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Crystallographic Study of the Structural Trans Effect. Molecular Structure of Oxoisopropoxobis(8-hydroxyquinolinato)vanadium(V)

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The quantitative stereochemical description of oxoisopropoxobis(8-hydroxyquinolinato)vanadium(V) comes from the determination by X-ray analysis of the atomic arrangement of the crystalline complex. The VO(O-*i*-Pr) group is in the cis configuration with an O–V–O angle of 101.9 (1)°; the V–O distances are 1.600 (1) and 1.774 (2) Å to the oxo and isopropoxo ligands, respectively. The two V–N complexing bonds are significantly different. The V–N bond trans to the oxo ligand is 2.317 (2) Å; the V–N bond trans to the isopropoxo ligand is 2.209 (3) Å. Two oxygen atoms of the 8-hydroxyquinolinato ligands, with V–O = 1.902 (2) and 1.925 (2) Å, complete the octahedral coordination group. The triclinic unit cell utilizes the space group $P\bar{1}$ with $a = 12.909$ (8), $b = 9.760$ (7), $c = 9.072$ (7) Å and $\alpha = 112.37$ (3), $\beta = 93.30$ (3), $\gamma = 109.87$ (3)°. An experimental density of 1.39 g/cm^3 compares favorably with a calculated density of 1.417 g/cm^3 for a cell content of 2 $VN_2O_4C_{21}H_{19}$. The intensities of all independent reflections having $(\sin\theta)/\lambda \leq 0.602$ Å^{-1} were measured with Mo Kα radiation by θ–2θ scanning on a computer-controlled four-circle diffractometer; the 3317 data retained as statistically observable were employed for structure determination and refinement by Patterson and least-squares techniques to a conventional R of 0.043.

Previous studies of the stereochemistry of mononuclear vanadium(V) complexes[2] utilized the oxalato and ethylenediaminetetraacetato (EDTA) chelates containing the dioxovanadium(V) cation, VO_2^+. A consistent stereochemical pattern for the dioxovanadium(V) complexes emerged from these studies. The configuration assumed by the VO_2^+ ion was found to be bent with two equivalent V–O bonds and an OVO angle that ranges from 104 to 107°. All three complexes utilize irregular octahedral coordination groups; the two donor atoms positioned opposite the oxo ligands in the coordination group are at abnormally long distances. The structural trans effect in these V(V) complexes is most clearly seen in the oxalato complex[2a] wherein the four complexing bonds to the oxalato oxygen atoms divide into two distinctive pairs accordingly as the position occupied by oxalato oxygen is cis to both oxo ligands or is trans to one and cis to the other. The V–O bond lengths in the first pair average to 1.980 Å; those in the second pair are 0.23 Å longer. Similar structural trans effects can be noted for many other oxometal complexes in which the metal ion has a high formal oxidation state. The usual preference of the vanadyl complexes for square-pyramidal five-coordination of the vanadium(IV) atom with no ligand trans to the oxo oxygen represents the extreme case of the structural trans effect. Other notable examples include $[MoO_2(acac)_2]$,[3a] the $[VO(C_2O_4)_2H_2O]^{2-}$ ion,[3b] and dioxobis(8-hydroxyquinolinato)molybdenum(VI)[3c] wherein the complexing bond trans to an oxo ligand is ≥0.1 Å longer than normal. It was suggested[2a] that through a synergistic mechanism the π bonding to the oxo oxygen atoms induced a strengthening of the σ bonding to the oxo ligands at the expense of the σ bonding of the ligands at the trans positions. The structural trans effect for platinum(II) complexes has been related to the ligand–metal σ overlap as $S^2/\Delta E$ where S is the overlap integral between the orbitals forming the bond and ΔE the energy separation between the orbitals being mixed.[4]

Because of our interest in the structural trans effect, we have determined and report herein the molecular structure of oxoisopropoxobis(8-hydroxyquinolinato)vanadium(V) (written as VO(O-*i*-Pr)(oxine)$_2$), a derivative of the $VO(OH)^{2+}$ cation. Several features of the molecular structure of this complex can be anticipated from the structures of the analogous VO_2^+ complexes. The VO(O-*i*-Pr) entity should have a cis configuration and the nitrogen atoms of the oxine ligands should be trans to one oxygen atom of the VO(O-*i*-PR) group and cis to the other. Furthermore, if the structural trans effect in oxometal complexes results from a synergistic strengthening of the σ bonding (and overlap) of the oxo ligand owing to its π-bonding properties, the V–N bond trans to the oxo ligand should be lengthened relative to the V–N bond trans to the weaker π-bonding isopropoxo ligand.

