TABLE III

BOND-LENGTH DATA FOR BORON TRIIODIDE

x	y(best fit)	Bond length	$y_{max.}$	Bond length	$y_{min.}$	Bond length
0.025	0.373	2.11 Å.	0.380	2.08 Å.	0.365	2.13 Å.
.030	.370	2.10 Å.	.375	2.08 Å.	.365	2.12 Å.
.035	.367	2.09 Å.	.375	2.07 Å.	.360	2.06 Å.

TABLE IV

CONDITIONS FROM OBSERVED INTENSITIES[6]
Reflection 23 > 10 ~ 13
Reflection 27 < 7 ≪ 10 ~ 13

Brockway[7] find 0.79 Å. as the trigonal radius and 0.89 Å. as the tetragonal radius. They interpret these results by remarking that the covalent radius for boron should change as the double bond character varies: when the boron–halogen π-bond character increases from 0 to $1/3$, the hybridization changes from trigonal to tetragonal and the boron covalent radius increases from 0.79 to 0.89 Å.

Nuclear quadrupole data can be used to obtain the π bonding in these compounds. This method gives 0.06, 0.12, and 0.16 as the halogen double-bond character in BCl_3,[8] BBr_3,[8] and BI_3,[2] respectively. Note that the two parameters—the nuclear quadrupole coupling constant and the asymmetry parameter—were obtained directly in BBr_3 and BI_3. In BCl_3, however, the parameters were determined on the assumption of a value for the ionic character of the B–Cl bond, which might lead to some error in this case. The preceding π-bond characters yield boron covalent radii of 0.82, 0.83, and 0.84 Å. for the trichloride, tribromide, and triiodide, respectively. With Coulson's values[9] for the halogen covalent radii and taking into account the electronegativity and π-bond contractions,[9] we calculate these bond lengths for BCl_3, BBr_3, and BI_3: 1.71, 1.88, and 2.09 Å., which compare well with the experimental values of 1.75 (Lipscomb[3a,4]), 1.87 (Levy and Brockway[7]), and 2.10 Å. (this paper).

(6) I_{obs} for reflections 23 and 27 weakened more by thermal motion than for the other three reflections.

(7) H. A. Levy and L. O. Brockway, *J. Chem. Soc.*, **59**, 2085 (1937).

(8) T. Chiba, *J. Phys. Soc. Japan*, **13**, 860 (1958).

(9) C. A. Coulson, "Valence," Oxford Press, 1952.

The Electronic Structure of the Vanadyl Ion[1]

BY C. J. BALLHAUSEN AND HARRY B. GRAY[2]

The bonding in the molecule ion $VO(H_2O)_5^{2+}$ is described in terms of molecular orbitals. In particular, the most significant feature of the electronic structure of VO^{2+} seems to be the existence of considerable oxygen to vanadium π-bonding. A molecular orbital energy level scheme is estimated which is able to account for both the "crystal field" and the "charge transfer" spectra of $VO(H_2O)_5^{2+}$ and related vanadyl complexes. The paramagnetic resonance g factors and the magnetic susceptibilities of vanadyl complexes are discussed.

Introduction

The high oxidation states of metal ions occurring at the beginning of the transition and actinium series usually are found in complex oxycations of the types MO^{n+} and MO_2^{n+}. The remarkable stability of these complexes, along with their interesting spectral and magnetic properties, has aroused considerable theoretical speculation concerning their electronic structures. The uranyl ion, UO_2^{2+}, has been discussed most often,[3] but partly due to the lack of good wave functions for

(3) For example, see R. L. Belford and G. Belford, *J. Chem. Phys.*, **34**, 1330 (1961).

the uranium atom, many features of the electronic structure of UO_2^{2+} are still uncertain.

One of the simplest oxycations of the above type is the vanadyl ion, VO^{2+}. It may be formulated as containing V^{4+}, with the electronic structure [Argon] $3d^1$, and an oxide ion. As might be expected, VO^{2+} always occurs coördinated to other groups both in the solid state and in solution, bringing the total coördination number of vanadium to five or six. Many complexes containing the VO^{2+} ion have been described, and in most cases they have a characteristic blue or purple color. For example, a number of common bidentate ligands form 2:1 complexes with VO^{2+}.[4]

The energy level scheme for vanadyl has been considered by Jørgensen[5] and by Furlani,[6] both using a simple crystal field model. Furlani's calculation considered only the $C_{\infty v}$ symmetry of VO^{2+} alone, and therefore cannot hope to account for all the observed levels. By considering VO^{2+} in aqueous solution as a tetragonal $VO(H_2O)_5^{2+}$ molecule ion, with axial destabilization, Jørgensen obtains a level scheme which qualitatively accounts for the "crystal field" part of the spectrum. However, Palma-Vittorelli, et al.,[7] first pointed out that the electrostatic model could not account for the observed magnetic properties of $VOSO_4 \cdot 5H_2O$ and concluded that π-bonding between vanadium and oxygen must be important.

There is now an appreciable collection of structural, spectral, and magnetic data available for the vanadyl ion and its complexes. Therefore it seems desirable to develop a theory of the electronic structure of VO^{2+} which will be consistent with its physical properties. It also might be hoped that an understanding of the principal features of the bonding in VO^{2+} will be a helpful guide in attempts to develop a general theory of the electronic structures of MO^{n+} and MO_2^{n+} complexes.

Structure of the Vanadyl Ion Complexes.— The structures of at least three different compounds containing vanadyl ion have been determined by X-ray methods. It is significant that VO_2 crystallizes in a highly distorted rutile (TiO_2) structure, in which there is one conspicuously short V–O bond (1.76 Å.) in each VO_6 unit.[8] Thus there seems to be a greater driving force to

form VO^{2+} in VO_2 than there is to form TiO^{2+} in TiO_2, since the TiO_6 units in the rutile structure contain no distinguishable TiO^{2+} fragments.

Anhydrous $VO(aca)_2$ (aca is acetylacetone) appears to be only five-coördinated in the crystal, with the VO^{2+} group perpendicular to the oxygen base of a square pyramid.[9] The V–O bond length in this complex is only 1.59 Å.

The structure of $VO(SO_4) \cdot 5H_2O$ is a distorted octahedron, which clearly contains the VO^{2+} group situated perpendicular to a base containing the four water oxygens.[7] The V–O bond length for VO^{2+} is 1.67 Å., while the V–O bond lengths to the water ligands are approximately 2.3 Å. A sulfate oxygen completes the tetragonal structure by occupying the other axial position. The V atom is coplanar with the water oxygens.

The vanadyl ion in aqueous solution presumably has an analogous tetragonal structure; a $V–O^{2+}$ group with five more distantly coördinated water molecules completing the coördination sphere. There are other possibilities for the solution structure, of course. For example, potentiometric measurements confirm the existence of the doubly-charged vanadyl cation in aqueous solutions of V^{4+}, but fail to tell us whether it is VO^{2+} or $V-(OH)_2^{2+}$.[10] However, the accumulated spectral and magnetic evidence, which will be discussed later, strongly support the assumption that the vanadyl ion actually retains its VO^{2+} identity in solution, and is surrounded by water molecules to complete a distorted octahedral array.

The electrostatic model for the hydrated vanadyl ion consists of V^{4+} situated in a tetragonal electric field caused by the oxide ion and five water dipoles. The crystal field energy level diagram for such a situation is given in Fig. 1.

The parameters Ds and Dt specify the degree of tetragonality present in the field.[11] If the tetragonal perturbation results in axial compression, as in $VO(H_2O)_5^{2+}$, the axial a_1 orbital is less stable than b_1, but the ordering of the e and b_2 orbitals depends on the relative values of Ds and Dt. Magnetic data on vanadyl complexes which will be discussed later indicate an orbitally non-degenerate ground state, and so the e orbitals are less stable than b_2 in this case. Thus for the ground state configuration the one d electron in

(4) M. M. Jones, Z. *Naturforsch.*, **12b**, 595 (1957).

(5) C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 73 (1957).

(6) C. Furlani, *Ricerca sci.*, **27**, 1141 (1957).

(7) M. B. Palma-Vittorelli, M. U. Palma, D. Palumbo, and F. Sgarlata, *Nuovo cimento*, **3**, 718 (1956).

