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Molecular Structure of Vanadyl(V) Chloride as Studied by Gas Electron Diffraction

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The molecular structure of $OVCl_3$ has been determined as follows by an analysis of electron diffraction intensities combined with the rotational constants for $OV^{35}Cl_3$, $OV^{37}Cl_3$ and $OV^{35}Cl_2{}^{37}Cl$ determined in a previous microwave study: $r_g(V–Cl) = 2.142 \pm 0.002$ Å, $r_g(O–V) = 1.570 \pm 0.005$ Å, $r_g(Cl\cdots Cl) = 3.530 \pm 0.002$ Å and $\angle Cl–V–Cl\ (r_{av}) = 111.3 \pm 0.1°$. The uncertainties represent estimated limits of error. An isotopic difference in the V–Cl distance, $r_{av}(V–{}^{35}Cl)–r_{av}(V–{}^{37}Cl)$, is estimated to be $(6 \pm 4) \times 10^{-5}$ Å.

Introduction

As part of a series of studies of the structures of inorganic halides by gas electron diffraction[1–3], the structure of $OVCl_3$ has been determined in the present study. The r_0 structure of this molecule was determined[4] in the recent microwave study of the authors using five rotational constants for $OV^{35}Cl_3$, $OV^{37}Cl_3$ and $OV\,{}^{35}Cl_2{}^{37}Cl$. Though this r_0 structure appeared to be an order of magnitude more precise than the earlier structure reported by Palmer[5] by visual electron diffraction, it was difficult to estimate the accuracy of the r_0 parameters, since the r_0 structure is liable to unknown systematic uncertainty[6]. One origin of the uncertainty consists in the harmonic terms in the rotational constants B_0, and hence, B_0 had to be converted to B_z by subtraction of the interaction terms[7].

Another important problem is the effect of isotopic substitution. Because of zero point vibration, isotope effects on the structural parameters cause another systematic uncertainty, which is frequently much larger than the random uncertainty due to experimental errors in the rotational constants[8, 9]; without precise knowledge about the force field, there is no reliable way at present for estimating the isotope effect. However, since electron diffraction intensity provides independent and complementary information on molecular geometry, a joint least squares analysis of electron diffraction and spectroscopic data can reduce strong correlation among molecular parameters including isotopic differences. This method has thus far been applied mostly to studies of organic structures[10, 11], but it should be equally effective for an analysis of inorganic structures, as demonstrated by Jacob *et al.*[12] for $XeOF_4$. In their joint least squares analysis they made careful selections of relative statistical weights and estimated random and systematic errors in the molecular parameters, although no explicit account seems to have been taken of the isotopic effect on the average structure.

In our previous study of CH_3CN[9], an isotopic difference in the C–H distance, $\delta r = r_{av}(C–H)–r_{av}(C–D)$, was treated as one of the independent parameters in a joint least squares analysis*. Since δr had to be assumed otherwise, this procedure alleviated the systematic errors originating from the isotopic effect, but δr was too small to be significantly determined. The ${}^{35}Cl–{}^{37}Cl$ isotopic effect in $OVCl_3$ is estimated to be so much smaller than the hydrogen–deuterium effect in CH_3CN that it seems even more difficult to detect. On the other hand, $OVCl_3$ has a more favorable condition than CH_3CN for an analysis of the isotopic difference, since the rotational constant C is available and since it has fewer structural parameters. In addition, the V–Cl bond distance, which is strongly correlated with the isotopic difference, can be determined accurately since the V–Cl pair has a large electron scattering power. Therefore, an attempt was made in the present study to observe an isotopic difference in the V–Cl distance and to determine a more accurate structure of $OVCl_3$ by a complementary use of electron diffraction and spectroscopic data.

Experimental

A commercial sample (purity over 99%) purchased from Nakarai Chemicals Co. was used without further purification. Since the sample decomposes rapidly in the presence of water ($2OVCl_3 + 3H_2O \rightarrow V_2O_5 + 6HCl$), it was handled in a dry box. A sample holder with a greaseless stopcock was used, because $OVCl_3$ is miscible in any proportion with grease. No red precipitate of V_2O_5 indicating hydrolysis of the sample was detected during the experiment.

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* See Ref. 6 for definitions of the structural parameters, r_{av}, r_a, r_α, $r_\alpha{}^0$, r_z and r_g, used in the present paper.

