or }2}$] (none known with certainty)
   ABC = $chel^{2-}$ [57]   *a* = see 7 above
9. [VO(ABA) (AA)] and [VO(ABC) (AA)] and [VO(ABA) (AB)] and [VO(ABC) (AB)]
   ABA, ABC = same as in 7 and 8
   AA = *o*-phen, dipy, $acac^-$
   AB = gly^-, $oxine^-$, $benzohydroxamate^-$, pic^-, etc.
10. [VO(AAAA)] and [VO(ABBA)] and [VO(ABBC)]
   AAAA = TPP^{2-}, pc^{2-} ABBA and ABBC = various Schiff bases[38-40]

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[a] References to the literature for a specific complex may be obtained from reference 1; references given in the Table are for new complexes.

[b] The generalized charge designation, e.g., $n\pm$, has been omitted outside each ion bracket.

B. THE COMPLEXES OF OXOVANADIUM(IV)

The large number of complexes of VO^{2+} may be best classified in terms of generalized formulae for the complexes, where we designate monodentate ligands by single lower-case letters, a, b, or c, and multidentate ligands by upper-case letters, such as AA, BB, ABA, etc., for symmetrical and AB, ABC, etc., for unsymmetrical multidentate ligands. Some examples of each type are listed in Table I.

(i) *X-ray studies*

Some additional X-ray diffraction data has been published since the last review[1] and all available pertinent data are collected in Table II, where it may be seen that the vanadyl $V{=}0$ bond lengths are, in general, shorter than most other V–X bond lengths by approximately 0.4–0.5 Å. It is interesting to note that the bond distance (2.22 Å) to the axially positioned H_2O in the ion, $[VO(NCS)_4(H_2O)]^{2-}$, is shorter than in the ion, $[VO(H_2O)_5]^{2+}$ (2.4 Å). It would seem that the stronger ligand NCS^- must weaken the $V{=}O$ bond sufficiently to allow a stronger attachment by H_2O *trans* to the multiply-bonded oxygen. Infrared data for $\bar{\nu}(V{=}O)$ support this hypothesis also, with values of 982, 963 cm^{-1} for the isothiocyanato complex[10] and 1003, 975 cm^{-1} for the aquo ion[17]. It would be particularly interesting and valuable to have X-ray data on some of the new low symmetry complexes which are to be discussed later. It is possible that we shall have just such data on a tartrate complex from Belford's laboratory[18].

TABLE II

SOME PERTINENT BOND LENGTH DATA FOR OXOVANADIUM COMPOUNDS[a,b]

Compound	*V–O length (Å)*[c]	*Other V–X lengths (Å)*	*Ref.*
$VOCl_3$	1.56 (1035)	2.12	2
$VO(acac)_2$	1.57 (996)	1.97	3, 4
V_2O_5	1.58 (1020)	1.77, 1.88, 2.02, 2.81	5, 6
$VOSO_4$	1.59	2.01, 2.05, 2.28	7, 8
$VO(bzacac)_2$	1.605 (995)	1.95, 1.98	4, 9
$(NH_4)_2[VO(NCS)_4(H_2O)] \cdot 4\,H_2O$	1.62 (982, 963)	2.04 (N), 2.22 (O)	10
$V_2O_4 \cdot 2\,H_2O$	1.65 (968)		11
$VO(H_2O)_5SO_4$	1.67 (1003, 975)	2.3, 2.4	12, 13
V_2O_4	1.76	1.86, 1.87, 2.01, 2.03, 2.05	14, 15

[a] Note that the first and third compounds are of *pentavalent* vanadium, included for comparison of $V{=}O^{3+}$ and $V{=}O^{2+}$ lengths.
[b] An X-ray investigation has been reported for monoclinic $(NH_4)_2VOF_4 \cdot H_2O$, space group C_{2h}^5–$P2_1/c$, and tetragonal $VO(ClO_4)_2 \cdot n\,H_2O$ (n=4 or 5), space group D_{4h}^{19}–$I4_1/amd$, but no bond lengths were given in the abstract of the Russian paper[16].
[c] Values in parentheses are assigned IR stretching frequencies, in cm^{-1}, for $V{=}O$.

(ii) *Infrared studies*

It is now well-known that metal–oxygen multiple bonds (and metal–nitrogen multiple bonds also for that matter) may be revealed by infrared bands in the NaCl region[19-21]. The following generalizations, valid for all of the transition metals forming multiple $M=O$ bonds may be made concerning the frequencies for such bonds: terminal $M=O$, 780–1100 cm^{-1}, and bridging[20] M–O–M, 650–920 cm^{-1}. The $V=O^{2+}$ frequencies generally fall in the range 960 ± 50 cm^{-1}, and the bands are usually very strong and sharp[17]. Relatively little new[22-25] IR work, *per se*, with vanadyl complexes has appeared since the previous review[1] but many papers dealing with other aspects of the chemistry also report IR data. Although there have been some very recent attempts made[22,29] to correlate $\bar{\nu}(V=O)$ with other properties of the vanadyl complexes, along the lines originally attempted by Selbin and co-workers[17,30], it is this author's opinion now that the stretching frequency, especially for a multiple bond, is simply too insensitive to other molecular changes to be of much value for such studies.

(iii) *Thermodynamic studies*

In 1961 the first efforts to obtain thermodynamic data on the act of coordination to vanadyl were made[31]. Enthalpies, entropies and free energies of coordination to the sixth, unsolvated position in the neutral complex, $VO(acac)_2$, were obtained by vapor pressure measurements and involved NH_3, $MeNH_2$, (*iso*-Pr)-NH_2 and (*tert*-Bu)NH_2. Enthalpy changes of approximately −15 kcal/mole were found, but the changes in free energies were relatively small in each case. Some interesting similarities were found in the thermodynamic data to the data found with adduct compounds of $(CH_3)_3B$, suggesting similarities in the act of coordination in the two cases. Recently a much more extensive study has appeared[32] in which enthalpy changes were measured calorimetrically in nitrobenzene for the reaction of many N- and a few O-donor ligands with $VO(acac)_2$. Values span the range −10.59 to −5.77 kcal/mole from *n*-decylamine to methanol. The equilibrium constants lie between ≥ 1000 and 0.55 l/mole for the same adducts. Both steric and inductive effects seem to control the ΔH_{rxn} values, but the results show that $VO(acac)_2$ is *not* a sensitive indicator of relative base strength. Some data obtained for $VO(F_3acac)_2$, allow some quantitative measure of the inductive effect in the chelate ring system.

The heat of combustion of $VO(acac)_2$, measured as −1276 kcal/mole, was used in a thermochemical cycle to obtain a value for the V–O bond energy (in the acac–O–V bond, *not* the $V=O$ bond)[33]. The value so obtained, 77.2 kcal/mole, is larger (by 7–28 kcal/mole) than every other M–O bond energy evaluated (where $M = UO_2^{2+}$, Cu^{2+}, Mg^{2+}, Co^{3+}, Fe^{3+}) except for $M = Th^{4+}$, for which case it is roughly equivalent. In view of the bond length data (Table II) for $VO(acac)_2$

(viz., V=O, 1.57 and V–O, 1.97), it seems to this author now that the large bond strength may be taken as an indication of a very strong σ-bond. While the existence of π-bonding also, from the acac–O, cannot be ruled out, it would seem that ionic bonding contributions must be considered as a more likely origin for the enhanced bond strength.