(8) G. Andersson, *Acta Chem. Scand.*, **10**, 623 (1956).

(9) R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, **35**, 55 (1961).

(10) F. J. C. Rossotti and G. S. Rossotti, *Acta Chem. Scand.*, **9**, 1177 (1955).

(11) W. Moffitt and C. J. Ballhausen, *Ann. Rev. Phys. Chem.*, **7**, 107 (1956).
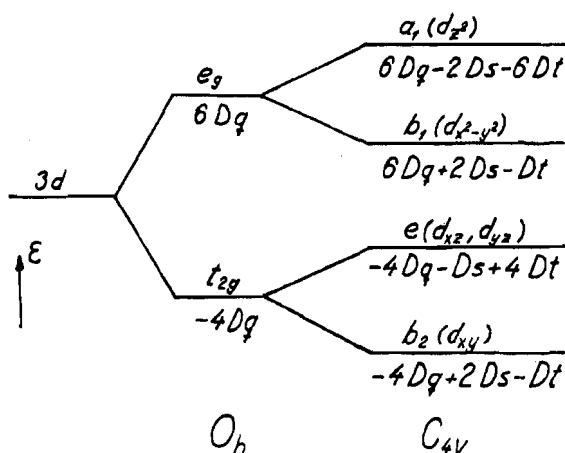
Fig. 1.—Energy levels in crystalline fields of O_h and compressed C_{4v} symmetry, with $(-3Ds + 5Dt) > 0$.

Fig. 2.—Structure of the $VO(H_2O)_5^{+2}$ molecule ion.

VO^{2+} is placed in the b_2 orbital. The predicted transitions are $b_2 \rightarrow e$ $(-3Ds + 5Dt)$, $b_2 \rightarrow b_1$ $(10Dq)$, and $b_2 \rightarrow a_1$ $(10Dq - 4Ds - 5Dt)$. The spectrum of $VOSO_4 \cdot 5H_2O$ in aqueous solution shows two crystal field bands, at 13,000 cm.$^{-1}$ and 16,000 cm.$^{-1}$, which from Fig. 1 can be assigned to the transitions $b_2 \rightarrow e$ and $b_2 \rightarrow b_1$, respectively. The $b_2 \rightarrow a_1$ transition is expected at higher energies, but it is not observed, presumably being covered by the broad charge transfer band which sets in at about 30,000 cm.$^{-1}$.

The value of $10Dq$ is obtained directly from the $b_2 \rightarrow b_1$ transition, which gives $Dq = 1600$ cm.$^{-1}$ for V^{4+} in aqueous solution. This Dq is considerably smaller than a value of 2600 cm.$^{-1}$ which might be expected for V^{4+} by extrapolating the Dq's for $V(H_2O)_6^{2+}$ (1220 cm.$^{-1}$) and $V(H_2O)_6^{3+}$ (1900 cm.$^{-1}$).[12] The values of Ds and Dt can be calculated by making the reasonable assumption that the $b_2 \rightarrow a_1$ transition for $VOSO_4 \cdot 5H_2O$ occurs at approximately 35,000 cm.$^{-1}$ (this transition is actually observed in a number of vanadyl complexes in the neighborhood of 30,000 cm.$^{-1}$). This calculation gives $Ds = -4570$ cm.$^{-1}$ and $Dt = -143$ cm.$^{-1}$. These values may be compared with the values $Ds = -117$ cm.$^{-1}$, $Dt = -33$ cm.$^{-1}$, for tetragonal cobaltous oxide.[13]

From these results it is clear that a rather exaggerated tetragonal distortion is present in $VO(H_2O)_5^{2+}$, and that a pure crystalline field model, that is, a model which only considers σ-bonding to be present, cannot provide an adequate description of the electronic structure of VO^{2+}. It thus is evident that an accurate description of the elec-
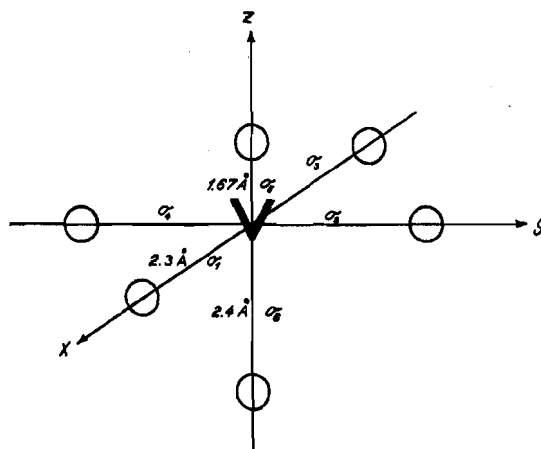
tronic structure of the vanadyl ion and its complexes must include provisions for π-bonding, and this will be accomplished by the method of molecular orbitals.

The Molecular Orbital Description of Vanadyl Ion.—Since the crystal structure of $VOSO_4 \cdot 5H_2O$ is known, the molecule ion $VO(H_2O)_5^{2+}$ will be taken as the example. The ligand oxygens will be numbered as shown in Fig. 2. In this model the axial sulfate oxygen, present in the crystal, is replaced with a water oxygen. Such a substitution does not affect any of the energy states of interest, and has a conceptual advantage for a discussion of the VO^{2+} ion in aqueous solution.

The 3d, 4s, and 4p metal orbitals will be used for bonding, along with the 2s, $2p_\sigma$ $(2p_z)$, and $2p_\pi$- $(2p_x, 2p_y)$ orbitals of oxide oxygen, and the sp_σ hybrid orbitals for the water oxygens. In view of the longer vanadium to oxygen bond lengths (2.3 Å.), π-bonding involving the water oxygens seems unlikely, and thus will be ignored.

The transformation scheme for the metal and ligand orbitals in C_{4v} is given in Table I. In specifying the form of the molecular orbitals, use has been made of the fact that the vanadyl VO bond is undoubtedly the strongest link, the four waters in the square plane are equivalent and are attached more strongly than the axial water molecule, which is the weakest link of all. With this in mind, the bonding in $VO(H_2O)_5^{2+}$ can be pictured as follows: a strong σ bond of symmetry a_1 between the sp_σ oxygen hybrid orbital and the $(4s + 3d_{z^2})$ vanadium hybrid orbital (there is some experimental justification for sorting out a localized σ molecular orbital involving only the $3d_{z^2}$ and 4s vanadium orbitals, and the 2s and $2p_\sigma$ oxygen orbitals—this is the fact that no nitrogen

(12) L. E. Orgel, *J. Chem. Phys.*, **23**, 1819 (1955).
(13) T. S. Piper and R. L. Carlin, *ibid.*, **33**, 1208 (1960).

TABLE I

ORBITAL TRANSFORMATION SCHEME IN C_{4v} SYMMETRY

Representation	Metal Orbitals	Ligand Orbitals
a_1	$3d_{z^2} + 4s$	σ_5
	$4s - 3d_{z^2}$	$\frac{1}{2}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$
	$4p_z$	σ_6
e	$3d_{xz}, 3d_{yz}$	$\pi_5(2p_x, 2p_y)$
	$4p_x, 4p_y$	$\frac{1}{\sqrt{2}}(\sigma_1 - \sigma_3), \frac{1}{\sqrt{2}}(\sigma_2 - \sigma_4)$
b_1	$3d_{x^2-y^2}$	$\frac{1}{2}(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)$
b_2	$3d_{xy}$	

hyperfine structure is found in the paramagnetic resonance spectrum of vanadyl porphyrins)[14,15]; two π bonds of symmetry e between the oxygen $2p_x$ and $2p_y$ orbitals and the vanadium $3d_{xz}$ and $3d_{xz}$ orbitals, making a total of three vanadium to oxygen bonds in VO^{2+}; four bonds involving the sp_σ hybrid orbitals of the equivalent water oxygens and vanadium $(4s-3d_z^2)(a_1)$, $4p_x$ and $4p_y(e)$, and $3d_{x^2-y^2}(b_1)$ orbitals; the sixth ligand, the axial water oxygen, is considered bonded to the remaining vanadium $4p_z(a_1)$ orbital; finally, the $3d_{xy}$ vanadium orbital, of symmetry b_2, is nonbonding.