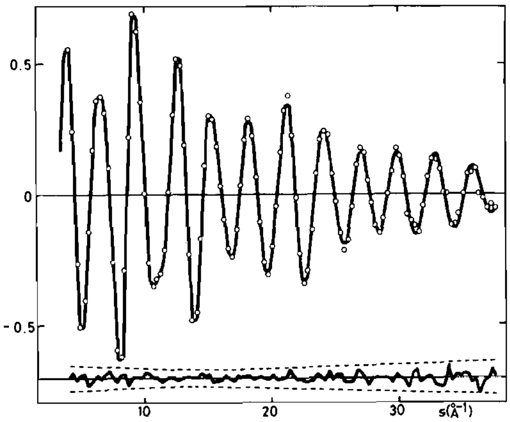

Figure 1. Experimental and best fit molecular intensities for $OVCl_3$ shown in open circles and the solid curve, respectively. The lower solid and broken curves represent residuals and error limits of the molecular intensity corresponding to a fractional error of 1×10^{-3} of the original photocurrent, respectively.

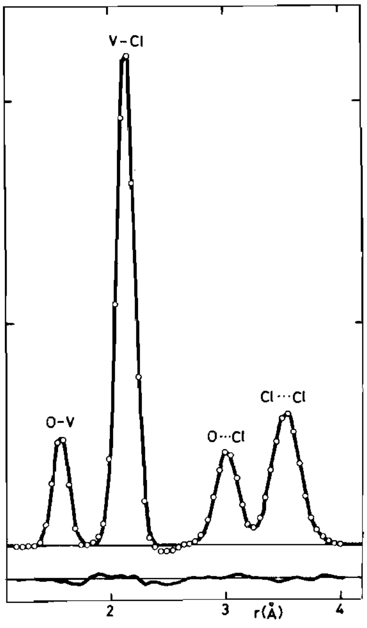

Figure 2. Experimental (open circles) and theoretical radial distribution curves for $OVCl_3$. The index of resolution is 0.74. The lower curve represents residuals. A damping factor, exp $(-0.0016\,s^2)$, was used.

Electron diffraction photographs were taken with an r^3-sector[13] at camera lengths of about 107.7 mm and 243.3 mm. The electron wavelength was about 0.06 Å. The sample gas was maintained in thermal equilibrium with its liquid phase at room temperature. The pressure of the sample was about 10 Torr. The exposure times for the short and long camera lengths were about 3 min and 1 min, respectively. Other experimental details are described elsewhere[13,14]. The scale factor was calibrated[13] with reference to the $r_a(C{=}O)$ distance (1.164_6 Å) of carbon dioxide measured under the same experimental conditions.

The optical densities (0.16–0.47) were assumed to be proportional to electron intensities. Observed molecular intensities covering the range $s = 4.0$–$37.7\ \text{Å}^{-1}$ were used in the analysis. The data taken with the short and long camera lengths were linked at $s = 9.4\ \text{Å}^{-1}$*. The elastic and inelastic scattering factors and the phase shifts were taken from the tables prepared by Schäfer *et al.*[15] Typical molecular intensities and the corresponding radial distribution curve are illustrated in Figure 1 and 2, respectively. Most of the calculations were carried out on a HITAC 8800/8700 operating system in the Computer Center of the University of Tokyo.

Analysis and Discussion

Force Constants

Mean square amplitudes and vibrational corrections[6] were calculated from the F_s matrix given in Table I. The force constants were obtained with reference to those for $OPCl_3$[16] and adjusted to reproduce the observed fundamental frequencies assigned by Clark and Mitchell[17]. The following sets of linear combinations of the internal coordinates defined in Figure 3 were selected as the internal symmetry coordinates:

For the A_1 species,

$$\begin{aligned} S_1 &= \Delta D \\ S_2 &= 3^{-1/2}(\Delta d_1 + \Delta d_2 + \Delta d_3) \\ S_3 &= 6^{-1/2}(\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{13} - \Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3) \end{aligned} \qquad (1)$$

and for the E species,

$$\begin{aligned} S_{4a} &= 6^{-1/2}(2\Delta d_1 - \Delta d_2 - \Delta d_3) \\ S_{5a} &= 6^{-1/2}(2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3) \\ S_{6a} &= 6^{-1/2}(2\Delta\alpha_{23} - \Delta\alpha_{12} - \Delta\alpha_{13}) \end{aligned}$$

$$\begin{aligned} S_{4b} &= 2^{-1/2}(\Delta d_2 - \Delta d_3) \\ S_{5b} &= 2^{-1/2}(\Delta\beta_2 - \Delta\beta_3) \\ S_{6b} &= 2^{-1/2}(\Delta\alpha_{13} - \Delta\alpha_{12}). \end{aligned}$$

The calculated frequencies listed in Table II agree with the observed frequencies to within 0.5 cm⁻¹. The calculated amplitudes and vibrational corrections are listed in Table III.

