CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY AND MATERIALS RESEARCH LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

# Electron Paramagnetic Resonance of Vanadyl Ion Doped into a Diamagnetic Chelate. Oxovanadium(IV) in Single Crystals of Bis(N-methylsalicylaldiminato)nickel(II)

BY M. A. HITCHMAN, B. W. MOORES, AND R. L. BELFORD[1]

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Successful attempts to substitute vanadyl ion ($VO^{2+}$) into single crystals of monoclinic ($\beta$) bis(N-methylsalicylaldiminato)-nickel(II) and measure the epr spectrum are reported. The orientations of the principal axes of the **g** and **A** tensors suggest that the guest molecule is tilted with respect to a corresponding substitutional host molecule so as to minimize steric repulsion between the oxygen atom of the vanadyl group and a methyl group of a neighboring molecule. The principal in-plane **g** tensor axes make angles of about 11° with the probable metal–ligand bond directions. The main cause of the in-plane **g** anisotropy seems to be the difference in coordinating ability between the oxygen and nitrogen ligands of the chelate ring, with the oxygen atom being the "stronger" ligand; the deviation of the in-plane $g$ directions from coincidence with the metal–ligand bonds may originate in a slight admixture of the $d_{3z^2-r^2}$ orbital into the ground state. Finally, the epr parameters suggest that, as in most other vanadyl compounds, the MO's involving the $\pi$-type metal orbitals $d_{x^2-y^2}$, $d_{xz}$, and $d_{yz}$ are quite ionic, a result also consistent with the absence of ligand hfs. The $\sigma$-type MO involving $d_{xy}$ is somewhat more covalent.

## Introduction

Epr spectroscopy has proved to be a very useful tool in the investigation of the energy levels and the nature of bonding in transition metal complexes. Two of us have recently described[2] the results of a detailed study of the spectrum of $^{63}Cu$ present as a slight impurity in the orthorhombic ($\alpha$) form of the diamagnetic complex Ni(mesalim)$_2$ (mesalim ≡ N-methylsalicylaldiminate anion). Here we report the results of a similar investigation of the epr spectrum of $VO^{2+}$ doped into single crystals of the monoclinic ($\beta$) form of Ni(mesalim)$_2$. The orientation of the paramagnetic molecules in the host lattice is discussed and the **g** and metal hyperfine tensors are interpreted in terms of the energy levels and bonding parameters of the vanadyl complex.

## Experiments and Data Analysis

**Preparation of Compounds.**—Ni(mesalim)$_2$ was prepared by the method of Klemm and Raddatz[3] and VO(mesalim)$_2$ by the method of Sacconi and Campigli.[4] Ni(mesalim)$_2$ exists in two distinct crystalline modifications: an $\alpha$ form,[5] obtained as long, flat needles from ethanolic solution, and a $\beta$ form,[6] obtained as diamond-shaped crystals from chloroform. The *molecular* structures in the two crystals are nearly identical. We did not find $VO^{2+}$ to substitute to any discernible degree into the lattice of the $\alpha$ form; the probable reason is discussed later. The following results refer to $VO^{2+}$ diluted in crystals of the $\beta$ form, substitution being found possible in this case.

Large diamond-shaped crystals of the substituted complex were obtained by dissolving 1 part (by weight) of VO(mesalim)$_2$ and 50 parts of Ni(mesalim)$_2$ in oxygen-free chloroform and allowing the solution to evaporate slowly at room temperature. Crystals also grew from solutions containing $VO^{2+}$:$Ni^{2+}$ ratios of 1:200 and 1:4, but no difference in the line width or number of lines was observed.

**Measurement of Spectra.**—Spectra were measured at room temperature using a Varian V-4502-12 spectrometer operating at 35 GHz (Q band); spectra measured at 80°K were identical with those obtained at room temperature. The magnetic field intensity was read from a Varian Fieldial accessory. The crystals were mounted by placing them upon a well-developed face on a quartz rod and screwing this into the cavity. The direction of the magnetic field was varied by rotating the magnet, and the crystal orientation was determined with an X-ray precession camera. Powdered DPPH was used as a reference in the determination of the $g$ values, the $g$ value of the radical being taken as 2.0036.

