transition is shifted to lower energy upon complexation with a metal ion.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. $[VO(sal)_2tn]_x$, 28630-97-9; $(DMF)VO(sal)_2tn$, 42578-14-3; $(py)VO(sal)_2tn$, 42578-15-4; $[Vo(sal)_2(+)tnCH_3]_x$, 42579-14-6; $VO(sal)_2(+)tnCH_3$, 31929-66-5; $(MeOH)VO(sal)_2(+)$-$tnCH_3$, 42578-17-6; $(DMF)VO(sal)_2(+)tnCH_3$, 42578-18-7; (py)-$VO(sal)_2(+)tnCH_3$, 42578-19-8; $[VO(3\text{-}iprsal)_2tn]_x$, 42579-15-7; $VO(3\text{-}iprsal)_2tn$, 42578-20-1; $(DMF)VO(3\text{-}iprsal)_2tn$, 42578-21-2; $(py)VO(3\text{-}iprsal)_2tn$, 42578-22-3; $[VO(7\text{-}CH_3sal)_2tn]_x$, 42745-97-1; $VO(7\text{-}CH_3sal)_2tn$, 42718-93-4; $(DMF)VO(7\text{-}CH_3sal)_2tn$, 42578-23-4; $(py)VO(7\text{-}CH_3sal)_2tn$, 42578-24-5; $(H\text{-}7\text{-}CH_3sal)_2(+)tnCH_3$, 42530-90-5.

Contribution from the Departments of Chemistry, University of Kentucky,
Lexington, Kentucky 40506, and West Virginia University, Morgantown, West Virginia 26506

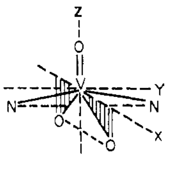
Electronic Structure of Bis(2-methyl-8-quinolinolato)oxovanadium(IV)

HENRY J. STOKLOSA,[1a] JOHN R. WASSON,*[1a] and B. JACK McCORMICK[1b]

Received July 18, 1973

The spectral and magnetic properties of bis(2-methyl-8-quinolinolato)oxovanadium(IV), $VO(quin)_2$, a low-symmetry complex possessing effective C_{2v} symmetry, are described. An explicit phenomenological crystal field model was developed which gave a good account of the electronic and electron spin resonance (esr) spectra of $VO(quin)_2$. Iterative extended-Huckel molecular orbital calculations for the model complex ion $VOCl_4^{2-}$ yielded results in qualitative agreement with the crystal field model. The esr spectrum of $VO(quin)_2$ in a toluene glass exhibited three g values and yielded spin-Hamiltonian parameters analogous to those found for bis(*N*-methylsalicylaldiminato)oxovanadium(IV) which also contains the $VO(N_2O_2)$ chromophore. Except for the splitting of the d_{xz} and d_{yz} levels, the Ballhausen–Gray energy level scheme for complexes with C_{4v} microsymmetry holds for $VO(quin)_2$.

A wide variety of oxovanadium(IV), vanadyl complexes have been prepared and characterized.[2,3] A square pyramidal (C_{4v}) geometry has been established or, more frequently, assumed for vanadyl compounds. In recent years two crystal structures[4,5] have appeared which serve to shake confidence in the usual assumptions concerning the structures of vanadyl chelates. Shiro and Fernando[4] have reported the structure of bis(2-methyl-8-quinolinolato)oxovanadium(IV), $VO(quin)_2$, which is five coordinate and has a trigonal bipyramidal coordination polyhedron about the vanadium in which the three oxygen atoms and the vanadium are in the equatorial plane and the two nitrogen atoms occupy apical positions, I. Similar structures have been reported for bis(trimethylamine)oxovanadium(IV) dichloride[6] and bis(tetramethylurea)oxovanadium(IV) dichloride.[7] It is noted that although these molecules are referred to as being trigonal bipyramidal they are more appropriately considered as having an effective C_{2v} distorted square pyramidal geometry.[6] The other unusual structure of importance to vanadyl chemistry is the one found[5] for the 4-phenylpyridine adduct of vanadyl acetylacetonate, $VO(acac)_2$, in which the 4-phenylpyridine added cis to the vanadyl oxygen atom rather than trans axially as is usually assumed for $VO(acac)_2$ adduct formation.



I

Here we address ourselves to the problem of the electronic structure of $VO(quin)_2$ since it was of interest to characterize the properties of a compound which could not be expected to be interpreted in terms of the familiar Ballhausen–Gray[8] model for vanadyl complexes possessing effective C_{4v} symmetry. To this end we have obtained the electronic and esr spectra of $VO(quin)_2$. A general crystal field model for complexes of this type was developed and iterative extended-Huckel molecular orbital calculations were performed for the model compound $VOCl_4^{2-}$ which was assumed to have bond angles appropriate to $VO(quin)_2$.

Experimental Section

2-Methyl-8-quinolinol was obtained from Aldrich Chemical Co., Milwaukee, Wis. and used without further purification. All other chemicals were of the best available reagent or spectroscopic grades. Optical and infrared spectra were measured with Cary Model 14 and Perkin-Elmer Model 621 recording spectrophotometers, respectively. Electron spin resonance spectra were measured with Varian E-3 and Magnion MVR-12X X-band spectrometers. The Magnion esr spectrometer operates at about 9.4 GHz using 6-kHz field modulation and a 12-in. electromagnet. The frequency was monitored with a calibrated absorption wavemeter incorporated in the microwave unit. Field calibration was checked using diphenylpicrylhydrazyl (DPPH) free radical for which $g = 2.0036$. Esr spectra of saturated ($\sim 10^{-3}$ *M*) toluene solutions of $VO(quin)_2$ were obtained using quartz capillary tubing. Frozen solution esr spectra were obtained with a finger dewar filled with liquid nitrogen which fit into the instrument sample cavity. Mass spectra were obtained using a double-focusing Hitachi Perkin-Elmer RMU-7 spectrometer. Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz.