Relatively few studies have been made of complex-ion formation constants for vanadyl complexes[1], but recently such data has been reported for (a) some lactate complexes, using circular dichroism and spectrophotometric measurements[34]; (b) an EDTA complex using spectrophotometry[35]; (c) chelates of picolinic and sulfosalicylic acids and salicyladehyde[36]; and (d) the addition of pyridine[26] to $VO(acac)_2$ and $VO(DBM)_2$.

(*iv*) *Solution studies*

Aside from spectral (including IR, vis–UV and ESR) and thermodynamic studies, relatively little solution work has appeared recently with VO^{2+} and its complexes and the earlier work has been thoroughly reviewed[1]. There have been however, at least three recent kinetics and mechanisms investigations involving the reaction[37] (a) between VO^{2+} and Cr^{VI} in dilute $HClO_4$; (b) between VO^{2+} and Cr^{2+} in acid solution[38]; and[39] (c) between VO^{2+} and V^{2+} in dilute $HClO_4$.

(*v*) *New compounds*

Many new compounds, or known compounds prepared by new methods for the purpose of new studies, have appeared since the previous review[1]. The following discussion will touch upon at least 95% of them.

Many compounds of the type $VO(OOCR)_2$ have been prepared recently[25,40] where R is H[41], CH_3, C_2H_5, n-C_3H_7, n-C_8H_{17}, $ClCH_2$, Cl_2CH, Cl_3C, C_6H_5, $(o\text{-}I)C_6H_4$, n-C_4H_9; and IR spectra have been run[9] for all but the last two. The $\bar{\nu}(V=O)$ values appear to be $\sim 100\ cm^{-1}$ lower than commonly found in VO^{2+} compounds (*vide supra*) and $V^-=O^+ \ldots V^-=O^+ \ldots V^-=O^+$ linkages have been proposed as an explanation[25]. Further support for this proposal is deduced from magnetic susceptibility studies at room temperature of 23 organic salts of VO^{2+} (including those above)[42] and chelates with dicarboxylic acids (such as malonic, succinic, glutaric and adipic [43], in which spin moments less than for the expected *one* electron were observed.

Complexes with picolinic acid, sulfosalicylic acid and salicylaldehyde have been prepared and stability constants determined[36]. Complexes of pyridine-2-carboxylic acid (pycH) of the types $[VO(pyc)_2H_2O]$ and $H[VO(pyc)_3] \cdot 3H_2O$ have been prepared and both yield $[VO(pyc)_2X]$ when treated further with X = pyridine, 2-picoline, aniline, *N,N*-dimethylaniline, etc.[44]. The pyridine-3-carboxylic acid is claimed to react similarly[5] whilst pyridine-2,6-dicarboxylic acid ($lutH_2$) gives shiny-blue $[VO(lut)(H_2O)] \cdot \frac{1}{2}H_2O$, which can be successively hydrated and dehydrated[44].

Complexes of the types $[VOa_4]b_2$ and $[VOa_5]b_2$ have been prepared from 4-substituted pyridine *N*-oxides where the substituted group was CH_3O- or CH_3-, whereas the ring deactivating 4-substituents Cl-, Br-, and NO_2- gave $[VO\,a_2b_2 \cdot H_2O]$ (where b = Cl^-, Br^-)[45]. However when ClO_4^- was the anion all substituted pyridine *N*-oxides gave complexes of the former types.

Some solid EDTA (H_4Y) compounds have been isolated, $M_2VOY \cdot x\,H_2O$ (M = $\frac{1}{2}$ Ba, NH_4, Li, Na, K, Rb, Cs) and $(VO)_2Y \cdot 8H_2O$, and their densities, water solubilities, heat stabilities, IR spectra, X-ray powder patterns and magnetic susceptibilities recorded[46]. Other recent work with the EDTA chelates includes two independent stability-constant determinations[35, 47].

Among what may now be considered the more *routine* types of oxovanadium-(IV) compounds, we have the solids, $VO(ox) \cdot 2\,H_2O$ and $VO(ox) \cdot 4\,H_2O$, described[48] along with their respective magnetic moment of 1.71 and 1.73 B.M., $\bar{\nu}(V{=}O)$ values of 986 and 988 cm^{-1}, and their aqueous-solution visible bands (in kK, with molar extinction coefficients): 12.82 (27.5); 16.67sh (7); 41.60sh (3000) and 45.50 (> 10,000). Also there are $[(Me_2N)_3PO]_2VO(NCS)_2$ reported by Ziegler and co-workers[49], a β,β'-bis(salicylaldimino)diethylamine chelate complex, reported with magnetic and IR data[50], chelates (all monohydrates) with salicylal-2′-hydroxyanalinate and its 5-chloro- and 5-bromo-derivates, which have μ_{eff} values of 1.84, 1.82, and 1.80 B.M., respectively, and which do not obey the Curie–Weiss law between 4.2–300 °K[51], and the solid, nicely crystalline, blue $[VO(H_2O)_5](ClO_4)_2$, shown by IR to involve no ClO_4^- coordination either in solution or in the solid and having $\mu = 1.70$ B.M. in solution[52].

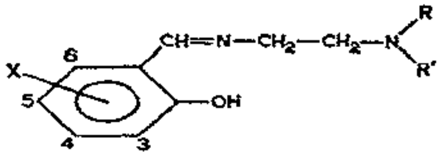
Of the more exotic compound types we have a complex with the sulfur-donor ligand, maleonitrile dithiolate (MNT), $[Ph_3PCH_3]_2[VO(MNT)_2]$, which has $\bar{\nu}(V{=}O)$ at 963 cm^{-1}, is monomeric in nitrobenzene, and which has very interesting electronic and ESR spectra[53]. Then there is $VO(cp)Cl_2$ prepared recently[54] by oxidation with O_2 of $V(cp)_2$. In our laboratory we[55] have succeeded in coordinating the diphosphine ethylenebis(diphenylphosphine), $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, to $VOCl_2$, yielding green, crystalline $[VO(diphos)Cl_2]$, with $\bar{\nu}(V{=}O)$ at 1005 cm^{-1} and visible bands at 13.7, 20.4–21.8, and ~24sh kK.

Perhaps the most interesting new compounds to appear recently are those aptly termed "low-symmetry" complexes. Interest in low-symmetry complexes, *per se*, seems to have started when Selbin and Morpurgo[56] prepared a solid tartrate complex in hopes that spectral studies of a low-symmetry complex would shed more light on the problem of assignments of electronic spectral data, all of which had previously been obtained with complexes of relatively high symmetry (generally C_{2v} or C_{4v}). This matter is considered in detail later in Section III.

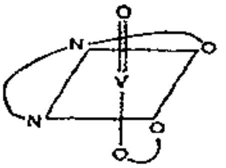
From the laboratory of Dutta has begun to flow a series of low-symmetry complexes, one of which, that with the tridentate pyridine-2,6-dicarboxylic (lutidinic) acid, has already been mentioned[44]. Recently "heterochelates" have been prepared from the tridentates: 4-hydroxypyridine-2,6-dicarboxylic (chelidamic) acid, pyridine-2,4,6-tricarboxylic (collidinic) acid, and iminodiacetic acid; all four tridentates appear to yield complexes of the types, VO(trident)$(H_2O)_2$ and VO(trident)(X)(H_2O), where X = pyridine, 2-picoline, aniline, etc., or VO(trident)(bident) with such bidentates as *o*-phen, dipy, acac, glycine, oxine, benzohydroxamic acid, and picolinic acid[57]. These latter heterochelates display magnetic moments in the somewhat high range of 1.82–1.86 B.M. Unfortunately no optical spectral data is yet available on these interesting compounds, but it is hoped that such data will be forthcoming.