**The Spectra.**—The $\beta$ form of Ni(mesalim)$_2$ belongs to the space group $P2_1/c$ and crystallizes with the (100) face well developed.[6] Spectra were measured with the magnetic field rotating in the (100), (010), and (001) crystallographic planes. Two sets of eight lines were observed for the (100) and (001) rotations, due to the interaction of the electron spin with the vanadium nuclear spin of $^7/_2$ for each of the two inequivalent positions in the unit cell. In agreement with the requirements of the space group, only a single set of lines was observed when the magnetic field was along the [010] direction or in the (010) plane. The spectrum with the field along [001] is shown in Figure 1. The observed line width was about 7 G.

**Forbidden Lines.**—When the magnetic field vector was close to the molecular $xy$ plane (see the next section for a precise definition of the $x$ and $y$ axes), several very weak lines were observed in addition to the eight allowed ($\Delta M_I = 0$, $\Delta M_S = \pm 1$) lines associated with each vanadium nucleus (see Figure 1; when the magnetic field is along [001] it makes an angle of about 10° with the $xy$ plane). These weak lines occurred in pairs between adjacent allowed lines; they clearly mark transitions in which $\Delta M_I = \pm 1$, $\Delta M_S = \pm 1$. Fourteen such transitions are possible; they are forbidden to first order but can gain intensity through both the vanadium nuclear quadrupole interaction and the vanadium nuclear Zeeman interaction. The latter mechanism certainly is required in this case, since the lines appearing between the middle two allowed lines are among the more intense of the forbidden transitions and the nuclear quadrupole interaction does not contribute to the intensity of these lines. (We note that some success is being obtained by H.-S. So and R. L. Belford in quantitatively accounting for similar "forbidden" lines by concerted action of both mechanisms in some re-

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[1] Work supported by Advanced Research Projects Agency Grant SD-131, assisted by a National Science Foundation grant.

[2] B. W. Moores and R. L. Belford, Paper No. S106, Division of Physical Chemistry, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 2, 1968. Also B. W. Moores, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1968.

[3] W. Klemm and K.-H. Raddatz, *Z. Anorg. Allgem. Chem.*, **250**, 207 (1942).

[4] L. Sacconi and U. Campigli, *Inorg. Chem.*, **5**, 606 (1966).

[5] M. R. Fox and E. C. Lingafelter, *Acta Cryst.*, **22**, 943 (1967).

[6] E. Frasson, C. Panattoni, and L. Sacconi, *J. Phys. Chem.*, **63**, 1908 (1959).

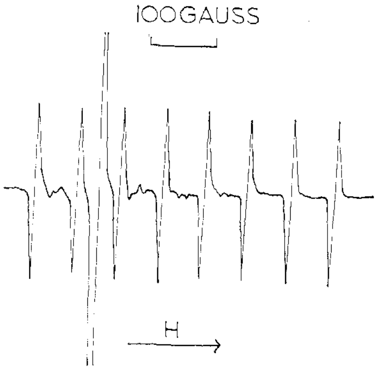

Figure 1.—Typical epr spectrum (derivative curve) of β-Ni(mesalim)$_2$ with dilute VO$^{2+}$ impurity, at 3.5 × 10$^{10}$ Hz. The large line is DPPH. The magnetic field is aligned along the crystallographic $c$ axis, about 10° from the molecular $xy$ plane.

lated systems. It is possible to extract accurate quadrupole coupling information from the behavior of these lines; details will be reported later.)

## Calculation of $g$ and $A$ Values

The method used to calculate the principal values and orientations of the **g** and **A** tensors has been described in detail elsewhere.[7] In brief, a least-squares computer analysis of the measured values of $g^2$ and $g^2K^2$ gave the tensors $\mathbf{g}^2$ and $\mathbf{g}^2\mathbf{K}^2$ in terms of an arbitrarily defined coordinate system. These tensors were then diagonalized by unitary transformations to yield the principal $g$ and $A$ values and the Euler angles relating the principal **g** and **A** directions to the arbitrary coordinate system, which is illustrated in Figure 2. The $y$ axis is defined by the vector from the nickel atom to the midpoint of the oxygen and nitrogen atoms of one chelate ring, with the $x$ axis at right angles to this and in the plane of these three atoms. The vanadyl complex probably has a square-pyramidal structure; our coordinate system for this compound is similar to that of the nickel complex, with the $z$ axis along the vanadyl group but with the chelate donor atoms lowered slightly out of the $xy$ plane in this case.