Bis(2-methyl-8-quinolinolato)oxovanadium(IV), $VO(quin)_2$, was prepared by adding an aqueous solution of the sodium salt of the ligand (obtained by adding the ligand to a stoichiometric amount of sodium hydroxide in about 50 ml of warm distilled water) dropwise to a stoichiometric amount of vanadyl sulfate in warm water. A pale green precipitate formed immediately which was collected by

---

[1] (a) University of Kentucky; (b) West Virginia University.

[2] J. Selbin, *Chem. Rev.*, 65, 153 (1965); *Coord. Chem. Rev.*, 1, 293 (1966); *Angew. Chem., Int. Ed. Engl.*, 5, 712 (1966).

[3] B. J. McCormick, J. L. Featherstone, H. J. Stoklosa, and J. R. Wasson, *Inorg. Chem.*, 12, 692 (1973), and references therein.

[4] M. Shiro and Q. Fernando, *Chem. Commun.*, 63 (1971).

[5] M. R. Caira, J. M. Haigh, and L. R. Nassimbeni, *Inorg. Nucl. Chem. Lett.*, 8, 109 (1972).

[6] J. E. Drake, J. Vekris, and J. S. Wood, *J. Chem. Soc. A*, 1000 (1968).

[7] J. Coetzer, *Acta Crystallogr., Sect. B*, 26, 872 (1970).

[8] C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, 1, 111 (1962).

filtration, washed successively with water, ethanol, and ether, and air dried. *Anal.* Calcd for $VO_3C_{20}H_{16}$: C, 62.67; H, 4.21; N, 7.31. Found: C, 63.66; H, 3.98; N, 7.20. The mass spectrum of the complex gives a parent peak agreeing with the calculated molecular weight. The compound was insoluble in most organic solvents but was slightly soluble in toluene.

Crystal field calculations were performed using the method of Companion and Komarynsky[9] and a computer program previously described.[10] Details of this explicit method,[9] its simplification using elementary group theory, and evaluation of ligand crystal field parameters are discussed elsewhere.[10,11] For both the crystal field and extended-Huckel molecular orbital calculations, the coordinate system in structure I was employed.

Extended-Huckel molecular orbital (EHMO) calculations were performed using Hoffmann's program[12] which was obtained from the Indiana University Quantum Chemistry Program Exchange and modified to permit inclusion of a central metal atom. Calculations were performed iteratively until the output charge on vanadium, obtained using a Mulliken population analysis,[13] was within 0.01 of the input charge. Calculations were performed for the model compound $VOCl_4{}^{2-}$ assuming a C_{2v} distorted square pyramidal geometry, a V=O distance of 1.60 A, and O=V–Cl angles consistent with the structure[4] of $VO(quin)_2$. A V–Cl distance of 2.42 A was taken in accord with the structure[14] of the $VOCl_4(H_2O)^{2-}$ anion.

The diagonal matrix elements (H_{ii}) are listed in Table I. The vanadium valence orbital ionization potentials (VOIP's) were those utilized by Schachtschneider, Prins, and Ros in their calculations[15] of vanadocene. The VOIP's are given by

$$H_{ii} = -(Aq^2 + Bq + C) \tag{1}$$

where A, B, and C are parameters obtained from spectroscopic data on the free atoms and ions and q is the net charge on the atom. Average ligand VOIP's were taken from the tabulation given by Ballhausen and Gray.[16]

The off-diagonal matrix elements of the effective Hamiltonian were estimated by the arithmetic mean or Mulliken-Wolfsberg-Helmholz[17] approximation, *i.e.*

$$H_{ij} = -0.5KS_{ij}(H_{ii} + H_{jj}) \tag{2}$$

with K set[12] equal to 1.75. Off-diagonal matrix elements were also evaluated by the geometric[8] and harmonic or reciprocal[18] mean approximations

$$H_{ij} = -KS_{ij}(H_{ii}H_{jj})^{1/2} \tag{3}$$

and

$$H_{ij} = -KS_{ij}[2(H_{ii}H_{jj})/(H_{ii} + H_{jj})] \tag{4}$$

respectively.

Slater orbital exponents for vanadium were those employed by Zerner and Gouterman[19] in their calculations for vanadyl porphyrins. Ligand atom Slater orbital exponents were simple averages of the energy optimized valence shell orbital exponents listed by Clementi and Raimondi.[20] All calculations were performed with the IBM 360-65 computer at the University of Kentucky Computer Center.