However, a large group of low symmetry complexes has been prepared in the laboratory of Sacconi[28] and their spectral properties have been studied. Seventeen compounds falling into two series are reported along with magnetic and spectral data (vibrational and electronic), the latter to be discussed later. The general formulae are: [X-salen-N(R) (R′)$]_2$VO, in which V is linked to two Schiff bases, and [(X-sal) (X-salen-N(R) (R′)]VO, in which V is linked to one salicylaldehyde group and one Schiff base (and X = H-, 5,6-benzo- or 5-chloro- and R = CH_3, H, C_2H_5, C_6H_5 etc.).

The Schiff bases have the general formula



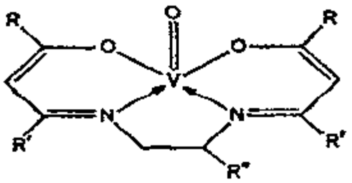
and they are presumably bidentate, coordinating through the oxygen and the imine nitrogen in the first type of complex mentioned. In the second type of complex having both the Schiff base molecule and a molecule of substituted salicylaldehyde bound to the VO^{2+}, the authors[28] believe that the former behaves as a tridentate ligand and the complex ion structure is of the type



However, this is by no means firmly established and it may also be that the Schiff base is still bidentate and possibly the structure distorts toward a trigonal bipyramidal arrangement with the vanadyl oxygen in the equatorial plane. We have made this suggestion for certain oxovanadium(IV) complexes before[30], and it would be most interesting and instructive to have an X-ray crystal structure determination made on one of these complex types.

One of the most exciting developments in oxovanadium(IV) chemistry which has occurred, necessarily with low-symmetry complexes, has been the resolution into optical enantiomorphs of several inner-complexes formed with asymmetric quadridentate ligands. The first report[58] (in 1965), was of the resolution of bis-(acetylacetonepropylenediimino)oxovanadium(IV) on a D-lactose column. Other complexes of quadridentate β-ketoimines were then partially resolved[59] and the rates of racemization (dextro samples) and mutorotation and racemization (laevo fractions) reported.

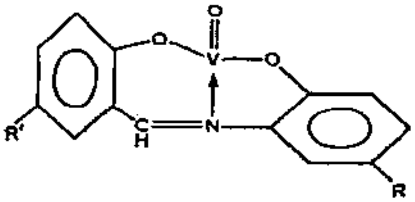
The general formula is as follows:



where $R = R' = R'' = CH_3$ (and $\bar{\nu}(V{=}O) = 978, 945\ cm^{-1}$) or $R' = R'' = CH_3$, $R = C_6H_5$ (and $\bar{\nu}(V{=}O) = 983\ cm^{-1}$). The compound should exist in the four forms, Dd, Ll, Dl and Ld. In a third paper in the series Martin and Ramaiah[60] report the separation into four optical enantiomers of the compound first resolved for VO^{2+}, by means of a double-column chromatographic technique employing D-lactose and elution with toluene. In that paper they also consider the kinetics of mutorotation and racemization of the diastereoisomeric mixtures and the kinetics of chelate exchange with a quadridentate ligand and with benzoylacetone. They find evidence for stereospecificity in the correlation of chelate exchange and the change in optical activity. They also present evidence that the primary separation yields two sets of diastereoisomers Ll, Dl (the laevo fraction) and Ld, Dd (the dextro fraction), and then the secondary separation gives much higher optical purities and the activity is stable over a period of days. Optical resolutions could not be obtained when bidentate β-ketoimines were used as ligands[59].

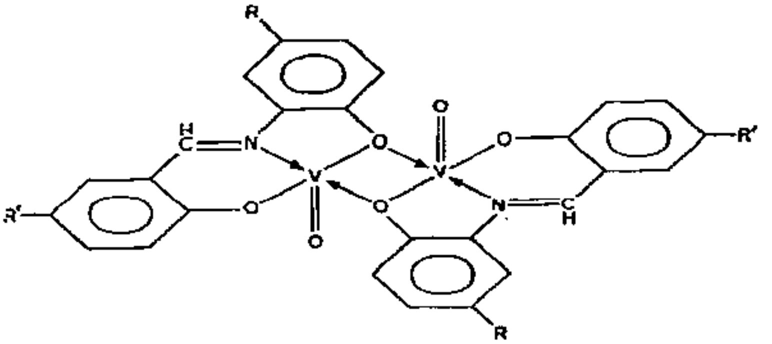
It is interesting to speculate at this point about the possibility of employing an optically-active sample of oxovanadium(IV) compound in a column to attempt to separate asymmetric organic molecules which may be capable of attaching weakly to the (pressumed) vacant sixth position in the molecule. Perhaps the kind of steric direction known to be given by, e.g., optically-active Co^{III} complexes, when they substitute ligands, can operate in the vanadyl case, only without in this system changing the basic structure and composition of the complex. At least in theory a continuous operation for isomer resolution could be envisaged.

Finally, in this section must be mentioned some very new and unusual oxovanadium(IV) low-symmetry type complexes. They have been made from several 5-substituted *N*-(2-hydroxyphenyl)salicylideneimines and have been studied[27] magnetically between 1.4 and 300 °K and by IR. Their general formula is



where R = H, R' = H, CH_3, Cl, Br, NO_2; and R = Cl, R' = H, Cl. When R = H and R' = Cl a monopyridine adduct forms, with $\bar{\nu}(V{=}O)$ at 970 cm^{-1} and μ_{eff} = 1.75 B.M. The low value for μ_{eff} = 1.62 B.M., when R = R' = NO_2, is unexplained. For all of the compounds the range for $\bar{\nu}(V{=}O)$ is 990 ± 20 cm^{-1}. Some of these compounds had already been prepared[61,62], and their abnormally low room-temperature magnetic moments (0.77–1.55 B.M.) prompted the recent work discussed here.

The temperature dependence of the magnetic susceptibility is characteristic of magnetically-isolated exchange coupled (antiferromagnetic) pairs. Thus the complexes are presumed to be dimeric with structure like the corresponding Cu^{II} compounds[63]:



The authors have derived exchange integrals for the vanadyl complexes by fitting the magnetic susceptibility to a theoretical equation for coupled pairs and the results are interpreted in terms of a direct σ metal–metal interaction between unpaired spins in the $3d_{xy}$ orbitals of vanadium atoms. This is in contrast to the analogous Cu^{2+} complexes where spin coupling occurs by superexchange through bridging oxygen atoms.

Although pairwise magnetic exchange is well known in d^9 Cu^{2+}-complexes (where the unpaired spin is in an orbital derived from the e_g set), the above results appear to be the first demonstration of this phenomenon in a d^1 system (where the unpaired spin is in an orbital derived from the t_{2g} set).