In order to minimize the errors inherent in the mounting of the crystals, we used two independent sets of data from the rotations in the (100) and (001) planes and four independent sets of data in the (010) plane. A total of 76 separate measurements were analyzed. The principal $g$ and $A$ values and the calculated Euler angles relating molecular axes to $g$ and $A$ axes are listed in Table I. The directions of the in-plane $g$ and $A$ values are illustrated in Figure 2 (the tilt out of the $xy$ plane has been ignored).

The in-plane $g$ and $A$ values could be obtained with unusual accuracy because the (010) crystallographic plane almost coincides with the molecular $xy$ plane, and for the rotation of the magnetic vector in the (010) plane any slight misalignment of the crystal produced sixteen rather than eight lines.

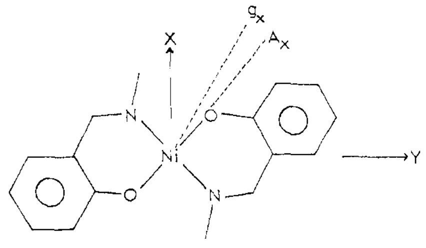

Figure 2.—Diagram illustrating the coordinate system defined for Ni(mesalim)$_2$ (the $z$ axis is orthogonal to $x$ and $y$) and the directions found for $g_x$ and $A_x$ (neglecting the tilt of these out of the $xy$ plane, *i.e.*, neglecting $\Omega_2$ in Table I).

Table I

Principal $g$ and $A$ Values for Vanadyl Ion Substituted into Ni(mesalim)$_2$, with the Euler Angles Relating the $g$ and $A$ Directions to the Chosen Coordinate System

| | $x$ | $y$ | $z$ | Rms error |
|---|---|---|---|---|
| $g$ | 1.9842 | 1.9796 | 1.9543 | 0.0004 |
| $10^4A$, cm$^{-1}$ | (−)59.7 | (−)48.4 | (−)156.3 | 1.0 |

| | $\Omega_1$,[a] deg | $\Omega_2$, deg | $\Omega_3$, deg |
|---|---|---|---|
| For $g$ | 67.9 ± 1.0 | 11.5 ± 0.5 | −34.0 ± 1.0 |
| For $A$ | 107.0 ± 1.0 | 9.7 ± 0.5 | −64.4 ± 1.0 |

[a] The Euler angles are defined as follows: to convert the molecular axes into the $g$ or $A$ axes rotate about $z$ by $\Omega_1$ to give $x'y'z$, about $x'$ by $\Omega_2$ to give $x'y''z'$, and then by $\Omega_3$ about $z'$ to give $x''y''z'$, with each rotation being counterclockwise to an observer in the positive octant. The errors in the angles were estimated by calculating g and A from independent sets of data and comparing the resulting Euler angles.

## Interpretation of $g$ and $A$ Values

**Orientation of the Vanadyl Complex in the Lattice.**—In order to deduce the orientation of the vanadyl complex in the host lattice we must first consider the probable position of the principal axes of the **g** and **A** tensors in the vanadyl chelate. It is highly probable that $g_z$ and $A_z$ coincide closely with the vanadium–oxygen bond of the vanadyl group. However, in a low-symmetry complex such as VO(mesalim)$_2$ it is not possible to predict the directions of the in-plane $g$ and $A$ directions. Inspection of the Euler angles (Table I) shows that $g_z$ and $A_z$, and therefore the V–O vanadyl bond direction, are tilted by ~10.5° away from the $z$ axis defined for Ni(mesalim)$_2$. The nickel atom in β-Ni(mesalim)$_2$ lies on a center of inversion, and its nearest intermolecular contact is with a methyl group 3.4 Å away and positioned approximately over the chelate oxygen atom.[6] The observed rotation of $g_z$ and $A_z$ is directed away from these neighboring methyl groups. It therefore seems likely that on substitution of a molecule of the vanadyl complex, this molecule is tilted relative to a corresponding host molecule so as to lessen the steric interference between the neighboring methyl group and the oxygen of the vanadyl group. If the vanadium atom occupied the exact position of a nickel atom, with the vanadium–oxygen bond of the vanadyl group along the $z$ axis defined for the nickel chelate, the distance from the vanadyl oxygen atom to the neighboring methyl group would be about 2.3 Å, rather less than the sum of their van der Waals radii (about 3.4 Å). Indeed, it is surprising that the five-coordinate vanadyl complex can substitute

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(7) M. A. Hitchman and R. L. Belford, paper presented at the Symposium on Esr of Metal Chelates, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 3, 1968; published in "Electron Spin Resonance of Metal Complexes," T. F. Yen, Ed., Plenum Press, New York, N. Y., 1969, Chapter 7, p 97.

at all into a lattice of large, well-packed planar molecules.