Experimental Section

VO(O-*i*-Pr)(oxine)$_2$ was prepared from VO(OH)(oxine)$_2$ (Eastman Kodak Co.) by the method of Blair, *et al.*[5] Crystals suitable for X-ray analysis were obtained by slow evaporation of isopropyl alcohol solutions of the complex. Preliminary X-ray photographic study established a two-molecule unit cell with $P1$ or $P\bar{1}$ as the space group. A crystal with approximate dimensions of 0.35 × 0.25 × 0.30 mm was cut from a larger crystal and used for the collection of intensity data. Lattice constants, $a = 12.909$ (8), $b = 9.760$ (7), $c = 9.072$ (7) Å and $\alpha = 112.37$ (3), $\beta = 93.30$ (3), and $\gamma = 109.87$ (3)° (20°, λ 0.71069 Å), came from a least-squares refinement that utilized the setting angles of 17 reflections with $2\theta \geq 30°$ given by the automatic centering routine supplied with the diffractometer. These constants led to a calculated density at 20 ± 1° of 1.417 g/cm^3 which compares well with the measured density of 1.39 g/cm^3.

Intensity data were measured on a Syntex $P\bar{1}$ diffractometer using the θ–2θ scanning technique with Zr-filtered radiation at a takeoff angle of ~4°. The range of each scan consisted of the base width of 1.6° at $2\theta = 0°$ and an increment, $\Delta(2\theta) = 0.692 \tan\theta°$, to allow for spectral dispersion; background counts were taken at the extremes of the scan for a time equal to the time required for the scan itself. A variable-2θ scan rate was used; the slowest was 0.5°/min; the fastest was 12.0°/min. The slowest scan rate was used for reflections with intensities less than 75 cps at the Kα_1 peak center; the fastest scan rate was used for reflections having intensities greater than 750 cps at the Kα_1 peak center. Intermediate scan

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[1] The Radiation Laboratory is operated by the University of Notre Dame, under contract with the Atomic Energy Commission. This is AEC Document No. C00-38879.

[2] (a) W. R. Scheidt, C. C. Tsai, and J. L. Hoard, *J. Amer. Chem. Soc.*, 93, 3867 (1971); (b) W. R. Scheidt, D. M. Collins, and J. L. Hoard, *ibid.*, 93, 3873 (1971); (c) W. R. Scheidt, R. Countryman, and J. L. Hoard, *ibid.*, 93, 3878 (1971).

[3] (a) B. M. Craven, K. C. Ramey, and W. B. Wise, *Inorg. Chem.*, **10**, 2626 (1971); (b) G. E. Form, E. S. Raper, R. E. Oughtred, and H. M. M. Shearer, *J. Chem. Soc., Chem. Commun.*, 945 (1972); (c) L. O. Atovmyan and Yu A. Sokolova, *Chem. Commun.*, 649 (1969).

[4] R. McWeeny, R. Mason, and A. D. C. Towl, *Discuss. Faraday Soc.*, 47, 20 (1969).

[5] A. J. Blair, D. A. Pantony, and G. J. Minkoff, *J. Inorg. Nucl. Chem.*, 5, 316 (1958).

rates were selected automatically by the control program based on a linear interpolation of the above limits. Three standard reflections that were well distributed in reciprocal space were used for periodic (every 50 reflections) checking on the alignment and possible deterioration of the crystal; no variation with time was noted. All independent data having $(\sin \theta)/\lambda \leqslant 0.602$ Å^{-1} were thus measured.