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* For a listing of the experimental total intensity and background data order document NAPS 02501 from ASIS-National Auxiliary Publications Service, c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016, remitting $1.50 for each microfiche or $5.00 for each photocopy.

TABLE I. F_s matrix for $OVCl_3$[a].

	A_1 species				E species		
S_1	7.72	0.20	0.077	S_4	2.07	−0.13	0.16
S_2		3.01	0	S_5		0.78	−0.19
S_3			0.625	S_6			0.52

[a] Force constants for internal symmetry coordinates S defined in Eq. (1). The units are md/Å for elements 11, 12, 22 and 44, md for 13, 45 and 46, and md/Å for 33, 55, 56 and 66.

TABLE II. Fundamental Frequencies for $OVCl_3$ (cm^{-1}).

Species		obsd[a]	calcd[b]	Description[a]
A_1	ν_1	1042.5	1042.6	V–O stretch
	ν_2	409.5	409.5	V–Cl stretch
	ν_3	163.0	162.8	VCl_3 deformation
E	ν_4	503.0	503.1	V–Cl stretch
	ν_5	246.0	246.1	O–V–Cl_3 rocking
	ν_6	124.5	124.5	VCl_3 deformation

[a] The vibrational modes were assigned by Clark and Mitchell, Ref. 17. [b] Calculated in the present study by use of the F_s matrix given in Table I.

Table III. Mean Amplitudes and Shrinkage Corrections for $OVCl_3$[a].

	l obsd[b]	l calcd[c]	r_a–r_α[d]
O–V	0.041 ± 0.006	0.0368	0.0038
V–Cl	0.048 ± 0.003	0.0492	0.0029
O···Cl	0.086 ± 0.009	0.0945	0.0015
Cl···Cl	0.112 ± 0.006	0.1165	−0.0020

[a] In Å units. [b] Uncertainties represent estimated limits of error. [c] Root mean square parallel amplitudes, $<\Delta z^2>^{1/2}$, calculated at 298 K from the force constants given in Table I. The range of uncertainties are about ± 5% and ± 10% for bonded and nonbonded pairs, respectively. [d] Shrinkage corrections calculated at 298 K.

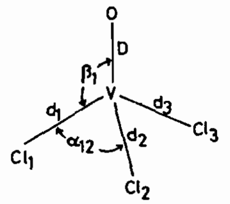

Figure 3. Internal Coordinates for $OVCl_3$.

Electron Diffraction Analysis and $r_\alpha{}^0$ Structure

Since this molecule has C_{3v} equilibrium symmetry, three parameters, r(O–V), r(V–Cl) and ∠Cl–V–Cl, were selected to define the molecular geometry. The asymmetry parameters $\varkappa$ for the O–V and V–Cl bonds were estimated[18] to be 0.6×10^{-6} and 1.9×10^{-6} Å^3, respectively, from the anharmonicity parameters a_3[19] for O–V and V–Cl assumed to be 2.0 Å^{-1}. The $\varkappa$ parameters for nonbonded pairs were ignored since the observed radial distribution peaks of the nonbonded pairs were symmetric within estimated experimental error[3].

A least squares analysis was carried out with an empirical diagonal weight matrix[20]. The observed indices of resolution for the long and short camera lengths were 0.87 ± 0.02 and 0.74 ± 0.03, respectively. Since these indices were appreciably smaller than those normally observed in our laboratory, a number of tests were made to investigate the origin of the discrepancies from unity. The following pieces of evidence indicated that the "local" indices of resolution (*i.e.*, the ratios of the experimental and theoretical intensity maxima) were essentially independent of s and that the discrepancies originated mainly from uniform secondary scattering of electrons:[21]

(a) The indices were reproducible. Blank exposures taken without the sample gas gave only weak and uniform photographic densities. In one experiment, diffraction patterns were taken of a sample exposed for several hours to a moist atmosphere, but the structural parameters and indices derived from them were essentially unchanged.