The hybrid atomic orbitals used can be written in the form

$$\psi(\text{hybrid}) = (\sin\theta)\Phi(s) \pm (\cos\theta)\Phi(p \text{ or } d) \quad (1)$$

The values of θ are estimated by methods described in the Appendix; this gives $\theta = 0.455$ for the sp_σ oxygen hybrid orbital and $\theta = \pi/4$ for the sd_{z^2} vanadium hybrid orbital. The tetrahedral hybrid, $\theta = \pi/6$, is used for the water oxygen σ orbital.

In order to obtain some idea of the relative strengths of the bonds, and thus the positions of the one electron molecular orbitals, overlap integrals were evaluated, using the SCF radial functions for vanadium given by Watson,[16] and oxygen radial SCF functions taken from data given by Hartree.[17] Bond distances used were taken directly from the $VOSO_4 \cdot 5H_2O$ crystal results, and are given in Fig. 2. The overlap results are summarized in terms of the usual group overlap integrals (G_{ij}'s) for each molecular orbital, and are given in Table II. The Appendix should be con-

(14) C. M. Roberts, W. S. Koski, and W. S. Caughey, *J. Chem. Phys.* **34**, 591 (1961).
(15) D. E. O'Reilly, *ibid.*, **29**, 1188 (1958).
(16) R. E. Watson, Quart. Prog. Rept., M.I.T., April, 1960.
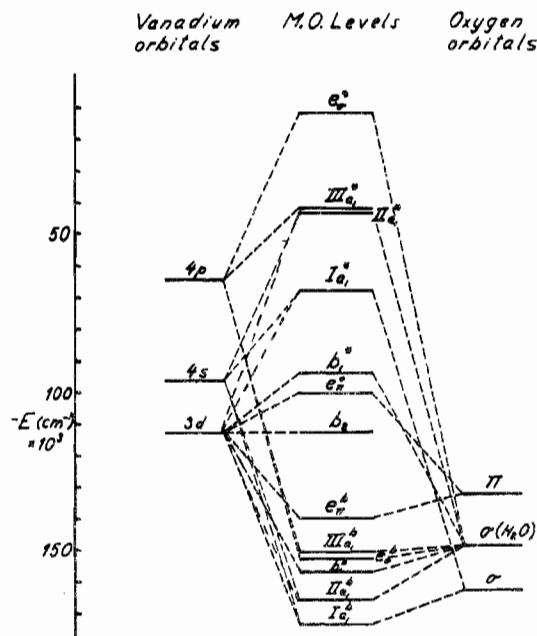(17) D. R. Hartree, "The Calculation of Atomic Structures," John Wiley, New York, N. Y., 1957, pp. 169-171.

Fig. 3.—Molecular orbital scheme for $VO(H_2O)_5^{2+}$. The levels are drawn to scale.

sulted for details concerning any of the calculations discussed in this section.

Using the criterion that bond strengths are proportional to overlap, the ordering of the molecular orbitals is shown in Fig. 3. It is gratifying to note that the order of increasing energy of the crystal field levels b_2, e_π^*, b_1^*, and Ia_1^* is the same as given in Fig. 1 for the crystal field model.

The bonding molecular orbitals all can be written

$$\psi^b = c_1\Phi(\text{metal}) + c_2\Phi(\text{ligand}) \quad (2)$$

and similarly the antibonding levels

$$\psi^* = c_1^*\Phi(\text{metal}) + c_2^*\Phi(\text{ligand}) \quad (3)$$

with

$$c_1 c_1^* + c_2 c_2^* + c_1 c_2^* G_{ij} + c_1^* c_2 G_{ij} = 0 \quad (4)$$

where Φ (metal) and Φ (ligand) refer to the proper combination of metal and ligand orbitals for the molecular orbital in question. Approximate values of the energies of these orbitals can be obtained by solving the secular equation $|H_{ij} - G_{ij}\epsilon| = 0$. The estimation of the one electron orbital energies follows closely the procedures outlined by Mulliken[18] and Wolfsberg and Helmholz.[19] The H_{ii} and H_{jj} integrals are approximated as the VSIE's (valence state ionization energies) which are discussed in Section A of the Appendix. The H_{ij} resonance integrals are set equal to $-2G_{ij}$.

(18) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1841 (1955).
(19) M. Wolfsberg and L. Helmholz, *ibid.*, **20**, 837 (1952).

TABLE II

GROUP OVERLAP INTEGRALS AND ESTIMATED ORBITAL ENERGIES FOR THE $VO(H_2O)_5{}^{2+}$ MOLECULE ION

Symmetry of M.O.	G_{ij}	Bonding levels $-\epsilon$ (cm.$^{-1}$)	c_1	c_2	Antibonding levels $-\epsilon$ (cm.$^{-1}$)	$c_1{}^*$	$c_2{}^*$
e_π	0.139	140,026	0.446	0.834	100,422	0.907	−0.567
b_1	.194	157,126	.381	.853	94,130	.946	−0.555
Ia_1	.305	173,500	.345	.883	68,158	.996	−0.620
IIa_1	.390	165,837	.409	.765	43,395	1.006	−0.770
$IIIa_1$	.313	150,750	.154	.941	42,750	1.042	−0.474
e	.467	152,931	.201	.888	10,244	1.113	−0.698

Atomic orbital	Coulomb energy (cm.$^{-1}$)
Vanadium 3d	−112,924
4s	− 96,792
4p	− 64,528
Oxygen ($2s + 2p_\sigma$)	−162,933
$2p_\pi$	−132,282
Oxygen(H_2O) ($2s + 2p_\sigma$)	−148,414

TABLE III

ANALYSIS OF THE $VOSO_4 \cdot 5H_2O$ SPECTRUM

Transition	Predicted energy (polarization) (cm.$^{-1}$)	Obsd.[a] (cm.$^{-1}$) for $VOSO_4 \cdot 5H_2O$	Predicted oscillator strength $f \cdot 10^4$	Obsd.
$^2B_2 \rightarrow {}^2E(I)$	12,502($\perp$)	13,060($\perp$)	3.9	1.1
$^2B_2 \rightarrow {}^2B_1$	18,794	16,000	Vibronic	0.45
$^2B_2 \rightarrow {}^2A_1$	44,766	Covered	Vibronic	...
$^2B_2 \rightarrow {}^2E(II)$	38,800($\perp$)	41,700($\perp$)	26.4	50.3
$^2B_2 \rightarrow {}^2B_2$	44,000($\parallel$)	~50,000	44.7	150

[a] Experimentally observed energies and f's refer to aqueous solution, 0.01–0.10 M in H_2SO_4. In the $VOSO_4 \cdot 5H_2O$ crystal the $^2B_2 \rightarrow {}^2E(I)$ and the $^2B_2 \rightarrow {}^2E(II)$ bands are observed at the same energies in $\perp$ polarization only.

$\sqrt{(H_{ii})(H_{jj})}$; the geometric mean is preferable since the resonance energy is expected to decrease rapidly as the difference in the coulomb energies becomes greater. Since the VSIE's for the different atoms vary considerably with the degree of ionization, a charge distribution for $VO(H_2O)_5{}^{2+}$ must be assumed for the initial calculation. After completing one calculational cycle, the resulting charge distribution is calculated, using Mulliken's suggestion[20] that the overlap contribution be divided equally between two atoms. This procedure is continued until a self-consistent answer appears. The final charge distribution is $V^{+0.97}$ $O^{-0.60}$ $(5H_2O)^{+1.63}$.

The VSIE's for atoms with fractional charges are obtained by extrapolation of VSIE vs. degree of ionization curves. This procedure is used for all the atoms except the vanadyl oxygen. In this case the coulomb energy is raised by the excess positive charge on the neighboring atoms, and it is senseless to adjust the VSIE for any fractional charge. Therefore the coulomb energies for the

(20) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

vanadyl oxygen are estimated as the proper σ and π VSIE's of the neutral oxygen atom.

The results of the calculation in terms of c_1, c_2, and ϵ values are given in Table II. For purposes of comparison, Fig. 3 is drawn to this energy scale.