With the cited dimensions of the crystal and a linear absorption coefficient of 0.57 mm^{-1} for Mo Kα radiation, the maximum error in any structure amplitude resulting from the neglect of absorption corrections was seen to be <3%. Consequently, the net intensities were reduced directly to a set of relative squared amplitudes, $|F_o|^2$, by application of the standard Lorentz and polarization factor (Lp). Standard deviations were calculated from

$$\sigma(F_o)^2 = [\mathrm{Ct} + k^2B + p^2(\mathrm{Ct} - kB)^2]/4|F_o|^2(\mathrm{Lp})^2$$

where Ct is the count of the scan, k is the ratio of scanning time to background counting time, B is the total background count, and the value of p was chosen as 0.04. All data having $F_o < 3\sigma F_o$ were taken to be unobserved, leaving 3317 independent data for the determination and refinement of structure (92% of the theoretical number possible).

The initial choice of the centrosymmetric space group $P\bar{1}$[6] was suggested by the negative result of tests for piezoelectricity and by all subsequent developments during the determination of structure. A three-dimensional Patterson synthesis gave trial positions for the vanadium atom; the positions of the remaining atoms were developed from Fourier syntheses with initial phasing based on the contribution of the vanadium atom to the structure amplitudes. Block-diagonal least-squares refinement[7] of the coordinates and isotropic thermal parameters using all independent data was followed by a difference Fourier synthesis which showed electron density concentrations appropriately located for all hydrogen atom positions. The hydrogen atom contributions were subsequently included in the least-squares minimization with fixed positional parameters and isotropic thermal parameters fixed one unit higher than that of its associated atom; this minimization was then carried to convergence using anisotropic thermal parameters for all other atoms. A final cycle of full-matrix least-squares refinement[8] was carried out varying only the coordinates of the heavy atoms; the output of this cycle was used to obtain the elements of the inverse matrix for the calculation of standard deviations. Empirical weights ($w = 1/\sigma^2$) were used in the later stages of refinement and were calculated from $\sigma = \Sigma_{n=0}{}^3 a_n |F_o|^n$, the a_n's being the coefficients from the least-squares fitting of the curve $||F_o| - |F_c|| = \Sigma_{n=0}{}^3 a_n |F_o|^n$; the values of $|F_c|$ came from a sensibly final description of the structure. The final value of $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ was 0.043; that of $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o{}^2)]^{1/2}$ was 0.064. The estimated standard deviation of an observation of unit weight was 1.28. The final parameter shifts were less than 10% of their estimated standard deviations during the last cycle. A final difference Fourier synthesis was judged to be free of significant features; the largest peak had a height of 0.6 e/A^3, about 10% of that of a carbon atom, and was apparently associated with the anisotropic scattering from the valence-shell electrons of the vanadium atom.

Atomic coordinates and the associated anisotropic thermal parameters in the asymmetric unit of structure are listed in Tables I and II, respectively.[9]

Discussion

The vanadium atom of the complex molecule (Figure 1)[10] is octahedrally complexed to the oxo ligand, the isopropoxo ligand, and the two nitrogen atoms and the two oxygen atoms of the oxine ligand. As expected, the two nitrogen atoms are coordinated trans to the oxo and isopropoxo ligands. The geometry of the octahedral coordination group is strikingly similar to the coordination groups in the $VO_2{}^+$ complexes.[2] Examination of Figure 1 along with the listing in Table III of the atomic displacements from the three principal coordinate planes of the octahedron shows that the vanadium atom is displaced by ~0.33 Å from the octahedral center toward the oxygen atoms of the oxo and iso-

Table I. Atomic Coordinates in Crystalline VO(O-*i*-Pr)(oxine)$_2$[a]