Results and Discussion

Table I. Valence Orbital Ionization Potentials and Orbital Exponents

Atom	Orbital	Exponent	−VOIP, eV
Vanadium	3d	2.3300	$1.959q^2 + 8.430q + 3.893$
	4s	1.3000	$1.060q^2 + 6.717q + 6.323$
	4p	1.3000	$0.924q^2 + 5.635q + 3.434$
Oxygen	2s	2.2363	32.348
	2p	2.2363	15.869
Chlorine	3s	2.1974	25.291
	3p	2.1974	13.761

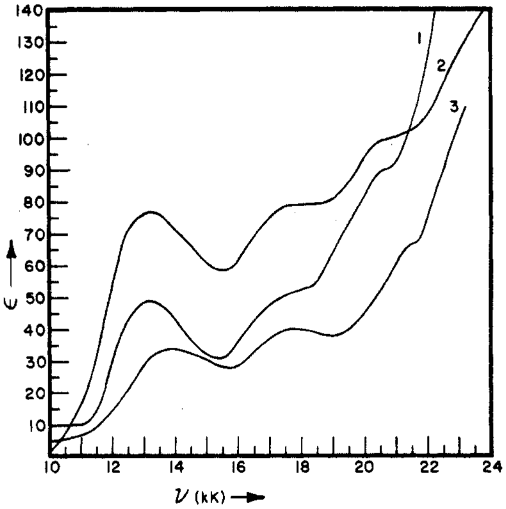


Figure 1. Electronic spectrum of $VO(quin)_2$: (1) toluene solution; (2) Nujol mull (absorptivity units are arbitrary); (3) diffuse relectance, $MgCO_3$ used as standard (absorptivity units are arbitrary).

Electronic Spectra. The electronic spectrum of $VO(quin)_2$ in toluene is shown in Figure 1 and spectroscopic data for $VO(quin)_2$ and related complexes are summarized in Table II. No bands are found at lower energies and no splitting of the low-energy band is found as is the case for $VO[N(CH_3)_3]_2Cl_2$.[6] $VO(TMU)_2Cl_2$, however, exhibits[21] an electronic spectrum very similar to that observed for $VO(quin)_2$. The larger extinction coefficients for $VO(quin)_2$ compared to the other complexes may arise from a greater metal-ligand bond covalency and/or a larger distortion from the C_{2v} symmetry assumed for the complex.

On the basis of a qualitative crystal field approach Wood, *et al.*,[6] have proposed the following energy level sequence: $a_2(xy) < b_1(xz) < b_2(yz) < a_1 < a_1$ to account for the electronic spectrum of $VO[N(CH_3)_3]_2Cl_2$ which has C_{2v} symmetry. Kuska and Yang[22] have proposed the energy level order: $a_2(xy) < b_1(xz) \approx b_2(yz) < a_1(x^2\text{-}y^2) < a_1(z^2)$ to account for the spectrum of $VO(TMU)_2Cl_2$ on the basis of Wolfsberg-Helmholz-type MO calculations. In order to check these results we have developed an explicit crystal field treatment of VOL_2X_2 (L = ligand, X = halide) complexes possessing C_{2v} symmetry. Of especial interest was the expression for the separation of the xy and yz levels.

As a consequence of C_{2v} point symmetry only six of the fifteen possible matrix elements need be evaulated. The d levels are given below

A_1	$d_{x^2-y^2}$	d_{z^2}
$d_{x^2-y^2}$	H_{11}	H_{13}
d_{z^2}	H_{13}	H_{33}

---

(9) A. L. Companion and M. A. Komarynsky, *J. Chem. Educ.*, 41, 257 (1964).

(10) J. R. Wasson and H. J. Stoklosa, *J. Chem. Educ.*, 50, 186 (1973).

(11) H. J. Stoklosa and J. R. Wasson, *J. Inorg. Nucl. Chem.*, 36, 227 (1974); D. K. Johnson, H. J. Stoklosa, J. R. Wasson, and H. E. Montgomery, *ibid.*, in press.

(12) R. Hoffmann, *J. Chem. Phys.*, 39, 1397 (1963).

(13) R. S. Mulliken, *J. Chem. Phys.*, 23, 1833, 1841 (1955).

(14) L. O. Atovmyan and Z. G. Aliev, *Zh. Strukt. Khim.*, 11, 782 (1970).

(15) J. H. Schachtschneider, R. Prins, and P. Ros, *Inorg. Chim. Acta*, 1, 462 (1967).

(16) C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, New York, N. Y., 1964, p 122.

(17) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, 20, 837 (1952).

(18) W. A. Yeranos, *J. Chem. Phys.*, 44, 2207 (1966).

(19) M. Zerner and M. Gouterman, *Inorg. Chem.*, 5, 1699 (1966).

(20) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, 38, 2686 (1963).

(21) J. G. H. du Preez and F. G. Sadie, *Inorg. Chim. Acta*, 1, 202 (1967).

(22) H. A. Kuska and P.-H Yang, "Bonding Studies of Bis(tetramethylurea)dichlorooxovanadium(IV)," submitted for publication; Abstracts of the 5th Central Regional Meeting of the American Chemical Society, Cleveland, Ohio, May 13-15, 1973.

Table II. Electronic Spectral Data

Compd	Medium	ν_1, kK	$\epsilon_1{}^a$	ν_2, kK	ϵ_2	ν_3, kK	ϵ_3
$VO(quin)_2$	Nujol mull	13.1		18.0		20.6	
	Toluene	12.66	35.0	17.09	41.2	20.8 sh	70
	Diffuse reflectance	11.90		15.87		19.61	
$VO(TMU)_2Cl_2{}^c$	Nitromethane	12.9 sh^b		15.0	43	24.9	
		11.76	45				
$VO[N(CH_3)_3]_2Cl_2{}^d$	Benzene	13.15	76	14.20	~12	27.03	12

^{a} Molar absorptivity. ^{b} Shoulder. ^{c} Reference 21. ^{d} Reference 6.