There are 17 electrons to place in the molecular orbitals shown in Fig. 2. The ground state is then $[(Ia_1{}^b)^2 \ (IIa_1{}^b)^2 \ (b_1{}^b)^2 \ (e_\sigma{}^b)^4 \ (IIIa_1{}^b)^2 \ (e_\pi{}^b)^4 \ (b_2)^1]$, $^2B_2$. There are several excited states with energies less than 50,000 cm.$^{-1}$ above the ground state. Table III gives the predicted energies of the transitions to these excited states, along with assignments of the solution spectrum of $VOSO_4 \cdot 5H_2O$, which is shown in Fig. 4. The oscillator strengths (f's) of the orbitally allowed transitions have been calculated using the M.O. wave functions, and also are given in Table III for purposes of comparison.

Consider first of all the so-called crystal field transitions; these involve moving the b_2 electron to the $e_\pi{}^*$, $b_1{}^*$, and $Ia_1{}^*$ M.O.'s, which are of course essentially the 3d metal orbitals, resulting in $^2E(I)$, $^2B_1$, and $^2A_1$ excited states, respectively. To a good approximation electron repulsion
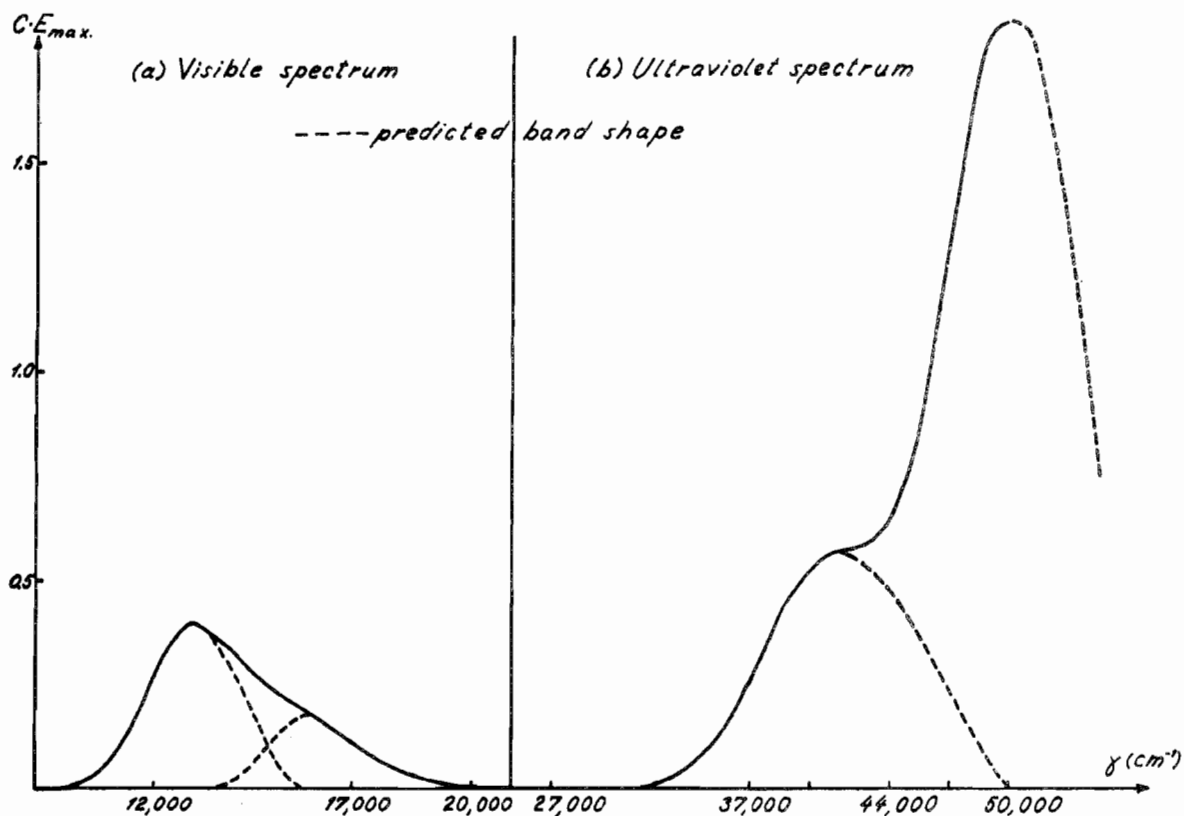
Fig. 4.—The electronic absorption spectrum of $VOSO_4 \cdot 5H_2O$ in aqueous. solution: (a) complex = 0.0237 M, H_2SO_4 = 0.1 M: (b) complex = 0.00237 M, H_2SO_4 = 0.01 M.

effects can be considered to be the same for all these states. Therefore transitions are expected to occur to $^2E(I)$, $^2B_1$, and $^2A_1$ in order of increasing energy. Since the electric dipole vectors transform as A_1 and E in C_{4v}, only transitions to B_2 and E excited states are orbitally allowed; thus the $^2B_2 \rightarrow {}^2E(I)$ transition is expected to have somewhat greater intensity than the other crystal field transitions. These observations support the assignment of the more intense first band (13,000 cm.$^{-1}$) of $VOSO_4 \cdot 5H_2O$ to the transition $^2B_2 \rightarrow {}^2E(I)$. The agreement is satisfactory between the calculated and the observed f values.

The second transition (16,000 cm.$^{-1}$) appears as a weak shoulder and is assigned to $^2B_2 \rightarrow {}^2B_1$, it is allowed vibronically and should appear in all polarizations. The $^2B_2 \rightarrow {}^2A_1$ transition apparently is hidden under the first charge transfer band of $VOSO_4 \cdot 5H_2O$; it is observed, however, at approximately 30,000 cm.$^{-1}$ in a few vanadyl complexes.

The charge transfer spectrum below 50,000 cm.$^{-1}$ is due to the promotion of an electron from the oxygen π orbital (e_π^b) to the crystal field levels b_2 and e_π^*. Denoting the inner core σ-bonding M.O.'s as IC, the first charge transfer

band (41,700 cm.$^{-1}$) is assigned

$$^2B_2[(IC)^{12}(e_\pi{}^b)^4(b_2)^1] \rightarrow {}^2E(II)[(IC)^{12}(e_\pi{}^b)^3(b_2)^2]$$
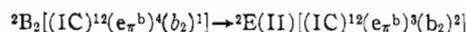
There is considerable repulsion energy involved in this transition, since an electron must be moved from a delocalized π orbital into an occupied b_2 orbital which is localized on the vanadium. This repulsion energy is estimated as *ca.* 11,700 cm.$^{-1}$ by comparing the positions of the first charge transfer band of VO^{2+} with the first band of VO-Cl_3.[21] This 11,700 cm.$^{-1}$ estimate is included in the predicted energy for the $^2B_2 \rightarrow {}^2E(II)$ transition. Both the predicted energy and the predicted f value agree well with the experimentally observed values.

Moving an electron from e_π^b to e_π^* results in the excited orbital configuration $[(IC)^{12} (e_\pi{}^b)^3 (b_2)^1 (e_\pi{}^*)^1]$. From this configuration doublet states can be constructed that transform as $^2A_1$, $^2A_2$, $^2B_1$, and $^2B_2$ in C_{4v}. Since only a transition to a $^2B_2$ state is orbitally allowed, the other states will not be considered. The energy of the first $^2B_2 \rightarrow$ $^2B_2$ transition can be predicted by adding together