Atom	10^4x	10^4y	10^4z
O_1	1228 (2)	2192 (2)	4731 (2)
O_2	3041 (2)	4817 (2)	6606 (2)
O_{11}	3318 (1)	2787 (2)	3710 (2)
O_{21}	1313 (1)	4823 (2)	4607 (2)
N_{11}	1587 (2)	2564 (2)	1911 (2)
N_{21}	3341 (2)	5756 (2)	4011 (2)
C_1	2657 (3)	4749 (4)	8045 (3)
C_2	2154 (5)	6008 (7)	8727 (5)
C_3	3577 (4)	4912 (2)	9219 (4)
C_{11}	3219 (2)	2050 (3)	2107 (3)
C_{12}	3983 (3)	1474 (4)	1379 (4)
C_{13}	3760 (4)	655 (5)	−340 (5)
C_{14}	2815 (4)	416 (4)	−1340 (4)
C_{15}	2032 (3)	1036 (3)	−627 (3)
C_{16}	1011 (3)	935 (4)	−1473 (4)
C_{17}	354 (3)	1618 (4)	−646 (4)
C_{18}	659 (2)	2462 (4)	1072 (4)
C_{19}	2254 (2)	1863 (3)	1087 (3)
C_{21}	1658 (2)	6156 (3)	4348 (3)
C_{22}	1006 (2)	7023 (3)	4390 (3)
C_{23}	1427 (3)	8416 (3)	4107 (3)
C_{24}	2481 (3)	8932 (3)	3768 (3)
C_{25}	3168 (2)	8057 (3)	3708 (3)
C_{26}	4265 (3)	8450 (3)	3398 (3)
C_{27}	4868 (2)	7548 (3)	3451 (4)
C_{28}	4377 (2)	6193 (3)	3749 (3)
C_{29}	2749 (2)	6675 (3)	4014 (3)
Atom	10^5x	10^5y	10^5z
V	22,387 (3)	36,605 (4)	45,741 (5)

[a] Figures in parentheses are the estimated standard deviations in the last significant figure.

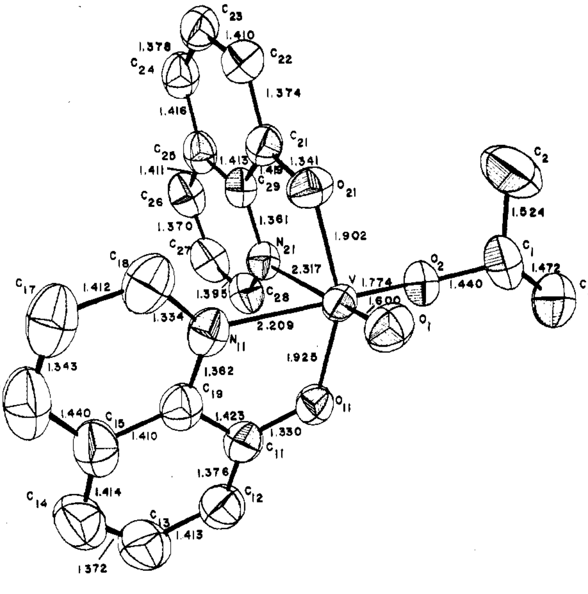

Figure 1. Model in perspective of the complex molecule carrying the pertinent bond distances (Å). Atoms are represented as ellipsoids having the shapes and relative sizes concomitant with the data in Table II.

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(6) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1965, p 75.

(7) The program REFINE, written by J. J. Park at Cornell University, was used. Atomic form factors were from D. T. Cromer and J. L. Mann, *Acta Crystallogr., Sect. A*, 24, 321 (1968), with real and imaginary corrections for anomalous dispersion in the form factor of the vanadium atom from D. T. Cromer, *Acta Crystallogr.*, 18, 17 (1965).

(8) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, a Fortran Crystallographic Least-Squares Program," Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(9) A table of the 3317 observed and calculated amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-1758.