where

$$H_{11} = -\frac{2}{7}\alpha_2{}^x(3\cos^2\theta_x - 1) - \frac{2}{7}\alpha_2{}^y(3\cos^2\theta_y - 1) + \alpha_4{}^x\left[\frac{5}{12}\cos^4\theta_x - \frac{5}{14}\cos^2\theta_x + \frac{1}{28} + \frac{5}{12}\sin^4\theta_x\right] + \alpha_4{}^y\left[\frac{5}{12}\cos^4\theta_y - \frac{5}{14}\cos^2\theta_y + \frac{1}{28} + \frac{5}{12}\sin^4\theta_y\right] + \frac{1}{21}\alpha_4{}^0 \tag{5}$$

$$H_{13} = \alpha_4{}^x\left[\frac{5\sqrt{3}}{42}\sin^2\theta_x(7\cos^2\theta_x - 1)\right] - \alpha_4{}^y\left[\frac{5\sqrt{3}}{42}\sin^2\theta_y(7\cos^2\theta_y - 1)\right] - \alpha_2{}^x\left[\frac{2\sqrt{3}}{7}\sin^2\theta_x\right] + \alpha_2{}^y\left[\frac{2\sqrt{3}}{7}\sin^2\theta_y\right] \tag{6}$$

$$H_{33} = \frac{2}{7}\alpha_2{}^x(3\cos^2\theta_x - 1) + \frac{2}{7}\alpha_2{}^y(3\cos^2\theta_y - 1) + \frac{2}{7}\alpha_2{}^0 + \frac{2}{7}\alpha_4{}^0 + \alpha_4{}^x\left[\frac{5}{2}\cos^4\theta_x - \frac{15}{7}\cos^2\theta_x + \frac{3}{14}\right] + \alpha_4{}^y\left[\frac{5}{2}\cos^4\theta_y - \frac{15}{7}\cos^2\theta_y + \frac{3}{14}\right] \tag{7}$$

$$A_2{:}\quad E_{d_{xy}} = -\frac{2}{7}\alpha_2{}^x(3\cos^2\theta_x - 1) - \frac{2}{7}\alpha_2{}^y(3\cos^2\theta_y - 1) - \frac{2}{7}\alpha_2{}^0 + \frac{1}{21}\alpha_4{}^0 + \alpha_4{}^x\left[\frac{5}{12}\cos^4\theta_x - \frac{5}{14}\cos^2\theta_x + \frac{1}{28} - \frac{5}{12}\sin^4\theta_x\right] + \alpha_4{}^y\left[\frac{5}{12}\cos^4\theta_y - \frac{5}{14}\cos^2\theta_y + \frac{1}{28} - \frac{5}{12}\sin^4\theta_y\right] \tag{8}$$

$$B_1{:}\quad E_{d_{xz}} = \alpha_2{}^x\left[\frac{1}{7}(3\cos^2\theta_x - 1) + \frac{3}{7}\sin^2\theta_x\right] + \alpha_2{}^y\left[\frac{1}{7}(3\cos^2\theta_y - 1) + \frac{3}{7}\sin^2\theta_y\right] - \frac{4}{21}\alpha_4{}^0 - \alpha_4{}^x\left[\frac{5}{21}\cos^4\theta_x - \frac{10}{7}\cos^2\theta_x + \frac{1}{7} - \frac{5}{21}\sin^2\theta_x(7\cos^2\theta_x - 1)\right] - \alpha_4{}^y\left[\frac{5}{21}\cos^4\theta_y - \frac{10}{7}\cos^2\theta_y + \frac{1}{7} - \frac{5}{21}\sin^2\theta_y(7\cos^2\theta_y - 1)\right] \tag{9}$$

$$B_2{:}\quad E_{d_{yz}} = \alpha_2{}^x\left[\frac{1}{7}(3\cos^2\theta_x - 1) - \frac{3}{7}\sin^2\theta_x\right] + \alpha_2{}^y\left[\frac{1}{7}(3\cos^2\theta_y - 1) + \frac{3}{7}\sin^2\theta_y\right] + \frac{2}{7}\alpha_2{}^0 - \frac{4}{21}\alpha_4{}^0 + \alpha_4{}^x\left[\frac{-10}{3}\cos^4\theta_x + \frac{20}{7}\cos^2\theta_x - \frac{2}{7} - \frac{5}{21}\sin^2\theta_x(7\cos^2\theta_x - 1)\right] + \alpha_4{}^y\left[\frac{-10}{3}\cos^4\theta_y + \frac{20}{7}\cos^2\theta_y - \frac{2}{7} + \frac{5}{21}\sin^2\theta_y(7\cos^2\theta_y - 1)\right] \tag{10}$$

$$E_{d_{xz}} - E_{d_{yz}} = \frac{10}{21}\left[\alpha_4{}^x\sin^2\theta_x(7\cos^2\theta_x - 1) - \alpha_4{}^y\sin^2\theta_y(7\cos^2\theta_y - 1)\right] \tag{11}$$

where the x, y, and 0 subscripts and superscripts refer to ligands in the xz and yz planes and the vanadyl oxygen atom, respectively. The above expressions are completely general for any VOL_2X_2 complex with C_{2v} symmetry. The angle θ is that made by the metal-ligand bond axis with the $z(C_2)$ molecular axis. The α_2 and α_4 values are ligand crystal field parameters. Experience[10,11,23] has shown that a realistic approach to the d levels in complexes requires that the α_2/α_4 ratio for a particular ligand be fixed at 0.9 or 1.0. It is noted that an α_4 value for a ligand is equal to *6Dq*, *i.e.*, 0.6 of the crystal field splitting for an octahedral complex. Using Jorgensen's expression[24]