It should be noted that in $\alpha$-Ni(mesalim)$_2$, in which no discernible vanadyl substitution occurred, the molecules are stacked one upon another in infinite chains, with a Ni–Ni distance of only 3.29 Å. It seems likely that vanadyl substitution does not occur in the $\alpha$ form because it would produce too much steric interference between the oxygen atom of the vanadyl group and a neighboring nickel atom.

Although we cannot be certain of it, since we cannot be certain of the directions of the principal $g_\perp$ and $A_\perp$ axes in the vanadyl chelate, it is probable that vanadyl substitution occurs without any significant rotation in the $xy$ plane. There seem to be no *obvious* steric reasons for such a rotation to occur. The most compelling evidence—though unfortunately not proof—is that the principal $A_\perp$ directions lie almost exactly along the Ni–O and Ni–N bonds (if we neglect the rotation out of the $xy$ plane). In the corresponding copper-doped crystal,[2] where substitution would occur without reorientation, we found the principal hyperfine directions to lie very close to the Ni–O and Ni–N bonds, although, as in the vanadyl complex, $g_x$ and $g_y$ were rotated somewhat from them.

**Energy Levels and Bonding Parameters.**—The methods by which $g$ and $A$ values are related to the energy levels and bonding parameters in transition metal complexes are by now well established.[8] In a complex such as VO(mesalim)$_2$, the ligand field can be considered as a strong $C_{4v}$ component with perturbations lowering the symmetry to $C_2$. The main effect of the low-symmetry perturbations is to introduce in-plane anisotropy into the **g** and **A** tensors. A treatment of the in-plane $g$ values of vanadyl complexes of $C_2$ symmetry has been given elsewhere,[9] but the relevant equations are complicated. For purposes of estimating approximate bonding parameters, a reasonable way to begin handling the epr data of a $C_2$ complex is to treat it in $C_{4v}$ symmetry and to use average $g_\perp$ and $A_\perp$ values.

In a $C_{4v}$ complex of this kind, if the *effective* charge on the metal ion is known, the $g$ and $A$ values depend to a good approximation only on the relative energies of certain of the excited electronic states and the coefficients of the d orbitals in the appropriate molecular orbitals. Therefore, if the excited-state energies can be estimated from the electronic spectrum of the complex, the MO coefficients can be estimated from the equations[8,10]

$$\Delta g_z = \frac{8\alpha^2\beta^2\xi}{\Delta E_{xy}} \qquad \text{(1a)}$$

$$\Delta g_y = \frac{2\alpha^2\gamma^2\xi}{\Delta E_{xz}} \qquad \text{(1b)}$$

$$\Delta g_x = \frac{2\alpha^2\delta^2\xi}{\Delta E_{yz}} \qquad \text{(1c)}$$

$$A_z = -P\left(\varkappa + \frac{4\alpha^2}{7} + \frac{3\Delta g_y}{14} + \frac{3\Delta g_x}{14} + \Delta g_z\right) \qquad \text{(1d)}$$

$$A_x = -P\left(\varkappa - \frac{2\alpha^2}{7} + \Delta g_x - \frac{3\Delta g_y}{14}\right) \qquad \text{(1e)}$$

$$A_y = -P\left(\varkappa - \frac{2\alpha^2}{7} + \Delta g_y - \frac{3\Delta g_x}{14}\right) \qquad \text{(1f)}$$

where $\Delta g_z = 2.0023 - g_z$, $\Delta g_y = 2.0023 - g_y$, and $\Delta g_x = 2.0023 - g_x$; $\alpha^2$, $\beta^2$, $\gamma^2$, and $\delta^2$ are the fractional contributions of $d_{x^2-y^2}$, $d_{xy}$, $d_{xz}$, and $d_{yz}$ orbitals, respectively, to the antibonding ligand field MO's; $\xi$ is the spin–orbit coupling constant of the vanadium ion in the complex; $\varkappa$ is the isotropic hyperfine constant in the complex; and $P$ is given by $P = 2.0023 g_N \beta_e \beta_N \langle r^{-3} \rangle$.