C. ELECTRONIC SPECTRAL STUDIES AND THEORETICAL MODELS

Of great interest in recent years are the near infrared, visible, and ultraviolet spectral bands observed for complexes of oxovanadium(IV). Closely related to these experimental studies, and often the main stimulus for them, is a theoretical model to account for the electronic details of the VO^{2+} d^1 system in its various chemical environs. No less than 50 papers contain results and/or interpretations of electronic spectra data, and yet, as we shall see, there is yet to be realized a clear, unambiguous theoretical interpretation of the varied and voluminous data.

In general, vanadyl complexes display three low-intensity, d–d or ligand-field absorption bands in their room-temperature spectra in the 7500–30,000 cm^{-1} region[1]. These bands commonly fall between 11 and 16 kK (I), 14.5 and 19 kK (II) and 20–30 kK (III), with molar extinction coefficients in the range 5–100. Often band III is either not observed (presumably because it is buried beneath a much more intense charge transfer (CT) band which often sets in above 30 kK), or it is seen as a shoulder on the first intense CT band. Increasing numbers of exceptions to this three-band pattern are being uncovered and these will be discussed later.

A decade ago crystal field models of VO^{2+} were elaborated in three independent papers by Furlani[64], Feltham[65], and Jørgensen[66]. But within five years they were shown to be quantitatively inadequate by Ballhausen and Gray[67]. These last authors used a modified self-consistent Wolfsberg–Helmholtz[68] molecular-orbital approach (recently questioned by Fenske[69]) to treat $VO(H_2O)_5{}^{2+}$.

The Ballhausen–Gray (BG) orbital transformation scheme for the C_{4v} species defines:

(a) a strong σ-bond (a_1 symmetry) between the ($3d_{z^2}+4s$) hybrid on vanadium and the sp_σ oxygen hybrid,

(b) two π-bonds (e symmetry) between the d_{xz} and d_{yz} 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) a σ-bond to the sixth ligand using the $4p_z$ vanadium orbital, and

(e) the non-bonding $3d_{xy}$ vanadium orbital (b_2 symmetry).

The resulting energy level scheme, drawn only roughly to scale, is shown in Fig. 1. They used their model to interpret optical, ESR, and magnetic properties of VO^{2+} complexes in general, and others have followed them using the same model to interpret and explain similar results for many more VO^{2+} complexes.

The Ballhausen–Gray (BG) scheme received some independent support from an entirely analogous ligand-field approach[17] applied to a general species $VOL_4{}^{n+}$. In that less rigorous treatment, the electronic structure of the isolated VO^{2+} entity was first elaborated and then the equatorial ligands were coupled to this molecule-ion in C_{4v} symmetry by inclusion of *both* out-of-plane and in-plane π-bonding as well as in-plane σ-bonding. The added feature (inclusion of in-plane π-bonding) 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 yet been unambigously settled experimentally, but it may turn out that in fact the energy levels in question are so close together that inversion of their order may occur from one complex to the next. There is an increasing amount of experimental data, some of which, curiously, is beautifully explained by the BG scheme, and some of which most decidedly cannot be accommodated by that scheme. We shall consider this problem in more detail later.

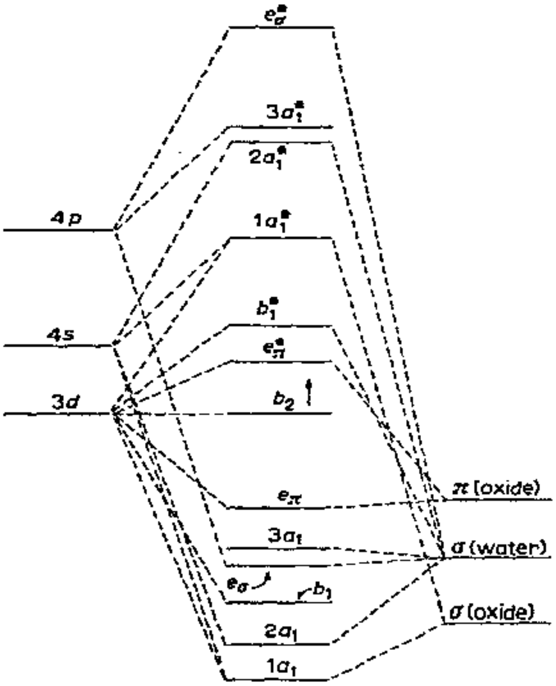


Fig. 1. Energy level diagram for $VO(H_2O)_5^{2+}$, according to Ballhausen and Gray[67]. The vanadium orbitals are on the left, oxygen orbitals are to the right and the molecular orbitals appear in the center. The unpaired electron is shown by the arrow in the nonbonding b_2 level.

But first it will be instructive to consider an interesting empirical observation made in the author's laboratory before the universality, if not the specific validity, of the BG scheme began to be questioned. The experimentally popular complex $VO(acac)_2$ was dissolved in a large number of pure solvents and the shifts produced in the optical bands recorded[70]. It was expected that a solvent molecule would add more or less strongly to the open sixth spatial position, thereby altering the magnitude of the strong (anisotropic) axial perturbation due to the strongly-bound oxygen *trans* to the solvent molecule. The effect was found to be quite sensitively recorded in a parameter, $D_{\mathrm{II,I}}$ the *difference* between the first and second *d–d* bands, or, more accurately, between bands I and II (since the correct assignment of all *d–d* bands is still sought). These are displaced in opposite directions with solvent changes. The value for $10Dq$, determined by the BG scheme to be the value of the band II maximum, changed by 1200 cm^{-1} through a solvent series, whereas $D_{\mathrm{II,I}}$ shows a spread of values nearly four times that large in the same solvent series. For example, for the solvent H_2O (at one end of the solvent ligand series), $10Dq = 17.82$ kK and $\mathrm{D_{II,I}} = 5.49$ kK, and for the solvent CCl_4 (at the other end of the series), $10Dq = 16.86$ kK and $D_{\mathrm{II,I}} = 1.07$ kK. Additional $D_{\mathrm{II,I}}$ data for $VO(acac)_2$ which could be added to Table VI of reference 1, has been published[22,26,29,32].

The first low-temperature (77 °K) spectral data for a vanadyl complex was reported from the author's laboratory[71] in 1963, and some additional low-temperature data became available soon thereafter[72–74]. These 77 °K spectra reveal a definite splitting of band I, always into *three* bands, one being a definite maximum, with a shoulder to either side (Table III). These split bands have been assigned to either an electronic[71,72] or a vibrational[73,74] origin, and the question is not yet satisfactorily settled, although there is additional evidence now, both from ESR and optical data that band I contains at least *two* electronic transitions beneath

TABLE III

EXPERIMENTAL BAND MAXIMA IN kK UNITS (= 1000 cm^{-1}) FOR SOME VO^{2+} COMPOUNDS[a] WHICH HAVE BEEN STUDIED AT LOW TEMPERATURE

Compound	*Medium*[b]	$T = 296$ °K	$T = 77$ °K
$VO(acac)_2$	2 : 5 : 5 ethanol : isopentane : ether	13.79, 17.00	12.98, 13.58, 14.18, 17.92
$VO(acac)_2$	3 : 7 isopropanol : isopentane	13.38, 16.94	12.04, 12.98, 13.60, 18.05
$VO(acac)_2$	3 : 1 : 3 triethylamine : isopentane : ether	13.50, 17.25	11.44, 12.55, 13.00, 17.50
$VO(acac)_2$	2 : 1 : 1 ether : toluene : ethanol	13.58, 16.88	13.00, 13.52, 14.07, 17.79
$VO(acac)_2$	KBr pellet	14.80, 16.00	13.95, 14.50, 15.10, 17.33
$VO(acac)_2$	thin crystal[c]		13.89, 14.50, 15.15, 17.39, 22.42, 22.78[d]
$(NH_4)_3VOF_5$	KBr pellet		13.16, 13.66, 14.10, 18.20
$(Et_4N)_3VO(NCS)_6$	KBr pellet		13.43, 14.00, 14.50, 19.23
$VOCl_5^{3-}$	in host lattice of $K_2TlCl_5 \cdot 2\,H_2O$[e]	15.50, 16.40	14.50(⊥), 15.50(⊥), 15,80(⊥), 26.00(⊥, ‖), also 16.20(‖)

[a] Data from reference 72 except where noted otherwise.