(b) The observed mean amplitudes, which have strong correlation with the indices of resolution, agree with the corresponding theoretical estimates within experimental error, as shown in Table III.

(c) The diffraction patterns for carbon dioxide, taken for reference under essentially the same experimental conditions but with exposure times of about one third of those of the $OVCl_3$ sample, gave indices of 1.00 ± 0.02 for both long and short camera lengths.

(d) Relative intensities of the observed radial distribution peaks (Figure 2) are consistent with the corresponding theoretical values within experimental error.

(e) The structural parameters derived from diffraction intensities are consistent with the rotational constants determined by microwave spectroscopy[4] as described in the following sections.

It was not possible, however, to make a quantitative account for the problem in terms of intramolecular[22], intermolecular and metal scattering or sample impurity[21].

The r_α parameters determined in the diffraction analysis were extrapolated to zero Kelvin neglecting the temperature dependence of the angle parameter and using a diatomic approximation for the bond parameters[6] with assumed a_3 parameters. The random errors σ_1 and σ_2 in the $r_\alpha{}^0$ parameters were estimated by use of their standard deviations and discrepancies among the parameters derived from different plates, respectively[20]. The σ_1 and σ_2 values are comparable with each other. Systematic errors in the scale factor were estimated to be ±0.06%. Uncertainties of 10% in the harmonic terms of the vibrational corrections are negligible, and the effect of uncertainties in the anharmonic corrections with a_3 values assumed to be 2 ± 1 Å^{-1} are also negligible except on the $r_\alpha{}^0$(V–Cl) parameter, ±0.0009 Å. Changes of 100% in the $\varkappa$ parameters for the bonded pairs and changes of $\pm 2.0 \times 10^{-6}$ Å^3 for the nonbonded pairs caused no significant systematic errors in the distances except in $r_\alpha{}^0$(V–Cl), ±0.0008 Å. The $r_\alpha{}^0$ structure with uncertainties estimated to be 2.5 times the random standard deviations plus the systematic errors estimated above is shown in Table IV.

r_z *Structure and the Influence of Isotopic Differences*

The rotational constants[4] B_0 for $OV^{35}Cl_3$ and $OV^{37}Cl_3$ and A_0, B_0 and C_0 for $OV^{35}Cl_2{}^{37}Cl$, listed in Table V, were transformed into the average rotational constants[23] A_z, B_z and C_z (abbreviated in a set as B_z). The corrections were estimated to have uncertainties of ±10%. Uncertainties in B_z originate mainly from those in the B_0 to B_z corrections, except for the C_z constant for $OV^{35}Cl_2{}^{37}Cl$, where the experimental error in C_0 is larger than the uncertainty in the correction. The rotational constants $B_\alpha{}^0$ calculated from the $r_\alpha{}^0$ structure determined in the foregoing electron diffraction analysis are compared with B_z in Table V. The diffraction and spectroscopic constants agree within the experimental error of the former.

Since the C axis of $OV^{35}Cl_2{}^{37}Cl$ approximately coincides with the molecular symmetry axis, the rotational constant C_z provides direct information on the r_z(Cl···Cl) parameter, $3.529_6 \pm 0.001_5$ Å. This is in agreement with the $r_\alpha{}^0$(Cl···Cl) determined by electron diffraction, 3.533 ± 0.005 Å. Therefore, it is convenient for the analysis of the rotational constants to choose the Cl···Cl nonbonded distance as one of the independent parameters and regard the Cl–V–Cl angle as a function of r(V–Cl) and r(Cl···Cl).

If isotopic differences in the parameters are completely ignored, the r_z(O–V) and r_z(V–Cl) parameters can be derived from the rotational constants B_z

TABLE IV. Average Structures for $OVCl_3$[a].