(10) C. K. Johnson, "ORTEP, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

Table II. Thermal Parameters[a]

Atom type	Anisotropic parameters, Å^2						B,[b] Å^2
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	
V	3.07 (2)	3.28 (2)	3.12 (2)	1.40 (1)	0.76 (1)	1.79 (1)	2.93
O_1	4.3 (1)	4.0 (1)	5.1 (1)	1.6 (1)	1.2 (1)	2.6 (1)	4.2
O_2	4.6 (1)	4.8 (1)	3.2 (1)	1.7 (1)	0.8 (1)	1.8 (1)	4.1
C_1	6.3 (2)	6.2 (1)	3.7 (1)	2.0 (1)	1.7 (1)	2.2 (1)	5.1
C_2	11.7 (3)	13.0 (4)	6.1 (2)	8.6 (3)	3.5 (2)	2.7 (2)	8.3
C_3	8.9 (2)	8.3 (2)	4.8 (2)	3.9 (2)	1.2 (2)	3.3 (2)	6.6
O_{11}	4.0 (1)	4.6 (1)	3.6 (1)	2.2 (1)	0.8 (1)	2.0 (1)	3.8
O_{21}	3.4 (1)	4.1 (1)	5.3 (1)	1.8 (1)	1.7 (1)	2.9 (1)	3.7
N_{11}	3.6 (1)	3.9 (1)	3.8 (1)	1.0 (1)	0.2 (1)	1.9 (1)	3.8
N_{21}	3.2 (1)	3.8 (1)	3.1 (1)	1.2 (1)	0.5 (1)	1.6 (1)	3.3
C_{11}	4.4 (1)	3.7 (1)	3.9 (1)	1.7 (1)	1.2 (1)	2.1 (1)	3.8
C_{12}	5.9 (2)	5.7 (1)	5.4 (1)	3.2 (1)	2.4 (1)	2.9 (1)	5.0
C_{13}	8.3 (2)	6.8 (2)	5.9 (2)	4.0 (2)	3.7 (2)	3.0 (1)	6.1
C_{14}	8.4 (2)	5.8 (2)	4.5 (1)	2.7 (2)	2.4 (1)	1.9 (1)	6.0
C_{15}	6.1 (2)	4.2 (1)	3.7 (1)	0.6 (1)	0.6 (1)	1.7 (1)	4.8
C_{16}	6.8 (2)	5.8 (1)	3.9 (1)	0.5 (1)	−0.6 (1)	1.9 (1)	5.7
C_{17}	5.3 (2)	6.8 (2)	4.9 (1)	1.0 (1)	−0.9 (1)	2.7 (1)	5.6
C_{18}	4.0 (1)	5.5 (1)	5.2 (1)	1.3 (1)	−0.2 (1)	2.7 (1)	4.8
C_{19}	4.4 (1)	3.4 (1)	3.8 (1)	0.9 (1)	0.8 (1)	1.9 (1)	3.8
C_{21}	3.8 (1)	3.7 (1)	3.3 (1)	1.5 (1)	0.7 (1)	1.8 (1)	3.5
C_{22}	4.2 (1)	4.5 (1)	4.2 (1)	2.1 (1)	0.9 (1)	2.1 (1)	4.1
C_{23}	6.0 (1)	4.4 (1)	3.8 (1)	2.7 (1)	0.6 (1)	1.9 (1)	4.3
C_{24}	6.5 (2)	3.7 (1)	4.0 (1)	1.8 (1)	0.9 (1)	2.1 (1)	4.4
C_{25}	4.9 (1)	3.3 (1)	3.2 (1)	0.9 (1)	0.6 (1)	1.4 (1)	3.8
C_{26}	5.5 (1)	3.7 (1)	4.4 (1)	0.5 (1)	1.5 (1)	1.9 (1)	4.5
C_{27}	4.0 (1)	4.7 (1)	4.5 (1)	0.4 (1)	1.3 (1)	1.5 (1)	4.7
C_{28}	3.4 (1)	4.6 (1)	3.5 (1)	1.1 (1)	0.6 (1)	1.5 (1)	4.0
C_{29}	3.6 (1)	3.5 (1)	2.7 (1)	1.0 (1)	0.4 (1)	1.4 (1)	3.3

[a] The number in parentheses that follows each B_{ij} value is the estimated standard deviation in the last significant figure. The B_{ij}'s (Å^2) are related to the dimensionless β_{ij}'s employed during refinement as $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$. [b] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/2}$.