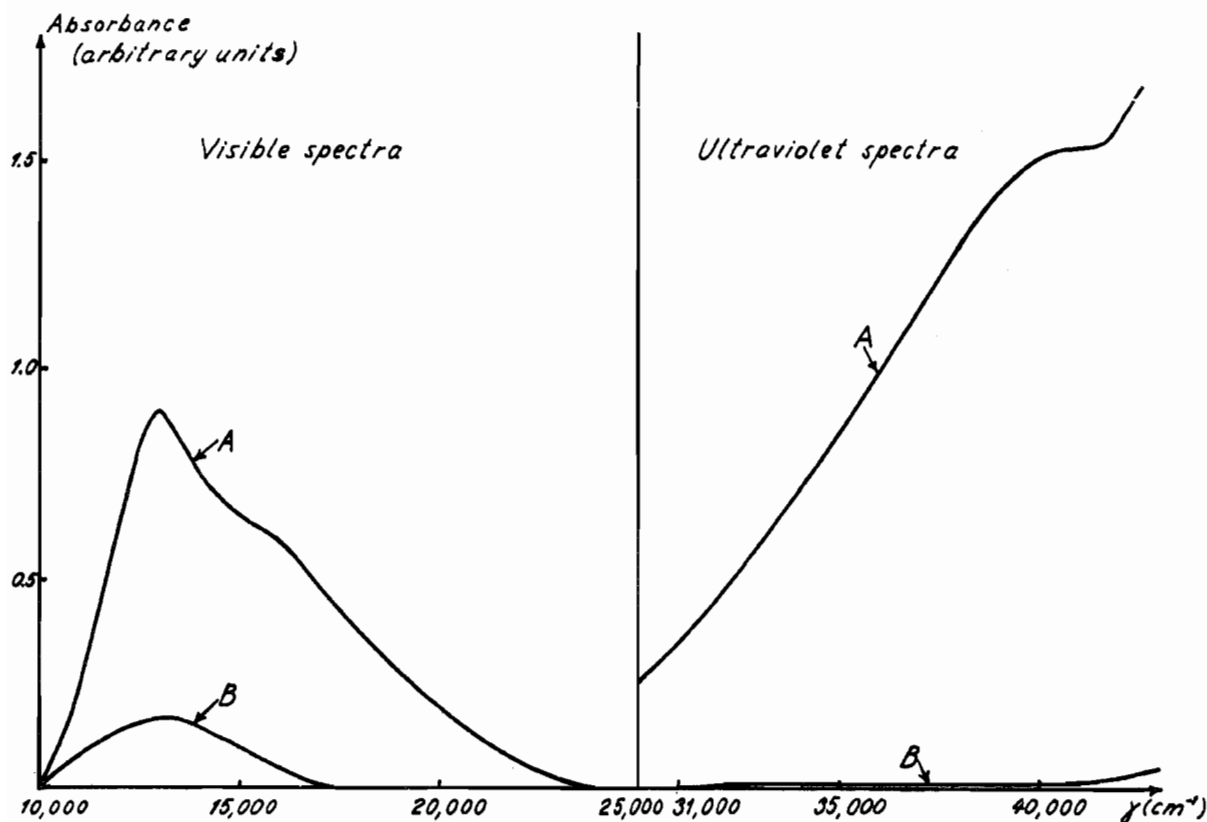(21) F. A. Miller and W. B. White, *Spectrochim. Acta*, **9**, 98 (1957).

Fig. 5.—Absorption spectra of a single crystal of $VOSO_4 \cdot 5H_2O$: Curve A (cm.$^{-1}$), light polarized $\perp$ to the V–O axis; Curve B, light polarized $\parallel$ to the V–O axis.

the orbital promotional energy and the repulsion energy contributions. The repulsion energy estimate of 11,700 cm.$^{-1}$ must be corrected for the difference in repulsion energy between the $^2E(II)$ and $^2B_2$ excited states. This difference can be expressed in terms of the usual coulomb and exchange integrals, calculated from the proper determinantal wave functions for the $^2E(II)$ and the most stable $^2B_2$ excited state. This calculation predicts that the $^2B_2 \rightarrow {}^2B_2$ transition should occur at about 44,000 cm.$^{-1}$.[22] Thus it is reasonable to assign the broad band found at about 50,000 cm.$^{-1}$ to the $^2B_2 \rightarrow {}^2B_2$ transition. Furthermore, the calculated f value agrees rather well with the f value which can be estimated from the band shape.

The Crystal Spectrum of $VOSO_4 \cdot 5H_2O$ and Spectral Properties of other Vanadyl Compounds.—The electronic absorption spectra of a single crystal of $VOSO_4 \cdot 5H_2O$ have been determined for light polarized both parallel and perpendicular to the molecular V–O axis. These spectra are shown in Fig. 5. It is important to note that the positions of the absorption maxima

found for the crystal are virtually the same as those found for an aqueous solution of $VOSO_4 \cdot 5H_2O$. This must mean that there are no significant structure changes in going from crystal $VOSO_4 \cdot 5H_2O$ to aqueous solution. The other important observation is that the 13,000 cm.$^{-1}$ band ($^2B_2 \rightarrow {}^2E(I)$) and the 41,700 cm.$^{-1}$ band ($^2B_2 \rightarrow {}^2E(II)$) appear principally in $\perp$ polarization, providing a rather convincing confirmation of these band assignments. Since it was not possible to obtain an accurate spectrum above 45,000 cm.$^{-1}$, the predicted $\parallel$ polarization of the second charge transfer band ($^2B_2 \rightarrow {}^2B_2$) could not be checked.

In addition to the above study, the reflectance spectrum of a powdered sample of $VOSO_4 \cdot 5H_2O$ has been determined, and the crystal field bands at 13,000 cm.$^{-1}$ and 16,000 cm.$^{-1}$ were resolved.

The reflectance spectrum of VO_2 has been measured by Rüdorff, Walter, and Stadler.[23] This measurement shows the charge transfer band at 41,700 cm.$^{-1}$ which is characteristic of vanadyl ion, but the crystal field bands were not resolved.

A survey of the spectra of common vanadyl

(22) Calculations of this type will be discussed in more detail by H. B. Gray and C. R. Hare in a forthcoming publication.

(23) W. Rüdorff, G. Walter, and J. Stadler, *Z. anorg. u. allgem. Chem.*, **297**, 1 (1958).

TABLE IV

SURVEY OF THE SPECTRA OF VANADYL COMPLEXES

Complex	Medium	Maxima ν (cm.$^{-1}$)	$f \cdot 10^4$	Assignment	Ref.
VO^{2+}	0.5 to 2 M HClO$_4$	13,100	1.1	$^2B_2 \rightarrow {}^2E(I)$	5
		16,000	0.48	$^2B_2 \rightarrow {}^2B_1$	
		41,700	50.8	$^2B_2 \rightarrow {}^2E(II)$	
VOSO$_4 \cdot$5H$_2$O	Crystal	13,000($\perp$)	...	$^2B_2 \rightarrow {}^2E(I)$	This work
		16,000	...	$^2B_2 \rightarrow {}^2B_1$	
		41,700($\perp$)	...	$^2B_2 \rightarrow {}^2E(II)$	
VO$_2$	Powder	41,700	...	$^2B_2 \rightarrow {}^2E(II)$	23
VOSO$_4 \cdot$5H$_2$O	Powder	12,900	...	$^2B_2 \rightarrow {}^2E(I)$	This work
		16,100	...	$^2B_2 \rightarrow {}^2B_1$	
VO(aca)$_2$	C$_5$H$_5$OH	12,800	2.6	$^2B_2 \rightarrow {}^2E(I)$	5
		17,300	1.0	$^2B_2 \rightarrow {}^2B_1$	
VO(enta)$^{2-}$	H$_2$O	12,800	1.5	$^2B_2 \rightarrow {}^2E(I)$	5
		17,200	1.2	$^2B_2 \rightarrow {}^2B_1$	
		29,800	2.0	$^2B_2 \rightarrow {}^2A_1$	
VO(oxalate)$_2^{2-}$	H$_2$O	12,600	2.5	$^2B_2 \rightarrow {}^2E(I)$	5
		16,500	0.70	$^2B_2 \rightarrow {}^2B_1$	
		29,400	15.6	$^2B_2 \rightarrow {}^2A_1$	
VO(tartrate)$^{2-}$	H$_2$O	$\{$11,000	1.7	$^2B_2 \rightarrow {}^2E(I)$	5
		$\{$17,000	1.4		
		18,800	2.2	$^2B_2 \rightarrow {}^2B_1$	
		25,300	4.1	$^2B_2 \rightarrow {}^2A_1$	

complexes is given in Table IV. The bands are assigned in a way consistent with the energies and intensities expected from a comparison with the VOSO$_4 \cdot$5H$_2$O spectrum. In fact, the main features of the spectra of vanadyl complexes are strikingly similar; a band at about 13,000 cm.$^{-1}$, followed by a second, less intense band at about 17,000 cm.$^{-1}$. For the enta, oxalate, and tartrate vanadyl complexes, the $^2B_2 \rightarrow {}^2A_1$ transition is observed before charge transfer spectra set in.