[b] The organic mixtures were employed because they formed good low temperature glasses.

[c] Data taken from Fig. 1 of reference 73, for 90 °K.

[d] Data from the Ph. D. Thesis of W. Yeranos (University of Illinois, 1965) for a single crystal of $VO(acac)_2$ shows a very low intensity band at 12.1 kK as well as the triply split band centered at 14.3 kK and another band at 17.3 kK.

[e] The room temperature peak at ~25.00 kK is split into many components, separated by ~0.7 kK, assumed to be a vibrational progression: 24.88, 25.51, 26.18, 26.88, 27.55, 27.93 kK.

its envelope (*vide infra*), and perhaps one more for certain low-symmetry complexes.

The observation of the four low-intensity bands below 20,000 cm^{-1} for these complexes prompted the semi-empirical delineation of what we may call the "clustered level" scheme of Ortolano, Selbin and McGlynn[72] (OSM). This "crystal field" scheme places all *d-d* transitions below 20,000 cm^{-1} and the first three excited levels (counting 2 for e_π^* and 1 for b_1^*) very close together, i.e., clustered, and only slightly removed from the next level. Thus the transitions were believed to be ordered as follows:

$$\left.\begin{array}{ll} b_2 \to e_\pi^*, b_1^* & \sim 13{,}000\ \text{cm}^{-1} \\ b_2 \to Ia_1^* & \sim 17{,}000\ \text{cm}^{-1} \end{array}\right\} \quad d\text{–}d$$

$$\begin{array}{lll} e_\pi^b \to b_2 & \sim 25{,}000\ \text{cm}^{-1} & \text{CT} \end{array}$$

Support for the BG scheme has been suggested by Wuthrich[75,76] from his ESR and optical data, but this matter is considered further in section IV where this support is questioned. Additional support is deduced by Jones and Larsen[77] from their absorption spectra and circular dichroism studies of some asymmetric complexes of VO^{2+}, employing optically-active lactate, tartrate, and propylenediamine-bis(acetylacetonate), as ligands. On the other hand, the BG scheme, or parts of it, are questioned by (a) the work of Belford and co-workers[73] who also disagree in part with the OSM assignments, but who make no definite committment from their own data; (b) by Wentworth and Piper[74], who at least for $VOCl_5^{3-}$, agree with the BG scheme for the first two transitions, but place the ($b_2 \to Ia_1^*$) transition even higher than the BG scheme would; (c) by Sacconi and Campigli[28], who deduce some support for the clustered level scheme from their spectral data on low-symmetry complexes; and (d) by Kuska and Rogers[78], who believe the 13.25 kK band for $VOSO_4$ in dilute H_2SO_4 contains both xy → xz, yz and xy → x^2-y^2 transitions, and who assign bands in the 16.2–26.0 kK region to xy → z^2.

It is the present opinion of this author that no one has yet put forth a completely acceptable energy-level scheme and coupled it in an entirely correct way to the bands observed in vanadyl complexes in general. And of course there is no *a priori* reason for believing that only one energy scheme will be satisfactory for all cases. In fact it appears from very recent data that energy levels may even cross one another from complex to complex and the only certainties at this writing are (a) that the ground level (singly occupied) is the non-bonding (in first approximation) b_2 orbital; (b) that somewhere above this level lie the antibonding orbitals e_π^* (doubly degenerate in C_{4v}, but split in lower symmetries) and b_1^*, but the *closeness and even the order of these levels is not always certain*; (c) that somewhere above these levels lies the antibonding Ia_1^*, which is now variously placed (*i*) below 20 kK, (*ii*) at 20–30 kK, or (*iii*) somewhere between 35 and 50 kK; and (d) that there is a relatively low intensity first charge transfer transition that might be occurring at as low an energy as 18–20 kK.

Other recent papers reporting new spectral data for relatively symmetrical VO^{2+} complexes are those of Wuthrich[75], Garvey and Ragsdale[45], Splinter and Tobias[29], and Arris and Duffy[79].

With this as background, let us turn now to the recent spectral studies of low-symmetry complexes. Selbin and Morpurgo[56] found that the tartrate, lactate, malate, mandelate and citrate complex in alkaline solutions yielded *three* distinct transitions before, and in addition to, a ~25 kK band: (1) 11.2–21.9 kK, (2) 14.9–16.8 kK, and (3) 18.0–19.3 kK. These were assigned, respectively, to $xy \rightarrow xz$; $xy \rightarrow x^2-y^2$; and $xy \rightarrow z^2$ and the fourth band, 24.3–25.1 kK, to the first CT transition. This was the first support for the OSM scheme from room temperature data. Then Sacconi and Campigli[28] found *three* bands in the same spectral regions for a large series of low-symmetry complexes (described earlier): (1) 11.5–12.3 kK, (2) 16.65–18.0 kK and (3) 18.2–20 kK. In fact they may even have resolved the first band into its expected two components in their pyridine-solution spectra, where this author counts *four* bands in their spectrum of $[H\text{-salen-}N(H)(C_6H_5)]_2$-VO in pyridine, at 12.5, 13.8, 16.65, and 18.6 kK! So unless we are willing to accept a rather large splitting of the $e_\pi{}^*$ level (approximately 4000 cm^{-1}), which might be possible but is very improbable, in these very low-symmetry complexes, it seems that we must alternatively accept either the proposition that all *d–d* transitions occur below 20,000 cm^{-1} or the proposition that the 18–20 kK band is of CT origin. Neither of these alternatives can yet be ruled out.

Now additional support for the proposal that the first band is composed of the two transitions $b_2 \rightarrow e_\pi{}^*$ and $b_2 \rightarrow b_1{}^*$ comes from recent unpublished work currently in progress in the author's laboratory[80]. The reflectance spectrum of $VO(F_6acac)_2$ displays bands at 10.60, 13.25, 16.67 and 21.28 kK. It is suggested here that the very low-intensity 10.60 kK band arises from the symmetry forbidden $b_2 \rightarrow b_1{}^*$ transition, which is reasonable if the σ-bonding from the β-diketone is as weak as is indicated by other known chemical properties of the complex. The 13.25 kK band then is proposed as the $b_2 \rightarrow e_\pi{}^*$ transition (note reversal of order of $b_1{}^*$ and $e_\pi{}^*$ levels), and the remaining two higher energy bands are $b_2 \rightarrow Ia_1{}^*$, and the first charge transfer transition, but here there is no certainty as to which is which. An initial vapor spectrum, the first such spectrum for a VO^{2+} complex, of $VO(F_6acac)_2$ has revealed bands at 14.84, 17.40, ~20 and 28.58 kK. Work is presently in progress to refine that spectrum and to see if more information can be obtained. But at the moment this data does support our previous assignments.