We note here that eq 1a–1f are derived from a zero-overlap model and that the general effect of this approximation will be to make the computed values of $\alpha^2$ a bit too large and, consequently, those of $\beta^2$, $\gamma^2$, and $\delta^2$ a bit too small for given values of $P$ and $\xi$. However, in view of the arbitrariness in choice of $P$ and $\xi$ as well as the considerable uncertainty in the values of $\Delta E_{xy}$, $\Delta E_{xz}$, and $\Delta E_{yz}$, it appears futile to attempt a correction from the zero-overlap model.

If we take $\xi = 18200P - 56$ cm$^{-1}$ as we have previously done for VO(benzac)$_2$,[10] the computed values of $\beta^2$ and $\gamma^2 = \delta^2$ are not very sensitive to the choice of $P$; they are considerably smaller than the corresponding parameters for VO(benzac)$_2$ and indicate that a smaller value of $P$ (corresponding to a lower metal ion charge) probably ought to be used in this case. The choice of the parameters is distressingly arbitrary, but the general conclusions are not really seriously affected by reasonable variations of the parameters.

Sacconi and Campigli[4] have measured the electronic spectrum of VO(mesalim)$_2$ in solution and in a mull. In both cases they reported band maxima at 11.90, 16.65, and 18.30 kK, which they assigned to $d_{x^2-y^2} \rightarrow d_{xz}, d_{yz}$; $d_{x^2-y^2} \rightarrow d_{xy}$; and $d_{x^2-y^2} \rightarrow d_{3z^2-r^2}$, respectively, in our coordinate system. These assignments (which it must be realized are not firmly established), together with the approximations $g_x = g_y = {}^1/_2(g_x + g_y)$ and $A_x = A_y = {}^1/_2(A_x + A_y)$, inserted into eq 1, result in the following metal orbital populations: $\alpha^2 = 0.98$, $\beta^2 = 0.66$, $\gamma^2 = \delta^2 = 0.80$, and $\varkappa = 0.73$, if $P = 0.0116$ cm$^{-1}$ ($\xi = 155$ cm$^{-1}$), corresponding to V$^{1.4+}$, d$^{3.6}$.

These values are generally reasonable in comparison with those for VO(benzac)$_2$ (benzac = CH$_3$COCHCO-C$_6$H$_5$) substituted into the Pd(benzac)$_2$[10] lattice: $\alpha^2 = 0.92$, $\beta^2 = 0.80$, $\gamma^2 = 0.96$, $\varkappa = 0.75$ if $P = 0.0123$ cm$^{-1}$ ($\xi = 168$ cm$^{-1}$), corresponding to V$^{1.7+}$, d$^{3.3}$. (An alternate set of values for $\varkappa = 0.73$, $P = 0.0125$ cm$^{-1}$ is: $\alpha^2 = 0.90$, $\beta^2 = 0.80$, $\gamma^2 = 0.96$.) The principal differences are these: (1) The $x^2 - y^2$ orbital is quite ionic in both cases but appears to be more so in the mesalim chelate. This may reflect nonavailability of nitrogen orbitals for in-plane $\pi$ bonding. (2) The covalency of the $xy$ molecular orbital relative to the $\pi(xz, yz)$ molecular orbitals is the same in both chelates. This conclusion is independent of the values of $P$ and $\xi$ and re-

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(8) See the review by B. R. McGarvey, *Transition Metal Chem.*, **3**, 89 (1966).

(9) M. A. Hitchman, C. D. Olson, and R. L. Belford, *J. Chem. Phys.*, **50**, 1195 (1969).

(10) M. A. Hitchman and R. L. Belford, *Inorg. Chem.*, **8**, 958 (1969).

sults from the fact that for the change VO(benzac)$_2$ → VO(mesalim)$_2$ the large decrease in $\Delta E_{xz}$ ($14.5 \rightarrow 11.9$) is accompanied by a comparable decrease in $\Delta g_z$ ($0.0615 \rightarrow 0.0480$). (3) The metal bonding is generally more covalent in VO(mesalim)$_2$ than in VO(benzac)$_2$.