$$10Dq \cong f(\text{ligand})g(\text{central ion}) \times 10^3\ \text{cm}^{-1} \tag{12}$$

and $g = 24.9$ for vanadium(IV), α_4 values of 11.92 and 18.68 kK (1 kK = 1000 cm^{-1}) can be estimated for oxygen (x) and nitrogen (y) ligands, respectively, from data on acetylacetonate and pyridine complexes. A value of $\alpha_4{}^{O^{2-}}$ of 94.50 kK was chosen for the vanadyl oxygen atom in accord with previous work.[10,11] With these parameters "d ← d" transitions $YZ \leftarrow XY$, $XZ \leftarrow XY$, $X^2 - Y^2 \leftarrow XY$, and $Z^2 \leftarrow XY$ are calculated to occur at 13.62, 15.73, 20.00, and 72.82 kK, respectively. The same calculation for the actual structure[4] of $VO(quin)_2$ yields $YZ \leftarrow X^2 - Y^2$, $XZ \leftarrow X^2 - Y^2$, $XY \leftarrow X^2 - Y^2$, and $Z^2 \leftarrow X^2 - Y^2$ transitions at 12.78, 15.67, 19.66, and 72.58 kK, respectively, with *all* of the d orbitals mixed into *each* state. The transitions from the calculation for the actual structure of $VO(quin)_2$ were assigned on the basis of

---

(23) A. L. Companion, *J. Phys. Chem.*, 73, 739 (1969); J. R. Angus, G. M. Woltermann, and J. R. Wasson, *J. Inorg. Nucl. Chem.*, 33, 3967 (1971).

(24) C. K. Jorgensen, *Struct. Bonding (Berlin)*, 1, 3 (1966); see also B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York, N. Y., 1966, pp 242-245.

greater than 75% of a particular level. The calculations for the idealized C_{2v} symmetry or the actual symmetry of VO(quin)$_2$ are in fairly good agreement with the experimental data in Table II as well as the energy level schemes proposed by Wood, *et al.*,[6] and Kuska and Yang.[20] Note that the position of the *XZ* and *YZ* levels can be interchanged by choice of the coordinates for the stronger field ligands. Our calculations were not "optimized" to obtain any sort of agreement with experiment. The $\alpha_2:\alpha_4$ ratio was chosen as 0.9 and the α_4 parameters were taken as described above. The unusually high value for the $Z^2 \leftarrow XY(X^2 - Y^2)$ transition is a consequence of the α_4 value for the vanadyl oxgyen atom.[10,11] In MO calculations additional $a_1(z^2) \leftarrow a_2$ transitions (orbitally forbidden in C_{2v} symmetry) are possible due to MO formation. In order to check the energy level sequence $d_{xy} < d_{xz} < d_{yz} < d_{x^2-y^2} < d_{z^2}$ found by the crystal field calculations, MO calculations for the *model* complex $VOCl_4^{2-}$ were performed.

The symmetry orbitals, generated by standard projection operator techniques, for VOL_2X_2 complexes possessing C_{2v} symmetry, are given in Table III. The symmetry combinations of basis functions show that the a_1 states involve considerable mixing of metal $d_{x^2-y^2}$, d_{z^2}, s, and p_z orbitals with each other and various ligand functions whereas the a_2 ground state is comparably simple. The large number of a_1 states arising from MO formation must be taken into account if the phenomenological crystal field model[9-11] is to be of utility in assigning electronic transitions. The first three (two if C_{4v} complexes are considered[10,11]) electronic transitions can be accounted for with an ionic model, but the highest energy transition so calculated corresponds (as seen below) to one of the higher energy transitions between MO's of the same classification as one occurring in the optical region. $A_1 \leftarrow A_2$ transitions are formally forbidden in C_{2v} symmetry but this selection rule is easily relaxed by slight distortion from the idealized C_{2v} geometry. The crystal field calculations discussed above showed that use of the actual geometry[4] for VO(quin)$_2$ did not significantly affect the transition energies although the orbital nature of the states was altered somewhat. The "d-p" and "s-p" mixing which can be invoked[11,25] to account for the spectral band intensities of noncentrosymmetric complexes can be seen to be of importance by inspection of valence orbitals involved in the various molecular states even though the actual calculation of spectral intensities must take other things, *e.g.*, charge transfer states,[26] into account.

Table IV summarizes the essential results of the iterative extended-Huckel MO calculations for $VOCl_4^{2-}$. The "d" level energy sequence was of particular interest as was d_{xz}-d_{yz} splitting since these could serve as a test of the ionic model. The calculated charge distributions are in accord with expectations for extended-Huckel calculations and vary little with the approximations chosen for the off-diagonal matrix elements. Except for the highest energy $a_1(z^2) \leftarrow a_2$ transitions the formula for the off-diagonal matrix elements does not significantly affect the positions of bands to be found in the optical region. The transition energies calculated for $VOCl_4^{2-}$ are not in very good agreement with experimental results[27] ($\nu_1 = 11.8$, $\nu_2 = 13.9$, and $\nu_3 = 24.0$ kK), but it must be kept in mind that the calculations did not employ structural data for $VOCl_4^{2-}$. The splitting of the d_{xz} and d_{yz} levels by about 2 kK shows that there is essential agreement between the ionic and MO models. Equation 11 shows that this splitting is not only a function of the difference in *Dq* values between the ligands other than vanadyl oxygen but also depends on the geometry of the complex. If the $XZ \leftarrow XY$ and $YZ \leftarrow XY$ transitions have large band widths, it may not be possible to resolve the transitions. Table IV shows that the "d" energy sequence $d_{xy} < d_{yz} < d_{xz} < d_{x^2-y^2} < d_{z^2}$ results from use of the MO model whereas the d_{yz} and d_{xz} levels are interchanged in the crystal field model. This interchange in the MO model can be attributed to the greater 3p(ligand)-3d(metal) orbital overlap (σ and π) which exists for the ligands in the *yz* plane. For VO(quin)$_2$ it is difficult to establish the d_{xz},d_{yz} ordering without recourse to a MO calculation or single-crystal optical spectroscopy. It is noted that the harmonic mean approximation for the off-diagonal matrix elements results in an $a_1 \leftarrow a_2$ transition (88.54 kK) which is in reasonable agreement with the 72.82 kK transition calculated for VO(quin)$_2$.