	$r_\alpha{}^{0}$ [b]	r_{av}[c]	r_z[d]
O–V	1.573 ± 0.008	$1.568_1 \pm 0.005$	1.569 ∓ 0.012
V–Cl	2.138 ± 0.002	$2.138_3 \pm 0.002$	2.138 ± 0.003
∠Cl–V–Cl	111.4 ± 0.4	$111.2_6 \pm 0.1$	111.3 ∓ 0.2
Cl···Cl	3.533 ± 0.005	$3.529_7 \pm 0.001_5$	$3.529_6 \pm 0.001_5$[e]

[a] Distances are in Å units and angles are in degrees. The final r_g structure is given in Table VII. See Ref. 6 for definitions of the structures. Uncertainties represent estimated limits of error. [b] Derived from electron diffraction intensities. [c] Derived from a joint analysis of electron diffraction intensities and rotational constants. [d] Derived from five rotational constants. The isotopic difference, $r_z(V\text{–}^{35}Cl) - r_z(V\text{–}^{37}Cl)$, is assumed to be $(6 \pm 4) \times 10^{-5}$ Å. The isotopic effect in the angle is assumed to be 0 ± 0.01°, and the secondary isotope effect is ignored. [e] Derived uniquely from the rotational constant C_z for $OV^{35}Cl_2{}^{37}Cl$.

TABLE V. Rotational Constants for $OVCl_3$[a] (cm^{-1}).

	B_0[b]	B_z[c]	$B_\alpha{}^{0}$ [d]	B_{av}[e]
B_1	0.0580975(3)	0.058037(5)	0.05800(15)	–
B_2	0.0555451(7)	0.055488(5)	0.05546(15)	–
A_3	0.0580381(20)	0.057977(5)	0.05794(15)	0.057977(5)
B_3	0.0564447(20)	0.056386(5)	0.05635(15)	0.056386(5)
C_3	0.037998(30)	0.037980(30)	0.03790(10)	0.037977(29)
$B_1 - B_2$	0.0025524(5)	0.0025490(5)	–	0.0025490(7)
$B_1 + B_2$	0.1136426(7)	0.113524(10)	–	0.113523(9)

[a] Rotational constants B for $OV^{35}Cl_3$ and $OV^{37}Cl_3$ and A, B and C for $OV^{35}Cl_2{}^{37}Cl$ are denoted as B_1, B_2, A_3, B_3 and C_3, respectively. Uncertainties attached to the last digits are given in parentheses. [b] Observed rotational constants taken from Ref. 4. [c] Average rotational constants calculated from B_0 with corrections for vibrational effects. The limits of error are estimated from uncertainties in the quadratic force constants used for calculating the corrections. [d] Rotational constants calculated from the $r_\alpha{}^0$ structure determined by the present analysis of ED intensities. [e] Best-fit rotational constants obtained from the joint least squares analysis of electron diffraction and spectroscopic data. Uncertainties represent 2.5 times the estimated standard deviations.

by use of an approximate two-dimensional diagram[4]. A cross section of the three-dimensional parameter space at r_z(Cl···Cl) = 3.5296 Å is shown in Figure 4. The relations given by the rotational constants B_z for $OV^{35}Cl_3$ and $OV^{37}Cl_3$, denoted as B_1 and B_2, respectively, form planes almost exactly parallel to the r(Cl···Cl) axis. Their cross sections form two straight lines in the r(O–V)–r(V–Cl) plane. The difference between the B_1 and B_2 slopes has been exaggerated but the crossing point P is correctly shown. The rotational constants A_z and B_z for $OV^{35}Cl_2{}^{37}Cl$ (A_3 and B_3), which give relations almost identical to B_1 and B_2 respectively, are not displayed in the figure. The most probable $r_\alpha{}^0$ parameters determined by electron diffraction are shown by R with the estimated uncertainty indicated by an ellipse. Since the ellipse crosses the lines, the diffraction and spectroscopic data are compatible.

However, small differences originating from the substitution of ^{35}Cl by ^{37}Cl should be carefully examined[6,8,9] for a critical comparison of the r_z parameters with the $r_\alpha{}^0$ parameters. If isotopic differences in the V–Cl distance and the O–V–Cl angle, $\delta r = r_z(\text{V–}^{35}\text{Cl}) - r_z(\text{V–}^{37}\text{Cl})$ and $\delta\alpha = \alpha(\text{O–V–}^{35}\text{Cl}) - \alpha(\text{O–V–}^{37}\text{Cl})$, respectively, and secondary isotope effects[24,25] are completely ignored, the most probable set of the r_z parameters corresponds to point P, where the two lines cross each other. This point is located outside the error ellipse of the $r_\alpha{}^0$ structure, and if the uncertainties in the r_z parameters are assumed to be nearly equal to those in the r_0 parameters, 0.005 Å and 0.001 Å for r(O–V) and r(V–Cl) respectively, these r_z parameters are significantly inconsistent with the $r_\alpha{}^0$ parameters. On the other hand, if δr is assumed to be 6×10^{-5} Å, the parameter set which satisfies the B_1 and B_2 conditions shifts from P to Q. The isotopic difference δr, $(6 \pm 4) \times 10^{-5}$ Å, brings the r_z(V–Cl) parameter into agreement with the $r_\alpha{}^0$(V–Cl) parameter determined by electron diffraction. The uncertainty in δr is estimated from the following sources: a) uncertainty in the $r_\alpha{}^0$(V–Cl) parameter, ±0.002 Å, b) uncertainty in the rotational constant C_z, $\pm 0.3 \times 10^{-4}$ cm^{-1}, c) uncertainty in the difference between the rotational constants B_1 and B_2, $\pm 0.5 \times 10^{-6}$ cm^{-1}, and d) the neglect of other isotope effects. By use of the diatomic approximation[8],