Table III. Atomic Displacements from the Three Principal Planes of the Coordination Octahedron

Equations of Planes

Plane I (O_2, O_{11}, O_{21}, N_{11}):[a]

$$0.673X + 0.724Y - 0.148Z = 1.732^b$$

Plane II (O_1, O_{11}, O_{21}, N_{21}):[a]

$$-0.249X + 0.029Y - 0.968Z = -3.853^b$$

Plane III (O_1, O_2, N_{11}, N_{21}):[a]

$$0.705X - 0.686Y - 0.177Z = -0.041^b$$

Atom type	Displacements from mean planes, Å		
	Plane I	Plane II	Plane III
V	0.28	0.22	−0.02
O_1	1.87	0.08	0.10
O_2	0.06	1.98	−0.10
O_{11}	−0.07	−0.07	−1.88
O_{21}	−0.06	−0.08	1.83
N_{11}	0.07	−1.98	−0.09
N_{21}	−2.03	0.08	0.09

[a] The coordinates of these atoms were employed for the determination by a least-squares fitting of the equation of the mean plane. [b] X, Y, and Z are orthogonal coordinates measured in angstroms along ($b \times c^*$), b, and c^*, respectively, of the crystallographic coordinate system.

propoxo ligands or ~0.1 Å less than the displacement of the vanadium atom in the VO_2^+ complexes.[2a]

Table IV is a listing of the complexing bond distances,[11] the octahedral edge lengths, and the angles subtended at the vanadium atom in the complex molecule, VO(O-*i*-Pr)(oxine)$_2$. The coordination group is tightly packed with none of the 12 octahedral edges as long as the sum of the appropriate van der Waals packing radii.[12] The irregularities of the tightly packed coordination group and the displacement of the vanadium atom from the octahedral center account for the markedly nonstandard bond angles listed in Table IV.

The VO(O-*i*-Pr) group has the expected cis configuration with an O_1VO_2 angle of 101.9 (1)°, slightly smaller than the 104–107° range for the cis VO_2 group in the mononuclear complexes[2] and the 103° value found in polymeric $K_2VO_2F_3$.[13] The vanadium oxo oxygen atom complexing link is 1.600 (1) Å, somewhat shorter than the 1.64-Å length typical of the VO_2^+ complexes and in the middle of the range of values (1.57–1.62 Å) reported for the complexing linkage in the vanadyl (VO^{2+}) ion.[3b,14] The complexing bond distance to the isopropoxo ligand is 1.774 (2) Å, comparable to the less precisely determined 1.76-Å average vanadium–methoxy oxygen distance in $VO(OCH_3)_3$.[15] Comparison with the sum of the ionic radii[13] of V^{5+} and O^{2-} (1.99 Å) or the proposed[16] 1.93-Å value for a V–O single-bond distance (in vanadates) suggests some multiple-bond character for this linkage.

As predicted (*vide supra*), the two V–N bond lengths are significantly different. The V–N linkage trans to the oxo ligand is 2.317 (2) Å, slightly shorter than the 2.360-Å average V–N distance found in the $[VO_2EDTA]^{n-}$ (n = 1, 3) complexes[2b,c] with the same coordination geometry. The

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(11) These calculations followed W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program," Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

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Table IV. Parameters of the Coordination Octahedron[a]

A. Bond and Edge Lengths, Å

Type	Length	Type	Length	Type	Length
O_1-O_2	2.623 (3)	O_2-N_{21}	2.836 (3)	$V-O_1$	1.600 (2)
O_1-O_{11}	2.778 (3)	$O_{11}-N_{11}$	2.585 (3)	$V-O_2$	1.774 (2)
O_1-O_{21}	2.603 (3)	$O_{11}-N_{21}$	2.795 (3)	$V-O_{21}$	1.902 (2)
O_1-N_{11}	2.749 (3)	$O_{21}-N_{21}$	2.626 (3)	$V-O_{11}$	1.925 (2)
O_2-O_{11}	2.754 (3)	$O_{21}-N_{11}$	2.738 (3)	$V-N_{11}$	2.209 (3)
O_2-O_{21}	2.796 (3)	$N_{11}-N_{21}$	2.941 (4)	$V-N_{21}$	2.317 (2)