In summary, a crystal field model yields transition energies for VO(quin)$_2$ which are in fair agreement with experiment.

Table III. Orbital Transformation Scheme for C_{2v} Symmetry

Representation	Metal orbitals	Ligand orbitals[a]
a_1	$3d_{x^2-y^2}$	s_O, Z_O
	$3d_{z^2}$	$s_{x_1} + s_{x_2}$
	4s	$X_{x_1} - X_{x_2}$
		$Z_{x_1} + Z_{x_2}$
	$4p_z$	
		$s_{y_1} + s_{y_2}$
		$Y_{y_1} - Y_{y_2}$
		$Z_{y_1} + Z_{y_2}$
a_2	$3d_{xy}$	$Y_{x_1} - Y_{x_2}$
		$X_{y_1} - Y_{y_2}$
b_1	$3d_{xz}$	$s_{x_1} - s_{x_2}$
	$4p_x$	$X_{x_1} + X_{x_2}$
		$Z_{x_1} - Z_{x_2}$
		$X_{y_1} + X_{y_2}$
		X_O
b_2	$3d_{yz}$	$Y_{x_1} + Y_{x_2}$
	$4p_y$	$s_{y_1} - s_{y_2}$
		$Y_{y_1} + Y_{y_2}$
		$Z_{y_1} - Z_{y_2}$
		Y_O

[a] The subscripts refer to atoms along the *x* and *y* axes (structure I); the numbers 1 and 2 referring to atoms with positive and negative coordinates (*x* or *y*), respectively. s, X, Y, and Z refer to ligand valence shell s, p_x, p_y, and p_z orbitals. The subscript O's refer to the vanadyl oxygen atom.

Table IV. Results of Extended-Huckel MO Calculations for $VOCl_4^{2-}$

Transition[a]	Arithmetic[b]	Geometric[b]	Harmonic[b]
$b_2 \leftarrow a_2$	6184	6265	6286
$b_1 \leftarrow$	8594	8812	8938
$a_1(x^2-y^2) \leftarrow$	9487	9888	10,161
$a_1(z^2) \leftarrow$	18,703	18,875	18,940
$a_1(z^2) \leftarrow$	156,132	117,782	88,540
Charges			
Vanadium	0.856	0.876	0.892
Oxygen	−1.108	−1.166	−1.211
Chloride 1[c]	−0.421	−0.411	−0.402
Chloride 2	−0.453	−0.445	−0.439

[a] For the a_1 levels the dominant d orbital is indicated in parentheses. [b] Arithmetic, geometric, and harmonic indicate the mean approximations employed for the off-diagonal matrix elements. [c] The chlorine atoms indicated by 1 are those along the *y* axis while those lying in the *xz* plane are indicated by 2.

---

(25) A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, Amsterdam, 1968.

(26) Z. Jaeger and R. Englman, *Chem. Phys. Lett.*, 19, 242 (1973).

(27) H. Kon and N. E. Sharpless, *J. Phys. Chem.*, 70, 105 (1966); J. E. Drake, J. E. Vekris, and J. S. Wood, *J. Chem. Soc. A*, 345 (1969).

Table V. Spin-Hamiltonian Parameters for Rhombic Vanadium(IV) Complexes

					10^4 cm^{-1}			
Compd	g_1	g_2	g_z	$\langle g\rangle^e$	A_1	A_2	A_z	$\langle A\rangle^f$
$VO(quin)_2$[a]	1.973	1.979	1.931	1.985	52.8	66.4	156.6	89.8
$VO(acac)_2$[b]	1.984	1.981	1.942	1.969	63.0	64.2	173.4	100.2
$V(\pi-C_5H_5)_2Cl_2$[c]	1.986	1.971	2.000	1.986	74.0	117.0	15.2	68.7
$VO(mesalim)_2$[d]	1.9842	1.9793	1.9543	1.973	59.7	48.8	156.3	88.3

[a] g_1, g_2, A_1, and A_2 values for $VO(quin)_2$ are labeled arbitarily whereas $g_1 = g_x$, $A_1 = A_x$, etc., for the other compounds listed. [b] Reference 28. Data for a (60:40) chloroform–toluene glass. [c] Reference 31. Since the ground state is predominantly d_{z^2}, g_z is very close to the free electron value 2.0023 as expected. [d] Reference 32. mesalim = *N*-methylsalicylaldimate. Data for the VO^{2+} complex doped into the corresponding diamagnetic nickel(II) compound. [e] $\langle g\rangle = {}^1/_3(g_1 + g_2 + g_z)$ except for $VO(quin)_2$ for which data was obtained in toluene solution. [f] $\langle A\rangle = {}^1/_3\langle A_1 + A_2 + A_z\rangle$ = isotropic vanadium electron spin–nuclear spin hyperfine coupling constant. The value for $VO(quin)_2$ was taken from the spectrum in toluene; all other values were calculated from the anisotropic data.