**The In-Plane $g$ and $A$ Anisotropy.**—The ligand field symmetry in VO(mesalim)$_2$ can be considered as predominantly $C_{4v}$ with an added along-the-bonds perturbation due to the inequivalence of the nitrogen and oxygen atoms and a between-the-bonds perturbation due to the chelate rings. A detailed discussion of in-plane $g$ and $A$ values and orientations has been given already;[9] we only remark here that two factors largely determine them: (1) the difference in energy and/or orbital coefficients between the $d_{xz}$ and $d_{yz}$ orbitals and (2) the mixing into the ground state of a small amount of $d_{3z^2-r^2}$. The excited-state energies and orbital coefficients will be affected by both the chelate ring perturbation and the difference in coordinating ability of the oxygen and nitrogen. However, the $d_{3z^2-r^2}$ mixing is only caused by the perturbation acting on the *ground-state* orbital, that is, in this case, only by the chelate effect. Also, the $d_{3z^2-r^2}$ mixing always tends to give principal $g_\perp$ directions lying along the directions of the ground-state orbital lobes, that is, along the $x$ and $y$ axes as they are defined here, while the $d_{xz}$ and $d_{yz}$ energy or coefficient differences can give principal $g_\perp$ directions anywhere in the $xy$ plane, depending on the precise nature of the ligand perturbations. Thus, if the principal $g_\perp$ directions lie along the ground-state lobe directions, it is quite likely that $d_{3z^2-r^2}$ is important in producing the $g_\perp$ anisotropy, while if the principal $g_\perp$ directions lie along the *nodes* of the ground-state orbital, then $d_{3z^2-r^2}$ does not contribute to the $g_\perp$ anisotropy, and it is likely (though not certain[9]) that the $g_\perp$ anisotropy can be interpreted solely in terms of the mixing of the $d_{xz}$ and $d_{yz}$ orbitals into the ground state.

For VO(mesalim)$_2$ the Euler angles suggest that the principal $g_\perp$ directions lie fairly close to the ground-state orbital nodes, being rotated from these nodes or from the metal–ligand bonds by ~11°. It therefore seems likely that the main perturbation on the $C_{4v}$ ligand field is caused by the inequivalence of the nitrogen and oxygen atoms with a much smaller perturbation due to the chelate ring effect, which introduces a slight admixture of $d_{3z^2-r^2}$ into the ground state and consequently produces a small rotation of the principal $g_\perp$ directions toward the $x$ and $y$ axes.[9]

If we neglect the $d_{3z^2-r^2}$ mixing and assume $\gamma^2 = \delta^2$, then, by eq 1b and 1c, the $g_\perp$ values indicate energies of $\Delta E_{xz} = 10.7$ kK and $\Delta E_{yz} = 13.4$ kK, where the $d_{xz}$ orbital is near the plane formed by the $g_y$ and $g_z$ directions (*i.e.*, nearer to the nitrogen atoms). However, a 2.7-kK difference is rather large; other factors, such as a difference between $\gamma^2$ and $\delta^2$, probably contribute significantly to the $g_\perp$ anisotropy. For example, $\gamma^2 = 0.84$, $\Delta E_{xz} = 11.2$ kk and $\delta^2 = 0.76$, $\Delta E_{yz} = 12.7$ kK fit the data.

The results $\Delta E_{yz} > \Delta E_{xz}$ and/or $\gamma^2 > \delta^2$ suggest that the oxygen atom is a "stronger" ligand than the nitrogen. It is noteworthy that for Cu(mesalim)$_2$,[2,9] in which the directions of the principal $g_\perp$ values also lie approximately along the metal–ligand bonds, there is a significant difference between the Cu–O (1.901 Å) and Cu–N (1.989 Å) bond lengths. Since one might reasonably suggest that the $g_\perp$ directions are largely determined by this difference, it is unfortunate that the corresponding bond lengths are not known for VO(mesalim)$_2$.

In Cu(mesalim)$_2$, hyperfine structure was observed from several ligand nuclei, but none was found in the vanadyl chelate. The absence of ligand hfs signifies that the nitrogen's contribution to the ground-state orbital is very small, as one expects for a largely ionic $d_{x^2-y^2}$ orbital slightly mixed with oxygen ps$^n$ ($n \ll 1$) orbitals. Ligand hfs is, indeed, seldom observed in epr spectra of vanadyl complexes.[10] However, the large (~7 G) line width in this compound suggests broadening by unresolved nitrogen and proton hfs.

**Acknowledgment.**—We thank Charles D. Olson for his generous assistance.