B. Bond Angles Subtended at the V(V) Atom, Deg

Type	Angle	Type	Angle	Type	Angle
O_1VO_2	101.87 (11)	O_2VO_{11}	96.15 (9)	$O_{11}VN_{11}$	77.09 (9)
O_1VO_{11}	103.58 (8)	O_2VO_{21}	98.99 (9)	$O_{11}VN_{21}$	81.85 (9)
O_1VO_{21}	95.62 (10)	O_2VN_{11}	166.67 (8)	$O_{21}VN_{11}$	83.16 (9)
O_1VN_{11}	90.95 (10)	O_2VN_{21}	86.68 (9)	$O_{21}VN_{21}$	76.27 (9)
O_1VN_{21}	169.15 (8)	$O_{11}VO_{21}$	152.49 (8)	$N_{11}VN_{21}$	81.84 (9)

[a] The figures given in parentheses are the estimated standard deviations.

V–N complexing bond trans to the isopropoxo ligand is 2.209 (3) Å; the 0.108-Å difference ($\Delta/\sigma = 32$) is highly significant according to the standard statistical tests.[17] The difference in the bond distances between the short V–N bond and the two V–O single bonds is greater than the ~0.20-Å difference suggested[2b] as appropriate for V–N and V–O single bonds, implying that the isopropoxo ligand still exerts some structural trans influence. In any case, the observed structural trans effects indeed correlate well with the qualitative predictions of the σ-overlap models.

The oxine oxygen-vanadium bond lengths are 1.902 (2) and 1.925 (2) Å, substantially shorter than the average 1.996-Å carboxylate oxygen-vanadium lengths in the oxalato and EDTA complexes of the VO_2^+ ion. This 0.08-Å shortening of the (nominally) V–O single bonds in the VO(O-*i*-Pr)$^{2+}$ complex compared to the VO_2^+ complexes (all of which are d^0 complexes) is most likely a consequence of the increase of the formal charge on the central VO(O-*i*-Pr)$^{2+}$ group. The difference in the length of the two oxine oxygen–vanadium bonds is in large part due to the rigidity of the chelate. This rigidity requires maintaining the fixed bite of the 8-hydroxyquinolinato ligand and nearly constant values for the internal angles of the chelate rings, while simultaneously allowing the two V–N bonds to assume substantially different values; consequently the V–O bond lengths in the chelates must also differ. (*Cf.* Figure 1 and Table V; $O_{11}\cdots N_{11} = 2.585$ Å; $O_{21}\cdots N_{21} = 2.626$ Å.)

Table V lists the parameters of the 8-hydroxyquinolinato ligands; the atoms of ligand 1 carry subscripts 1*n*; those of ligand 2 have subscripts 2*n*. The values listed are typical of those found in other 8-hydroxyquinolinato complexes.[18]

Table V. Bond Parameters of the 8-Hydroxyquinoline Chelates and the Isopropoxo Ligand[a]

A. Bond Lengths, Å

Bond	Length	Bond	Length	Bond	Length
$O_{11}-C_{11}$	1.330 (3)	$C_{17}-C_{18}$	1.412 (5)	$C_{25}-C_{29}$	1.413 (3)
$C_{11}-C_{12}$	1.376 (4)	$C_{18}-N_{11}$	1.334 (3)	$C_{25}-C_{26}$	1.411 (4)
$C_{11}-C_{19}$	1.423 (4)	$C_{19}-N_{11}$	1.362 (3)	$C_{26}-C_{27}$	1.370 (4)
$C_{12}-C_{13}$	1.413 (5)	$O_{21}-C_{21}$	1.341 (3)	$C_{27}-C_{28}$	1.395 (4)
$C_{13}-C_{14}$	1.372 (5)	$C_{21}-C_{22}$	1.374 (4)	$C_{28}-N_{21}$	1.324 (3)
$C_{14}-C_{15}$	1.414 (5)	$C_{21}-C_{29}$	1.419 (3)	$C_{29}-N_{21}$	1.361 (3)
$C_{15}-C_{19}$	1.410 (4)	$C_{22}-C_{23}$	1.410 (4)	C_1-O_2	1.440 (3)
$C_{15}-C_{16}$	1.440 (5)	$C_{23}-C_{24}$	1.378 (5)	C_1-C_2	1.524 (6)
$C_{16}-C_{17}$	1.343 (5)	$C_{24}-C_{25}$	1.416 (4)	C_1-C_3	1.472 (5)