Magnetic Properties of Vanadyl Compounds.— The paramagnetic resonance of VO^{2+} has been investigated for a number of complexes and $< g >$ values are all very nearly 2.[7,14,15,24-29] A survey of g values for different complexes is given in Table V. In the molecular orbital description of VO(H$_2$O)$_5^{2+}$, the formulas for the g values become

$$g_\perp = 2\left(1 - \frac{(c_1^*)^2\xi}{\Delta E(^2B_2 \rightarrow {}^2E(Ig\perp))}\right) \quad (5)$$

$$g_\parallel = 2\left(1 - \frac{(c_1^*)^2 4\xi}{\Delta E(^2B_2 \rightarrow {}^2B_1)}\right) \quad (6)$$

$$\langle g \rangle = \frac{1}{3}(2g\perp + g\parallel) \quad (7)$$

if it is assumed that $\left| \hat{L} + 2\hat{S} \right| \psi_2 > = 0$.

Since the approximate charge on vanadium is $+1$ in the M.O. approximation, a value of the spin orbital coupling constant $\xi = 135$ cm.$^{-1}$ is taken for V$^+$.[30] The calculation then gives $g_\perp = 1.983$, $g_\parallel = 1.940$, with $\langle g \rangle = 1.969$. This is in excellent agreement with the accurately known $\langle g \rangle = 1.962$ value for aqueous solutions of VO^{2+}.[25-27] The measurements on powdered samples of the vanadyl sulfates also give $\langle g \rangle$ values in reasonable agreement with this calculation.

Several measurements have been made which clearly show the predicted anisotropy of the g factor. In the case of VO(etioporphyrin II) $g_\perp = 1.988$ and $g_\parallel = 1.947$,[14] which indicates that this complex has an electronic structure which resembles VOSO$_4 \cdot$5H$_2$O. The somewhat lower g values indicate that the energy levels are closer together, which is reasonable since the porphyrin nitrogens probably can π bond with the b_2 (3d$_{xy}$) metal orbital, thus raising its energy relative to e$_\pi$* and b$_1$*.

It is possible to study V^{4+} in a more symmetrical environment by substituting it into the TiO$_2$ lattice.[31] The symmetry is almost octahedral and presumably the dominant axial field of VO^{2+}

(24) C. A. Hutchinson, Jr., and L. S. Singer, *Phys. Rev.*, **89**, 256 (1953).

(25) R. N. Rogers and G. E. Pake, *J. Chem. Phys.*, **33**, 1107 (1960).

(26) N. S. Garif'ianov and B. M. Kozyrev, *Doklady Akad. Nauk S.S.S.R.*, **98**, 929 (1954).

(27) B. M. Kozyrev, *Discussions Faraday Soc.*, **19**, 135 (1955).

(28) R. J. Faber and M. T. Rogers, *J. Am. Chem. Soc.*, **81**, 1849 (1959).

(29) F. W. Lancaster and W. Gordy, *J. Chem. Phys.*, **19**, 1181 (1951).

(30) T. M. Dunn, *Trans. Faraday Soc.*, **57**, 1441 (1961).

(31) H. J. Gerritsen and H. R. Lewis, *Phys. Rev.*, **119**, 1010 (1960).

TABLE V

PARAMAGNETIC RESONANCE g FACTORS FOR VANADYL COMPLEXES

Compound	Details	$g\perp$	$g\parallel$	$\langle g \rangle$	Ref.
$VOSO_4 \cdot 5H_2O$	Powder, temp. range 4–300°K.	...	...	1.99	7
$VOSO_4 \cdot 2H_2O$	Powder	...	...	1.96	24
VO^{2+}	Aq. soln.	...	...	1.962	25–27
VO^{2+}	Alcohol or glycerol soln., temp. 90°K.	...	...	1.96	27
VO(etioporphyrin II)	Castor oil soln.	1.988	1.947	1.974	14
VO(etioporphyrin I)	Petroleum oil soln.	1.987	1.948	1.974	15
VO^{2+}	Adsorbed on (a) IR-100	1.983	1.93	1.97	28
	(b) Dowex-50	1.979	1.88	1.95	
	(c) Charcoal	1.983	...	...	
	(d) IR-4B	1.989	1.93	1.97	
$VOCl_2$	Powder	...	...	2.0	29

is eliminated. This means that an increase in $\Delta E(^2B_2 \rightarrow {}^2B_1)$ is expected, accompanied by a corresponding decrease in $\Delta E(^2B_2 \rightarrow {}^2E$ (I)). The observed values of $g_\perp = 1.914$ and $g_{||} = 1.957$ strongly support this interpretation. A reasonable value of $\xi = 150$ cm.$^{-1}$ gives $\Delta E(^2B_2 \rightarrow {}^2B_1) = 28,000$ cm.$^{-1}$ and $\Delta E(^2B_2 \rightarrow {}^2E(I)) = 3500$ cm.$^{-1}$. Recall that for the crystal field model, $\Delta E(^2B_2 \rightarrow {}^2B_1)$ is equal to 10 Dq, and the value 28,000 cm.$^{-1}$ is now in agreement with expectations for V^{4+}.

The other magnetic property of interest for VO^{2+} complexes is the susceptibility. The theoretical expression for the magnetic susceptibility is of the form[32]

$$\chi = \frac{C}{T} + \chi_{H.F.} \qquad (8)$$

where C is the Curie constant and $\chi_{H.F.}$ stands for the temperature independent contributions to the susceptibility (high-frequency terms). In this case

$$C = \frac{N\beta^2(g_{||}^2 + 2g_\perp^2)}{12k} \qquad (9)$$

$$\chi_{H.F.} = 2/3\, N\beta^2 \sum_i \frac{|<\psi_0|\hat{L} + 2\hat{S}|\psi_i>|^2}{\Delta E_{0,i}} \qquad (10)$$

where β is the Bohr magneton, N is Avogadro's number, and where $\Delta E_{0,i}$ is the transition energy from ψ_0 to ψ_i. Since values of $g_\perp$ and $g_{||}$ have been calculated above for $VO(H_2O)_5{}^{2+}$, they will be used to calculate C. The major contributions to $\chi_{H.F.}$ are from the $^2B_1$ and $^2E(I)$ excited states; contributions from the other excited states will be ignored. Thus eq. 8 becomes

$$\chi = \frac{N\beta^2(g_{||}^2 + 2g_\perp^2)}{12kT} + {}^2/_3 N\beta^2 \sum_i \frac{|<\psi_0|\hat{L} + 2\hat{S}|\psi_i>|^2}{\Delta E_{0,i}} \qquad (11)$$

$$\chi = \frac{N\beta^2[(1.940)^2 + 2(1.983)^2]}{12kT} + \\ 2/3N\beta^2 \frac{(1+1)(c_1{}^*)^2}{\Delta E(^2B_2 \rightarrow {}^2E(I))} + \frac{(4+4)(c_1{}^*)^2}{\Delta E(^2B_2 \rightarrow {}^2B_1)} \qquad (12)$$

so

$$\chi_{calc.} = \frac{0.363}{T} + 100 \times 10^{-6} \qquad (13)$$

The magnetic susceptibility of $VOSO_4(3.5\, H_2O)$ has been measured by Perrakis[33] over a temperature range of 145°. A plot of χ vs. $1/T$ gives a straight line with slope 0.335 and intercept 130×10^{-6}. Thus

$$\chi_{exp.} = \frac{0.335}{T} + 130 \times 10^{-6} \qquad (14)$$

in satisfactory agreement with the predicted equation (13).

Several room temperature magnetic susceptibility measurements have been made for both powdered samples and aqueous solutions of vanadyl complexes.[34,35] The effective magnetic moments arrived at are listed in Table VI. The

TABLE VI

MAGNETIC SUSCEPTIBILITY DATA FOR VANADYL COMPLEXES

Component[a]	Temp., °C.	μ_{eff} B.M.	Ref.
$VOSO_4 \cdot 5H_2O$	26	1.73	This work
VO^{2+} (aq. $HClO_4$)	20	1.72	34
$VO(aca)_2 \cdot H_2O$	17.5	1.72	35
$VO(aca)_2$	22.5	1.73	This work
VO(salicylaldehydeethylene-diimine)	18.5	1.68	35
VO(salicylaldehyde-O-phenyl-enediimine)	17	1.68	35
$(NH_4)_2[VO(malonate)_2] \cdot 3H_2O$	17	1.70	35

[a] Powder sample unless otherwise indicated.