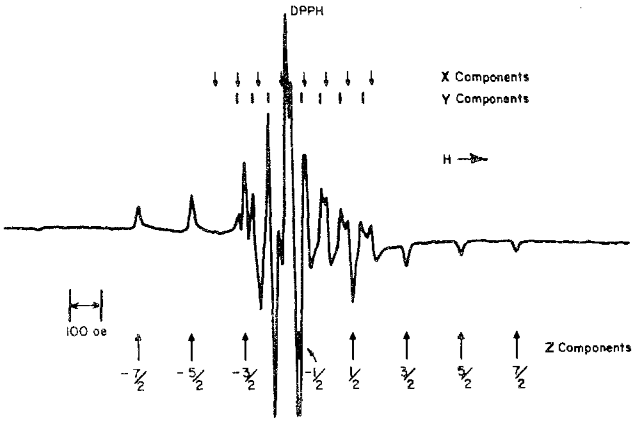


Figure 2. Electron spin resonance spectrum of $VO(quin)_2$ in a toluene glass ($T \cong 77°K$). The numbers at the bottom indicate the m_I values of the transitions.

Adjustment of parameters could be employed to yield a better fit of the observed spectrum, but that was not the purpose of the calculations. However, general expressions were developed for all VOL_2X_2 complexes which can be used to fit spectral data. MO calculations for $VOCl_4^{2-}$ show that the crystal field model gives a good account of the magnitude of the d_{xz}-d_{yz} splitting and the first three bands of VOL_2X_2 complexes.

Electron Spin Resonance Spectra. The esr spectrum of $VO(quin)_2$ in toluene exhibits the eight-line pattern characteristic of vanadyl complexes. The isotropic vanadium electron spin-nuclear spin hyperfine coupling constant, A_0, is 96.3 G. A_0 was obtained by averaging the separation of the $-m_I$ to $+m_I$ transitions. This was done since the separation of these transitions has no second-order dependence on A_0. The spectrum was interpreted using the usual spin Hamiltonian

$$\hat{H} = g\beta H\cdot\hat{S}_z + A\hat{I}_z\hat{S}_z \tag{13}$$

which for $S = {}^1/_2$ systems, when second-order perturbation theory is employed, yields

$$H_0 = H_m + A_0 m_I + A_0^2[I(I+1) - m_I^2]/2H_0 \tag{14}$$

and $H_0 = h\nu/g_0\beta$ where h is Planck's constant, β is the Bohr magneton, ν is the microwave frequency, and g_0 is the isotropic g value. H_m is the resonance field position of the m_I component of the solution spectrum.

The spectrum of $VO(quin)_2$ in toluene at 77°K (liquid nitrogen) is shown in Figure 2. The anisotropic spectrum of the complex exhibits rhombic rather than axial symmetry; at least 20 lines are discernible compared to the 16 lines expected for an axial spectrum. The spectrum was interpreted using the following equations obtained by Stewart and Porte[28] and cast into a different form.

$$H_m^z = H_0^z - A_z m_I - \left[\frac{g_x^2A_x^2 + g_y^2A_y^2}{4g_z^2H_0^z}\right][I(I+1) - m_I^2] \tag{15}$$

$$H_m^x = H_0^x - A_x m_I - \left[\frac{g_y^2A_y^2 + g_z^2A_z^2}{4g_x^2H_0^x}\right][I(I+1) - m_I^2] - \frac{Q^2}{4g_xA_x}[2I(I+1) - 2m_I^2 - 1]m_I \tag{16}$$

$$H_m^y = H_0^y - A_y m_I - \left[\frac{g_x^2A_x^2 + g_z^2A_z^2}{4g_y^2H_0^y}\right][I(I+1) - m_I^2] - \frac{Q^2}{4g_yA_y}[2I(I+1) - 2m_I^2 - 1]m_I \tag{17}$$

The symbols have their usual meanings and H_0^α ($\alpha = x, y, z$) is related to g_α by $h\nu = g_\alpha\beta H_0^\alpha$. Q is the nuclear quadrupole coupling constant expressed in gauss. The quadrupole term is estimated to contribute *ca.* ∓0.8 G for $m_I = \pm{}^7/_2$ transitions and *ca.* ∓4.0 G for $m_I = \pm{}^1/_2$ transitions. The $m_I - {}^1/_2$ transition has an "extra absorption" associated with it and, thus, its position is uncertain. In accord with general practice we have chosen to ignore the quadrupole term in our interpretation of the powder spectrum. Equations 15–17 were also obtained by assuming $\theta = 0°$, $\phi = 0°$; $\theta = 90°$, $\phi = 0°$; $\theta = 90°$, $\phi = 90°$ and substituting these values into the general equations for rhombic spectra given by Bleaney[29] and Atherton[30] where quadrupole terms were also ignored. The esr parameters are summarized in Table V.

Table V enables comparison of esr spectral parameters for a variety of vanadium(IV) compounds which exhibit rhombic spectra. The g_z value of 2.00 for $(\pi-C_5H_5)_2VCl_2$ results from the molecule having essentially a d_{z^2} ground state unlike the other molecules where some d_{z^2} metal orbital character may be mixed in due to low-symmetry components. If vanadium electron spin-nuclear spin hyperfine coupling constants, A, are employed as a measure of metal-ligand covalency, A decreasing with increasing covalency, it is noted that the Schiff-base complex[31] $VO(mesalim)_2$ and $VO(quin)_2$ exhibit comparable covalency. Both complexes contain the $VO(O_2N_2)$ chromophore but it is unlikely that they have

---

(28) C. P. Stewart and A. L. Porte, *J. Chem. Soc., Dalton Trans.*, 1661 (1972).