Additionally, spectral data for the lower-symmetry β-diketone complex, $VO(bzacac)_2$ reveals that in non-coordinating solvents, such as benzene and CCl_4, where the "first" band shifts to higher energy and drops in intensity, that there appears a very weak intensity, very broad, low-energy band (at ~10.0–12.0 kK) which may well be the $b_2 \rightarrow b_1{}^*$ transition in this system[80]. Thus we postulate that the $b_2 \rightarrow e_\pi{}^*$ transition moves to higher energy as a sixth ligand is removed and the V=O oxygen p_π orbitals can get a greater share of the e_π orbitals (d_{xz}, d_{yz}) of the vanadium.

Finally, for purposes of comparison it is perhaps pertinent to at least look at what transition energies and respective energy-level assignments are available for *non*-oxovanadium(IV) complexes. These complexes are expected to be more symmetrical and to have stronger covalent bonds than all of the bonds in VO^{2+} complexes with the exception of the V=O bond.

TABLE IV

SOME SPECTRAL DATA FOR NON-OXOVANADIUM(IV) COMPLEXES

Complex	*Medium*	*Obsd. Bands, kK*	*Assignment*
VCl_6^{2-}	diff. refl.[81]	15.10	$^2E_g \leftarrow {}^2T_{2g}$
		~20.40	C.T.
	CH_3CN soln.[81]	14.90 ($\varepsilon = 65$)	$^2E_g \leftarrow {}^2T_{2g}$
		21.30 ($\varepsilon = 310$)	C.T.
	CH_3CN soln.[82]	15.40 ($\varepsilon = 89$)	$^2E_g \leftarrow {}^2T_{2g}$
		21.05 ($\varepsilon = 1040$)	C.T.
VF_6^{2-}	KCl pellet[85]	20.12 sh	$^2E_g \leftarrow {}^2T_{2g}$
		(20.70 calcd.)	
$VCl_4 \cdot x$ L	diff. refl.[83,84]	13.6–20.0	$^2B_{1g} \leftarrow {}^2B_{2g}$
		18.18–22.2	$^2A_{1g} \leftarrow {}^2B_{2g}$

L = *o*-phen, dipy, CH_3CN, THF, dioxane, benzophenone, pyrazine, tetrahydropyran.

The VCl_6^{2-} ion has been studied by Fowles and Walton[81] and by Kilty and Nicholls[82], and their data is given in Table IV. A series of complexes $VCl_4 \cdot x$ L (x = 1 or 2 and L = *o*-phen, dipy, MeCN, THF, diox, THP, benzophenone, and pyrazine), assumed to possess D_{4h} symmetry, have also been studied[83,84]. In this symmetry the T_{2g} and E_g levels (of O_h) split into B_{2g}, E_g and B_{1g}, A_{1g}, respectively, with the splitting of $E_g(O_h)$ predicted to be larger than the splitting in T_{2g}. A Wolfsberg–Helmholtz MO treatment of VF_6^{2-} has recently been reported[85] and the calculated and observed values for $E_g \leftarrow T_{2g}$ are also given in Table IV. It seems to this author that the energies involved in these *d–d* transitions make more reasonable the suggestions offered here for the VO^{2+} transitions.

D. ELECTRON-SPIN RESONANCE STUDIES

Electron-spin resonance studies are being carried out very extensively on VO^{2+} and its compounds, and in general there are two quite distinct motives stimulating these researches. There are those chemists and physicists whose primary interest is in ESR spectroscopy, and who study vanadyl compounds because these compounds are so amenable to the technique (and the variables of the technique) and yield such beautiful spectra (see Introduction). And then there are the inorganic chemists whose primary interest is in basic knowledge about VO^{2+} and its complexes, and for them ESR is merely a very elegant tool. (Admittedly there are a few instances where it is very difficult to judge the real source of the author's interest in doing the ESR work). Many of the ESR papers referenced in the earlier review[1] fall into the first of the above categories, but several very fine and very important papers in the second category have appeared since the last review and these will be discussed here. References will only be given for the recent papers which come under the first category[86-94].

For the uninitiated it might be mentioned at the outset that from ESR spectra we get "average" g-factors (g_0 or $\langle g \rangle$ in the literature) and "average" hyperfine splitting (hfs) values (a or $\langle a \rangle$ or $\langle A \rangle$) from *solutions* studies; and the corresponding anisotropic quantities from *solids studies*: $g_\parallel$ and $g_\perp$ (or g_x, g_y, g_z if possible) where generally,

$$\langle g \rangle = \tfrac{1}{3}(g_\parallel + 2g_\perp) = \tfrac{1}{3}(g_x + g_y + g_z) \tag{1}$$

and A and B (or $A_\parallel$ and $A_\perp$) where, generally, $\langle a \rangle = 1/3(A+2B)$. Of pertinence also for our discussion here are the equations which permit $g_\parallel$ and $g_\perp$ to be calculated from optical spectral data providing certain other parameters may be determined or cleverly guessed. These equations for VO^{2+} case are:

$$g_\parallel = 2.0023\left[1 - \frac{(\varepsilon_\pi{}^*)^2\xi}{\Delta E(e_\pi{}^* \leftarrow b_2)}\right] \tag{2}$$

$$g_\perp = 2.0023\left[1 - \frac{4(\beta_1{}^*)^2\xi}{\Delta E(b_1{}^* \leftarrow b_2)}\right] \tag{3}$$

where ξ is the spin–orbit coupling constant for VO^{2+}, generally taken to be between 135 and 200 cm^{-1}; $\varepsilon_\pi{}^*$ and $\beta_1{}^*$ are the molecular-orbital bonding coefficients, best discussed by Kivelson and Lee[95]; and the denominators of the second terms are the energies (in cm^{-1}) of the first and second d–d transitions within the VO^{2+} ion, according, to the Ballhausen and Gray[67] energy scheme.

In 1964, Kivelson and Lee[95] reported their ESR studies of $VO(acac)_2$ and VO(TPP) in various liquid solvents and frozen glasses. They confirmed the placing of the unpaired electron in a $b_{2g}{}^*$ orbital (where they used the asterisk to imply to this orbital some antibonding character which has, however, never been assumed to be more than very slight and is usually taken to be insignificant). The extra hyperfine splitting (*ehfs*) (sometimes called superhyperfine splitting (*shfs*)), which should arise from the interaction of the unpaired electron with the nuclei of the bonded pyrrole nitrogens, was observed only for VO(TPP) dissolved in $CHCl_3$ or CS_2, but in no other media, and was found to be very isotropic. This indicates that the $b_{2g}{}^*$ orbital is localized on the vanadium in the porphyrin complex and that therefore the in-plane π-bonding is at most slight. The g-tensor analysis suggests that the spin–orbit coupling constant, $\xi \gtrsim 170$ cm^{-1}, and that the in-plane σ-antibonding and out-of-plane π-antibonding orbitals are delocalized, with the delocalization increasing in the order $VO(H_2O)_5^{2+} < VO(acac)_2 < VO(TPP)$. Vanadyl ions in frozen glasses of ethylenediamine or methylamine did not exhibit *ehfs* either. Values for the in-plane σ-bonding and out-of-plane π-bonding coefficients, β_1^* and ε_π^*, respectively were estimated[95] as follows:

Compound	$(\beta_1^*)^2$	$(\varepsilon_\pi^*)^2$
$VO(H_2O)_5^{2+}$	0.89	0.82
V^{4+} in GeO_2	(0.91)	1
$VO(acac)_2$	0.84	0.90–0.95
VO(TPP)	(0.73)	(0.6)

The preceeding results for VO(TPP) were supported by Assour[96], except that he found no *ehfs* in either CS_2 or $CHCl_3$ at low temperature. Furthermore, in an ESR study from the same laboratory[97] no *ehfs* was observed for VO(pc) magnetically diluted in metal-free- and zinc phthalocyanine salts and in H_2SO_4 solution. The spin–orbit coupling constant was assumed to be 165 cm^{-1}, being the value for V^{2+} (a d^3 system). Based upon their data, they[97] state their *belief* that for VO(pc) there is *zero* in-plane π-bonding, but they admit that *conclusive* evidence is still lacking. In this connection it is interesting that ESR results on analogous Cu^{2+} complexes often do show nitrogen *ehfs* components. However it is noteworthy that both Cu and V nuclei have quadrupole moments which can cause line broadening, but that the moment of V is twice that for either of the Cu isotopes. Consequently it is possible that one will never observe ligand hyperfine splittings in VO^{2+} complexes, unless they are abnormally large. This author, for one, is convinced that the degree of delocalization to the in-plane ligands is not zero, and that it may be merely a question of finding the right ligand to prove it. Such a ligand might be a diarsine, since the ^{75}As nucleus has 100% abundance, an $I = 3/2$, and more overlap with the vanadium atom should be possible. No complexes of VO^{2+} have yet been reported, however, containing the V–As bond. Nevertheless, since As has a magnetic moment about four times that of N, the splitting might be large enough to overcome the line width problems[98].

Gutowsky and co-workers[99] have obtained ESR data for $VOCl_5^{3-}$ in dilute (~1 mole %) single crystals of $(NH_4)_2[InCl_5(H_2O)]$ at room temperature (the data at −165° did not differ appreciably). They conclude that the semiempirical method which Ballhausen and Gray[67] used to estimate bonding coefficients overestimates the covalency of transition-metal complexes. They further conclude that the in-plane σ-bonding appears greater in the chloro than the aquo ion, and that the Mo^V in the analogous $MoOCl_5^{2-}$ ion is more covalently bonded than the V^{IV} in $VOCl_5^{3-}$.

Wuthrich[75] has measured ESR ⟨g⟩ and ⟨a⟩ values, as well as visible spectra, for a large number of vanadyl complexes in solution. He accepts as correct the BG energy-level scheme, assigning the first visible band (11.8–13.6 kK) to be $e_\pi^* \leftarrow b_2$ and the second (16.0–19.7 kK) to $b_1^* \leftarrow b_2$ and he proceeds to calculate

$\langle g \rangle$ values from the optical-spectral data using the formulas (1)–(3) given earlier, $\xi = 170\ \text{cm}^{-1}$, and the following bonding coefficient values:

	$\varepsilon_\pi{}^*$	$\beta_1{}^*$
for $VOSO_4$ and $VO(NCS)_n{}^{(2-n)+}$	0.907	0.946
for the polycarboxylic acid complexes	0.950	0.915
for the PS and dipy compounds	0.78	0.87

However it can easily be demonstrated how relatively *insensitive* is the $\langle g \rangle$ value calculated from electronic spectral data to the positions of the first and second bands. Indeed it is possible by choosing the right value of ξ (or for that matter, of $\beta_1{}^*$ and $\varepsilon_\pi{}^*$), to assign the same energy value to *both* of the first two *d–d* transitions, thus assuming that they are under the envelope of the first broad band, I. Indeed this author has checked much of the recent ESR data in this fashion (for example that of Bernal and Rieger[100] and Wuthrich[75] and must conclude that agreement between ESR-measured $\langle g \rangle$ values and optical-spectral-calculated $\langle g \rangle$ values does *not* constitute unequivocal support for the Ballhausen–Gray band assignments. This statement will now be briefly supported by a specific example.

In a separate paper, Wuthrich[76] describes his ESR investigation of $VO(TIR)^{2-}$, $VO(TIR)^{6-}$, $VO(SSA)^{-}$ and $VO(SSA)_2{}^{4-}$. His data is summarized as follows:

Compound	*Band I, assigned* $e_\pi{}^* \leftarrow b_2$	*Band II, assigned* $b_1{}^* \leftarrow b_2$	$\langle g \rangle$	a	$\langle g \rangle_{\text{calcd.}}$
$VO(TIR)^{2-}$	13.0 (24)	19.0 (17)	1.966	101.5	1.966
$VO(TIR)^{6-}$	15.5 (64)	19.2 (40)	1.972	86.0	1.970
$VO(SSA)^{-}$	12.35 (34)	17.3 (11)	1.963	106.0	1.963
$VO(SSA)^{4-}$	12.55 (35)	17.7 (16)	1.966	96.5	1.965

The data in the last column is obtained by calculation using equations (1)–(3), the optical data given, $\xi = 170\ \text{cm}^{-1}$, $\varepsilon_\pi{}^* = 0.950$ and $\beta_1{}^* = 0.915$. However, by using the *same* bonding coefficients and changing only the spin–orbit coupling constant to $\xi = 135\ \text{cm}^{-1}$, one can calculate $\langle g \rangle$ for $VO(TIR)^{2-}$ as 1.967, *using* 13,000 cm^{-1} *for both* $\Delta E(b_\pi{}^* \leftarrow b_2)$ *and* $\Delta E(b_1{}^* \leftarrow b_2)$!

Kon and Sharpless[101] investigated the ESR spectra of $VOCl_n{}^{(2-n)+}$ in several environments and $VOF_5{}^{3-}$, and their data is included in Table V, along with other new ESR data. Kuska and Rogers[78] used ESR hyperfine splittings, $\langle A \rangle$, to obtain an empirical linear correlation with the ratio (ρ) of axial to equatorial charge where, from crystal field theory:

$$\rho = \frac{\rho_4{}^{z+} + \rho_4{}^{z-}}{2\rho_4{}^{xy}} = \frac{\text{axial charge}}{\text{equatorial charge}}$$

and $\rho_4{}^{z+}$ is the field strength along the V=O axis, $\rho_4{}^{z-}$ is the same *trans* to V=O, and $\rho_4{}^{yx}$ is the in-plane field strength. In terms of transition energies we

TABLE V. SOME RECENT ESR DATA ON VO^{2+} COMPLEXES[a]