(32) J. H. Van Vleck, "Electric and Magnetic Susceptibilities," Oxford University Press, 1932.

(33) N. Perrakis, *J. phys. radium*, **8**, 473 (1927).

(34) S. Freed, *J. Am. Chem. Soc.*, **49**, 2456 (1927).

(35) R. W. Asmussen, "Magnetokemiske Undersøgelser over Uorganiske Kompleksforbindelser," Gjellerups Forlag, Copenhagen, 1944.

moments all are approximately equal to the spin only value of 1.73 B.M. for one unpaired spin, as is expected when the orbital contribution is completely quenched in the low symmetry field.

Discussion

It is worthwhile to summarize the main points of evidence concerning the structure of the vanadyl ion in solution. First, the position of the $^2B_2 \rightarrow {}^2E(I)$ band (13,000 cm.$^{-1}$) is the same in the crystal and for an aqueous solution of $VOSO_4 \cdot 5H_2O$. Also, the first charge transfer band (41,700 cm.$^{-1}$) is found at the same place in an aqueous solution of VO^{2+}, in the reflectance spectrum of powdered VO_2, and in the absorption spectrum of crystalline $VOSO_4 \cdot 5H_2O$. Since these transitions involve the VO^{2+} π orbitals, it is convincing evidence that the solution structure at least contains the VO^{2+} entity. Protonation of VO^{2+}, resulting in $V(OH)_2{}^{2+}$, would significantly affect the amount of π-bonding, and thus completely change the positions of the energy levels.

Secondly, the magnetic data are consistent with the VO^{2+} formulation for the vanadyl ion in solution. For example, the values of $\langle g \rangle$ reported for vanadyl complexes are approximately the same both for the crystal, powder, and aqueous solution measurements. A smaller $\langle g \rangle$ value would be expected for the more symmetrical $V(OH)_2{}^{2+}$ ion, similar to the $\langle g \rangle = 1.938$ found for V^{4+} in the TiO_2 lattice. Finally, the magnetic susceptibility of an aqueous solution of VO^{2+} is the same as the susceptibility of powdered $VOSO_4 \cdot 5H_2O$, within experimental error, and corresponds to the spin only moment of 1.73 B.M. This constancy might not be expected if the complex undergoes a structural change in going from the crystal to aqueous solution, although it must be admitted that the susceptibility difference for a structural change would hardly lie outside the realm of experimental error.

The resistance of VO^{2+} to protonation can be understood in terms of the M.O. bonding scheme. With the oxygen 2p orbitals used for π-bonding, only the non-bonding sp_σ hybrid is left for a proton; it has considerable 2s character, and is energetically unsuited for bonding purposes.

The extreme importance of ligand to metal π-bonding in the oxycations must be emphasized. In the case of VO^{2+}, this π-bonding accounts for the drastic reduction ($\sim$45%) of the free ion ζ value,[36] the resistance of VO^{2+} to protonation,

(36) Reference 30 gives a value of 250 cm.$^{-1}$ for the ζ of V^{4+}.

and the charge transfer features of the electronic spectrum of $VOSO_4 \cdot 5H_2O$. Indeed, it is clear that any complete discussion of the electronic structures of the oxycations of the transition and actinium series must allow for substantial oxygen to metal π-bonding. Furthermore, it can be qualitatively understood why ions of this type in the first transition series usually have the formula $MO^{n+}(TiO^{2+}, VO^{2+}, CrO^{3+})$, while similar ions in the actinium series are invariably $MO_2{}^{n+}(UO_2{}^{2+}, NpO_2{}^{2+})$. The two $2p_\pi$ orbitals on oxygen can satisfy the π-bonding capacities of the two $3d_\pi$ orbitals of a first transition series metal ion, but it takes at least two oxygens to satisfy the combined π-bonding capacities offered by the 5f and 6d orbitals of the metal ions in the actinium series.

Appendix

A. Radial Functions and Atomic Orbital Energies.

—Self-consistent field (SCF) radial functions for vanadium 3d and 4s orbitals were taken from Watson's report.[16] Watson gives no 4p function, so it is estimated as having approximately the same radial dependence as the 4s function. Analytic 2s and 2p oxygen SCF radial functions were obtained by fitting the numerical functions given by Hartree[17] with a linear combination of Slater functions. These radial functions are summarized

$$\text{Vanadium } R(3d) = 0.5243\phi_3(1.83) + 0.4989\phi_3(3.61) + 0.1131\phi_3(6.80) + 0.0055\phi_3(12.43) \quad (15)$$

$$\begin{aligned}(4s) = &-0.02245\phi_1(23.91) - 0.01391\phi_2(20.60) \\ &+ 0.06962\phi_2(10.17) + 0.06774\phi_3(9.33) \\ &- 0.09708\phi_3(5.16) - 0.2462\phi_3(3.51) \\ &+ 0.04412\phi_5(3.87) + 0.3607\phi_5(1.88) \\ &+ 0.6090\phi_5(1.15) + 0.1487\phi_5(0.78) \quad (16)\end{aligned}$$

$$R(4p) = \phi_3(1.024) \quad (17)$$

$$\text{Oxygen } R(2s) = 0.5459\phi_2(1.80) + 0.4839\phi_2(2.80) \quad (18)$$

$$R(2p) = 0.6804\phi_2(1.55) + 0.4038\phi_2(3.43) \quad (19)$$

where $\phi_n(\mu) = N\mu r^{n-1}e^{-\mu r}$, and $N\mu$ is a normalization constant.

Valence state ionization energies for σ and π electrons in these orbitals are calculated for different degrees of ionization using the formulas and methods given by Moffitt[37] along with the spectroscopic data compiled by Moore.[38]

The degree of mixing in the hybrid orbitals

$$\psi(\text{oxygen } \sigma) = (\sin\theta)\Phi(2s) \pm (\cos\theta)\Phi(2p_z) \quad (20)$$

$$\psi(\text{vanadium } \sigma) = (\sin\theta)\Phi(4s) \pm (\cos\theta)\Phi(3d_{z^2}) \quad (21)$$

is estimated by requiring that the quantity

(37) W. Moffitt, *Repts. Progr. Phys.*, **17**, 173 (1954).

(38) C. E. Moore, "Atomic Energy Levels," U. S. Natl. Bur. Standards Circular 467, 1949 and 1952.

$\dfrac{\text{VSIE}(\theta)}{S(\theta)}$ be a minimum, where $S(\theta)$ is the overlap between the hybrid orbital and the appropriate orbital on the neighboring atom, and VSIE(θ) is the valence state ionization energy for different amounts of mixing θ. This gives $\theta = 0.455$ for the oxygen σ and $\theta = \pi/4$ for the vanadium σ. The sp$_\sigma$ tetrahedral hybrid orbital, $\theta = \pi/6$, is used for the water oxygen.

B. Overlap Integrals.—The two atom overlap integrals (S_{ij}'s) between the various atomic orbitals were found in the tabulations available in the literature.[39-42] The group overlap integrals (G_{ij}'s) of interest in the M.O. calculation are related to the S_{ij}'s as

$$G(e_\pi) = S(2p_\pi, 3d_\pi) \tag{22}$$

$$G(b_1) = \sqrt{3}S(te\sigma, 3d_\sigma) \tag{23}$$

$$G(Ia_1) = S(\sigma_b, sd_\sigma) \tag{24}$$

$$G(IIa_1) = \frac{1}{\sqrt{2}}[2S(te\sigma, 4s) + S(te\sigma, 3d_\sigma)] \tag{25}$$

$$G(IIIa_1) = S(te\sigma, 4p_\sigma) \tag{26}$$

$$G(e_\sigma) = \sqrt{2}S(te\sigma, 4p_\sigma) \tag{27}$$

where teσ is the tetrahedral sp$_\sigma$ hybrid for the water oxygens, and the oxygen orbitals are always listed first in parentheses.

C. Intensity Calculations.—The theoretical expression for the oscillator strength of a transition is given by[43]

$$f = 1.085 \times 10^{-5}(\nu_{\text{cm.-1}}) \, [av_1 \, \Sigma_{\text{II}} \mid \int \psi_{\text{I}}^* \mid \vec{r} \mid \psi_{\text{II}} \, d\tau \mid {}^2] \tag{28}$$

where ψ_{I} and ψ_{II} refer to the initial and final states, respectively, and $\vec{r} = i_x + j_y + k_z$.