(29) B. Bleaney, *Phil. Mag.*, 42, 441 (1951).

(30) N. M. Atherton and C. J. Winscom, *Inorg. Chem.*, 12, 383 (1973).

(31) M. A. Hitchman, B. W. Moores, and R. L. Belford, *Inorg. Chem.*, 8, 1817 (1969); see also M. A. Hitchman, C. D. Olson, and R. L. Belford, *J. Chem. Phys.*, 50, 1195 (1969).

very similar structures. This suggests that it is the number and types of atoms bonded to the VO^{2+} ion which primarily determine the metal–ligand covalency rather than the spatial arrangement of ligands.

The A_2 ground state of a vanadyl complex possessing effective C_{2v} symmetry can be expressed by

$$\psi_{A_2} = \alpha|d_{xy}\rangle + \alpha' L \qquad (18)$$

where α and α' are normalized molecular orbital coefficients and L represents appropriate combinations of ligand symmetry orbitals. Proceeding in the conventional manner[31] the following expressions are obtained as good approximations for the g values

$$g_x = 2.002 - \frac{2\alpha^2\gamma^2\zeta}{E_{xz} \leftarrow E_{xy}} \qquad (19)$$

$$g_y = 2.002 - \frac{2\alpha^2\delta^2\zeta}{E_{yz} \leftarrow E_{xy}} \qquad (20)$$

$$g_z = 2.002 - \frac{8\alpha^2\beta^2\zeta}{E_{x^2-y^2} \leftarrow E_{xy}} \qquad (21)$$

where the denominators are the indicated transition energies (reciprocal centimeters), $\alpha^2, \beta^2, \gamma^2$, and δ^2 are metal d_{xy}, $d_{x^2-y^2}$, d_{xz}, and d_{yz} orbital populations, respectively, and ζ is the spin–orbit coupling constant of the vanadium ion in the complex. Since many low-symmetry vanadyl chelates do not exhibit significant in-plane g anisotropy ($g_x - g_y << 0.01$),[31] it was of interest, in view of the g anisotropy observed for $VO(quin)_2$, to see if the above expressions could yield any information on the "d" level sequence. In the calculations summarized in Table VI the spin–orbit coupling constant, ζ, was obtained by fitting g_z to experiment and then evaluating g_x and g_y for various values of the other parameters. As is readily seen the results for both the crystal field and MO models yield the result $g_x > g_y$ and this, along with the other data in Table V, indicates that our g_1 and g_2 and the corresponding A values should be interchanged. In particular, it is noted that the spin–orbit coupling constant evaluated using MO results is anomalously high even though the calculated in-plane g anisotropy is not in terribly bad agreement with experiment. However, the crystal field model results, employing experimental optical data, are in good agreement with experiment as are the crystal field results employing the somewhat idealized C_{2v} symmetry. The data indicate that the d_{xz} level lies above the d_{yz} level in contrast to the MO results on the model complex ion $VOCl_4^{2-}$. The spin–orbit coupling constants found using the crystal field model are in the range expected for vanadyl complexes.[31-33]

Table VI. Comparison of Calculated and Experimental g Values for $VO(quin)_2$

	Crystal field		
	a	*b*	MO[c]
α^2	0.874	1.000	0.846
β^2	0.986	0.978	0.722
γ^2	0.769	1.000	0.823
δ^2	0.854	1.000	0.863
ζ, cm^{-1}	169	174	237
g_x	1.984	1.980	1.976
g_y	1.982	1.976	1.975
$g_x - g_y$	0.002	0.004	0.001

[a] $E_{x^2-y^2} \leftarrow E_{xy} = 17.09$ kK; $E_{xz,yz} \leftarrow E_{xy} = 12.66$ kK; $g_x - g_y$ (exptl) = 0.006. Experimental data and crystal field results for the actual structure of $VO(quin)_2$. [b] $E_{x^2-y^2} \leftarrow E_{xy} = 20.00$ kK; $E_{xz} \leftarrow E_{xy} = 15.73$ kK; $E_{yz} \leftarrow E_{xy} = 13.62$ kK. Results for C_{2v} model (see text). [c] Using experimental data in footnote *a* and d orbital populations for $VOCl_4^{2-}$ (harmonic mean).

The preceding experimental and theoretical results for $VO(quin)_2$ show that the Ballhausen–Gray energy level scheme[8] for vanadyl complexes possessing effective C_{4v} symmetry is only slightly modified upon further reduction of the microsymmetry of vanadyl complexes. This is undoubtedly due to the dominance of the strong axial field of the vanadyl oxygen atom. The separation of the d_{xz} and d_{yz} levels can result in in-plane g anisotropy in low-symmetry vanadyl complexes. In the present study the phenomenological crystal field model was found capable of giving an adequate interpretation of the spectral and magnetic properties of the low-symmetry $VO(quin)_2$ complex.

Acknowledgment. The authors are grateful to Professor Quintus Fernando, University of Arizona, for valuable discussion concerning $VO(quin)_2$.

Registry No. $VO(quin)_2$, 31323-29-2.

(31) C. P. Stewart and A. L. Porte, *J. Chem. Soc., Dalton Trans.*, 722 (1973).

(33) H. G. Hecht and T. S. Johnson, *J. Chem. Phys.*, **46**, 23 (1967).