B. Bond Angles, Deg

Type	Value	Type	Value	Type	Value
$VO_{11}C_{11}$	120.6 (2)	$C_{18}N_{11}V$	129.8 (2)	$C_{26}C_{25}C_{29}$	115.5 (2)
$O_{11}C_{11}C_{12}$	124.7 (2)	$C_{19}N_{11}V$	111.1 (2)	$C_{25}C_{26}C_{27}$	120.5 (3)
$O_{11}C_{11}C_{19}$	117.0 (2)	$N_{11}C_{19}C_{11}$	114.2 (2)	$C_{26}C_{27}C_{18}$	119.7 (2)
$C_{12}C_{11}C_{19}$	118.3 (2)	$N_{11}C_{19}C_{15}$	123.8 (3)	$C_{27}C_{28}N_{21}$	121.9 (3)
$C_{11}C_{12}C_{13}$	119.3 (3)	$C_{11}C_{19}C_{15}$	122.1 (3)	$C_{28}N_{21}C_{29}$	118.7 (2)
$C_{12}C_{13}C_{14}$	123.1 (3)	$VO_{21}C_{21}$	122.3 (2)	$C_{28}N_{21}V$	132.9 (2)
$C_{13}C_{14}C_{15}$	118.8 (3)	$O_{21}C_{21}C_{22}$	123.1 (2)	$C_{29}N_{21}V$	108.3 (2)
$C_{14}C_{15}C_{19}$	118.3 (3)	$O_{21}C_{21}C_{29}$	117.6 (2)	$N_{21}C_{29}C_{21}$	115.5 (2)
$C_{14}C_{15}C_{16}$	126.8 (3)	$C_{22}C_{21}C_{29}$	119.4 (2)	$N_{21}C_{29}C_{25}$	123.5 (2)
$C_{16}C_{15}C_{19}$	114.9 (3)	$C_{21}C_{22}C_{23}$	119.9 (2)	$C_{21}C_{29}C_{25}$	121.0 (2)
$C_{15}C_{16}C_{17}$	120.8 (3)	$C_{22}C_{23}C_{24}$	121.6 (2)	VO_2C_1	125.8 (3)
$C_{16}C_{17}C_{18}$	120.5 (3)	$C_{23}C_{24}C_{25}$	119.7 (2)	$O_2C_1C_3$	110.3 (3)
$C_{17}C_{18}N_{11}$	120.9 (2)	$C_{24}C_{25}C_{29}$	118.5 (2)	$O_2C_1C_2$	108.9 (3)
$C_{18}N_{11}C_{19}$	119.1 (2)	$C_{24}C_{25}C_{26}$	126.0 (2)	$C_2C_1C_3$	114.1 (3)

[a] The figures in parentheses are the estimated standard deviations.

No atom of ligand 2 departs by more than 0.02 Å from the mean plane of the ligand. The departures of ligand 1 from the mean plane are somewhat larger (⩽0.05 Å) owing primarily to the deviation of atom O_{11}. The chelate ring of ligand 1 departs from planarity, the consequence of a 2.5° folding along the $O_{11}\cdots N_{11}$ edge of the coordination polyhedron; the chelate ring of ligand 2 is planar. The structural parameters of the isopropoxo ligand are also listed in Table V.

The complex molecules are well separated in the crystal. The most notable short intermolecular contacts involve O_1 and neighboring 8-hydroxyquinoline ligands (distances >3.25 Å) and partially overlapped aromatic residues of the ligands (distances >3.45 Å).

Registry No. VO(O-*i*-Pr)(oxine)$_2$, 40031-92-3.

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