For the transition ${}^2B_2 \rightarrow {}^2E(II)$

$$\psi_{\text{I}} = [(IC)^{12}(e^b\pi_x)(e^b\pi_x)(e^b\pi_y)(e^b\pi_y)(b_2)] = B_2 \text{ (orbital)} \tag{29}$$

$$\psi_{\text{II}} = \left\{ \begin{array}{l} [(IC)^{12}(e^b\pi_x)(e^b\pi_x)(e^b\pi_y)(b_2)(b_2)] \\ [(IC)^{12}(e^b\pi_x)(b_2)(e^b\pi_y)(e^b\pi_y)(b_2)] \end{array} \right\} = E(II)(\text{orbital}) \tag{30}$$

Simplifying, eq. 28 reduces to

$$({}^2B_2 \rightarrow {}^2E(II)) = 1.085 \times 10^{-5}(\nu_{\text{cm.-1}}) \left[\frac{N_{2p}c_2}{2N_{3d_{xy}}{}^{\mu_{2p}}} \right] \times$$
$$2[S(3d_\delta{}^{\mu_{2p}}, 3d_\delta)]^2 \tag{31}$$

where N_{2p} is the normalization constant for the

original ligand orbitals, and $N_{3d_{xy}}{}^{\mu_{2p}}$ is the normalization constant a 3d$_{xy}$ orbital would have with an exponential factor μ_{2p} in the radial function.

Supplying the proper values of c_2 and $\nu_{\text{cm.-1}}$ for the ${}^2B_2 \rightarrow {}^2E(II)$ transition, and obtaining the overlap integral from Jaffé's table,[41] $f = 2.64 \times 10^{-3}$ is calculated.

For the ${}^2B_2 \rightarrow {}^2E(I)$ transition, the same integrals are involved as in the above calculation. Only the constants $\nu_{\text{cm.-1}}$ and c_2 are different. Thus eq. 31 is written

$$({}^2B_2 \rightarrow {}^2E(I)) = 1.085 \times 10^{-5}(\nu_{\text{cm.-1}}) \left[\frac{N_{2p}c_2^*}{2N_{3d_{xy}}{}^{\mu_{2p}}} \right]^2 \times$$
$$2[S(3d_\delta{}^{\mu_{2p}}, 3d_\delta)]^2 = 3.92 \times 10^{-4} \tag{32}$$

For the ${}^2B_2 \rightarrow {}^2B_2$ transition

$$\psi_{\text{II}} = \frac{1}{\sqrt{2}} \{ [(IC)^{12}(e^b\pi_x)(e^*\pi_x)(e^b\pi_y)(e^b\pi_y)(b_2)] +$$
$$[(IC)^{12}(e^b\pi_x)(e^b\pi_x)(e^b\pi_y)(e^*\pi_y)(b_2)] \} = B_2(\text{orbital}) \tag{33}$$

and therefore

$$f({}^2B_2 \rightarrow {}^2B_2) = 1.085 \times 10^{-5}(\nu_{\text{cm.-1}}) \times$$
$$\left[\frac{\sqrt{2}(c_1c_2^* + c_1^*c_2)N_{2p}}{N_{3d_{xz}}{}^{\mu_{2p}}} \right]^2 [S(3d_\pi{}^{\mu_{2p}}, 3d_\pi)]^2 = 4.47 \times 10^{-8}$$

Experimental

Anhydrous VO(aca)$_2$ was prepared as described in the literature.[44] Analyzed VOSO$_4 \cdot 5H_2O$ was obtained from Struers Co., Copenhagen. Solution spectral measurements were made using a Zeiss instrument. Reflectance spectra were obtained with a Beckman DU equipped with a standard reflectance attachment. Magnesium oxide was used as a standard. The resolution of the bands in the reflectance spectrum of VOSO$_4 \cdot 5H_2O$ did not differ from the resolution achieved for the crystal absorption spectrum A shown in Fig. 5.

The crystal absorption spectra were obtained with a Zeiss instrument modified for double beam operation. It was equipped with a calcite polarizer and quartz optics which allowed accurate spectral measurements up to 45,000 cm.$^{-1}$. The optical system was designed to record spectra of very small crystals (about 2 mm.). The details of the design and operation of the crystal spectrophotometer will be reported elsewhere.[45]

The prismatic crystals of VOSO$_4 \cdot 5H_2O$ have four molecules in the monoclinic cell, with the VO groups arranged approximately parallel to the wedge of the prism. The A spectrum in Fig. 5 was recorded with the light incident on the 110 face and vibrating in a plane perpendicular to the wedge of the prism; the B spectrum was recorded with the light vibrating in a plane parallel to the wedge.

The magnetic susceptibilities of VOSO$_4 \cdot 5H_2O$ and VO-

(39) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

(40) H. H. Jaffé and G. O. Doak, *ibid.*, **21**, 196 (1953).

(41) H. H. Jaffé, *ibid.*, **21**, 258 (1953).

(42) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 354 (1954).

(43) C. J. Ballhausen, *Progr. in Inorg. Chem.*, **2**, 251 (1960).

(44) *Inorganic Syntheses*, **5**, 115 (1957).

(45) A. E. Nielsen, to be published.

(aca)$_2$ were determined by the Gouy method.[46]   Sample tubes were calibrated with Hg[Co(SCN)$_4$].

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(46) Chap. 6 in "Modern Coördination Chemistry," by B. N. Figgis and J. Lewis, edited by J. Lewis and R. G. Wilkins, Interscience Publishers, Inc., New York, N. Y., 1960.

The Reactions of Some Oxygen Donors with Molybdenum Pentachloride: Coordination Compounds of Molybdenum(V) Oxotrichloride and Molybdenum(VI) Dioxodichloride

By S. M. HORNER AND S. Y. TYREE, JR.

The reactions of the donor molecules triphenylarsine oxide, triphenylphosphine oxide, and dimethylsulfoxide with molybdenum pentachloride have been investigated.   The new compound MoCl$_5$·(C$_6$H$_5$)$_3$AsO has been prepared, but analogous compounds using triphenylphosphine oxide and dimethylsulfoxide could not be prepared. Some complexes of the oxychlorides of molybdenum have been prepared by two routes: the reaction of the donor molecules with solutions of molybdenum pentachloride or with solutions of the oxychlorides themselves.   The new compounds MoOCl$_3$·2(C$_6$H$_5$)$_3$PO, MoO$_2$Cl$_2$·2(C$_6$H$_5$)$_3$PO, MoOCl$_3$·2(CH$_3$)$_2$SO, MoO$_2$Cl$_2$·2(CH$_3$)$_2$SO, MoOCl$_3$· 2(C$_6$H$_5$)$_3$AsO, MoO$_2$Cl$_2$·2(C$_6$H$_5$)$_3$AsO, MoOCl$_3$·(C$_6$H$_5$)$_3$AsO·(CH$_3$)$_2$CO, and MoO$_2$Cl$_2$·2C$_5$H$_5$NO have been prepared. The compounds have been characterized by magnetic moment measurements, melting points, and infrared spectra.

Introduction

In recent years, considerable attention has been focused upon the donor behavior of various oxygen-type donor molecules toward metal salt acceptor species.   Several decades ago the syntheses of triphenylphosphine oxide–metal complexes were reported.[1]   Recently the behavior of phosphine oxides as ligands has been elucidated more fully.[2,3] Lindqvist[4] has reported complete structure determinations for a few crystalline complexes of phosphine oxides with metal halides.   Cotton[5] has published a complete analysis of the infrared spectra of triphenylphosphine oxide complexes. A study of the donor properties of triphenylarsine oxide has been carried out in this Laboratory,[6]

while compounds of triphenylarsine oxide with some metal carbonyls have been reported from Hieber's laboratory.[7,8]

The preparation and properties of compounds using dimethylsulfoxide as the donor group have been reported[9-11] and Drago[12] has prepared and studied the infrared spectra of some similar complexes.   Complexes of pyridine N-oxide have been reported by Quagliano and workers in our own Laboratory,[13] along with a complete study of their infrared spectra.[14]   Other compounds of pyridine-N-oxide have been synthesized by Carlin,[15] and some visible spectra measurements reported.

We wished to extend the study of oxygen donor

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