Compound	*Medium*	$g_{\parallel}$	$g_{\perp}$	$\langle g \rangle$	*A*	*B*	$\langle a \rangle$	*Ref.*
$VOCl_2$	3 *N* HCl	1.932	1.981	1.965	182.6	71.8	106.4	101
	3 *N* H_2SO_4	1.933	1.980	1.965	182.6	71.7	106.2	101
	12 *N* HCl	1.933	1.978	1.968	182.0	70.4	101.9	101
$VOCl_4^{2-}$	HAc–HCl	1.944	1.979	1.969	172.9	66.2	101.4	101
VO(TPP)	$CHCl_3$	1.966	1.985	—	161	55	—	96
	CS_2	1.965	1.990	—	159	57	—	96
	H_2TPP	1.966	1.985	—	161	55	—	96
VO(pc)	H_2pc	1.966	1.989	—	158	56	—	97
	Znpc	1.966	1.933, 1.981[b]	—	158	55, 52[b]	—	97
	H_2SO_4 soln.	1.965	1.988	—	159	59	—	97
$VO(acac)_2$	CS_2	—	—	1.968	—	—	99.5	95
	$CHCl_3$	1.948	1.981	1.970	166.5	63.5	97.8	95
	THF	1.945	1.981	1.969	169.0	61.8	97.5	95
	CH_3NH_2	1.944	1.980	1.969	167.4	59.5	95.5	95
	NH_3	1.947	1.979	1.968	165.0	59.9	95.0	95
	liq. toluene	1.943	1.979, 1.985[b]	1.969	—	—	—	88
VO(TPP)	CS_2	1.961	1.988	1.980	159.1	55.8	90.2	95
	THF	1.964	1.989	1.981	159.1	54.2	88.7	95
	$CHCl_3$	1.961	1.989	1.979	161.2	51.7	88.2	95
$VO(H_2O)_5^{2+}$	[c]	1.933	1.981	1.965	182.8	72	119	102
$VOCl_5^{3-}$	[d]	1.945	1.985	1.972	173.0	63.8	109.4	99
$VOSO_4$	aq. soln.	—	—	1.961	—	—	115.5	75
$VO(NCS)_n^{(2-n)+}$	aq. soln.	—	—	1.964	—	—	108.0	75
$VO(ox)_2^{2-}$	aq. soln.	—	—	1.964	—	—	106.0	75
$VO(MS)_2^{2-}$	aq. soln.	—	—	1.967	—	—	102.0	75
$VO(Pht)_2^{2-}$	aq. soln.	—	—	1.963	—	—	109.0	75
$VO(dipy)_2^{2+}$	aq. soln.	—	—	1.974	—	—	95.0	75
VO(IDA)	aq. soln.	—	—	1.966	—	—	104.0	75
$VO(EDTA)^{2-}$	aq. soln.	—	—	1.967	—	—	102.5	75
$VO(DTPA)^{3-}$	aq. soln.	—	—	1.967	—	—	102.0	75
$VO(NTA)^{-}$	aq. soln.	—	—	1.963	—	—	109.0	75
$VO(NTA)(OH)^{2-}$	aq. soln.	—	—	1.963	—	—	106.5	75
VO(PIDA)	aq. soln.	—	—	1.966	—	—	105.0	75
$VO(PIDA)(OH)^{-}$	aq. soln.	—	—	1.966	—	—	100.5	75
$VO(PS)_2$	aq. soln.	—	—	1.970	—	—	99.0	75
$VO(PS)_2(OH)^{-}$	aq. soln.	—	—	1.968	—	—	96.0	75
$VO(TIR)^{2-}$	aq. soln.	—	—	1.966	—	—	101.5	76
$VO(TIR)_2^{6-}$	aq. soln.	—	—	1.972	—	—	86.0	76
$VO(SSA)^{-}$	aq. soln.	—	—	1.963	—	—	106.0	76
$VO(SSA)_2^{4-}$	aq. soln.	—	—	1.966	—	—	96.5	76
VO mandelate	pH = 1	—	—	1.967	—	—	113.1	103
	pH = 3	—	—	1.967	—	—	98.4	103
	pH = 5	—	—		—	—	89.1	103
	pH = 7	—	—	1.975	—	—	89.4	103
	pH = 9	—	—	1.974	—	—	89.4	103
VO tartrate	pH = 9	—	—	1.974	—	—	88.5	103
VO malate	pH = 9	—	—	1.974	—	—	89.2	103
VO lactate	pH = 9	—	—	1.973	—	—	90.0	103
VO citrate	pH = 9	—	—	1.969	—	—	96.9	103

[a] The data does not include any reported in Table III of ref. 1. [b] These values are g_x and g_y or B_x and B_y respectively. [c] In $Zn(NH_4)_2(SO_4)_2 \cdot 6\,H_2O$. [d] 1 mole % in $(NH_4)_2[InCl_5(H_2O)]$.

obtain[70]:

$$\rho = \frac{3[\Delta E(\mathrm{xy} \rightarrow \mathrm{z}^2)] - 4[\Delta E(\mathrm{xy} \rightarrow \mathrm{xz, yz})]}{2[\Delta E(\mathrm{xy} \rightarrow \mathrm{x}^2 - \mathrm{y}^2)]} - \tfrac{1}{2}$$

ρ values range from +0.210 to −0.450 while ⟨A⟩ values go from 102.3 to 116 for a series of 13 relatively symmetrical complexes. Although they assign the optical transitions as follows:

$\mathrm{xy} \rightarrow \mathrm{xz, yz}$	$\mathrm{zy} \rightarrow \mathrm{x}^2 - \mathrm{y}^2$	$\mathrm{xy} \rightarrow \mathrm{z}^2$
12.4−15.5 kK	14.1−17.45 kK	16.2−26.0 kK

Kuska and Rogers do believe that the 13.25 kK band for $VOSO_4$ in dil. H_2SO_4 contains *both* of the first two transitions. For $VO(CN)_5{}^{3-}$ they obtained a ^{13}C ESR hyperfine splitting of 11.3 gauss, indicating a significant covalency and as this ion does not fit their linear correlation they say, quite understandably, that ρ is not reliable when covalency is significant. Furthermore their correlation does not hold for low-symmetry complexes[103].

Summarizing, it must be stated that the VO^{2+} ESR work, while it has been extensive and intensive, has not provided unambiguous assignments for the electronic energy transitions which are taking place in VO^{2+} complexes.

Abbreviations used in this review

acac,	acetylacetonate ion	MNT,	maleonitrile dithiolate ion
big,	biguanide ion	*o*-phen,	orthophenanthroline
bzacac,	benzoylacetylacetonate ion	ox,	oxalate ion
cat,	catecholate ion	oxine,	8-hydroxyquinoline
chel,	4-hydroxypyridine-2,6-dicarboxylate ion	pc,	phthalocyanine ion
coll,	pyridine-2,4,6-tricarboxylate ion	Ph,	phenyl
cp,	cyclopentadienyl ion	pic,	picolinate ion
DBM,	dibenzoylmethanate ion	py,	pyridine
diphos,	ethylenebis(diphenylphosphine)	pyc,	pyridine-2-carboxylate ion
dipy,	dipyridyl	pyNO,	pyridine-*N*-oxide
DMSO,	dimethylsulfoxide	R,	alkyl
EDTA,	ethylenediaminetetraacetate ion	sal,	salicylaldehyde ion
F_3acac,	trifluoroacetylacetonate ion	THF,	tetrahydrofuran
F_6acac,	hexafluoroacetylacetonate ion	TPP	tetraphenylporphine
gly,	glycinate ion	X,	halide ion
lut,	pyridine-2,6-dicarboxylate ion	X-sal,	substituted salicylaldehyde
Me,	methyl	X-salen-N(R)(R′),	substituted salicylaldehydeethylenedimine

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