$$a_3 \cong (2r \cdot \delta r + \delta\langle\Delta\varrho^2\rangle)/3r \cdot \delta\langle\Delta z^2\rangle \qquad (2)$$

where $\delta\langle\Delta z^2\rangle$ and $\delta\langle\Delta\varrho^2\rangle$ denote the isotopic differences in the parallel and perpendicular mean square amplitudes, respectively, the anharmonicity parameter a_3 for the V–Cl pair is estimated from δr to be $1._9 \pm 1$ Å^{-1}. This order estimate is consistent with those found in many diatomic molecules[19], 1.6–2.4 Å^{-1}.

As listed in Table IV, r(O–V) can be determined by electron diffraction data with an uncertainty several fold as large as that in r(V–Cl), since the scattering power of the O–V pair is only about 21% of that of the V–Cl pair. This is also the case for the r_z(O–V) and r_z(V–Cl) determined by spectroscopic data. However, uncertainty in the angle parameter can be decreased by a joint analysis, since $r_\alpha{}^0$(V–Cl) is defined well by electron diffraction data and r_z(Cl···Cl) is defined well by spectroscopic data.

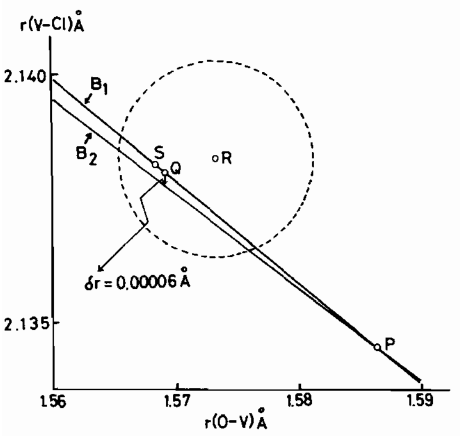

Figure 4. A cross section of the three-dimensional parameter space, where r(Cl···Cl) equals 3.5296 Å. Two straight lines B_1 and B_2 represent the relations given by the rotational constants B_z for $OV^{35}Cl_3$ and $OV^{37}Cl_3$, respectively. The difference between the B_1 and B_2 slopes is exaggerated. When the isotopic differences are ignored, the most probable set of the r_z parameters corresponds to point P. If the isotopic difference in r(V–Cl), $\delta r = r_z(\text{V–}^{35}\text{Cl}) - r_z(\text{V–}^{37}\text{Cl})$, is assumed to be 0.00006 Å, the parameter set satisfying the condition set by B_1 and B_2 shifts to Q. The most probable $r_\alpha{}^0$ parameters determined by a joint least squares analysis of electron diffraction and spectroscopic data are shown by S.

Joint Analysis of Electron Diffraction and Spectroscopic Data

As schematically shown in Figure 4, information on the effect of isotopic substitution is provided by the difference between the rotational constants B_1 and B_2. The uncertainty in B_1–B_2 was estimated to be 0.5×10^{-6} cm^{-1}, while the uncertainties in B_1 and B_2 were about 0.5×10^{-5} cm^{-1}, because various systematic errors in the B_0 to B_z corrections in B_1 and B_2 cancel each other. Accordingly, the rotational constants $B_1 \pm B_2$, A_3, B_3 and C_3 listed in Table V were combined with the diffraction intensities, and the V–Cl isotopic difference δr was taken as an additional structural parameter. The isotopic difference $\delta\alpha$ was assumed to be 0 ± 0.01° and held constant, and the secondary isotope effect was ignored.

The relative weights for the rotational constants were adjusted empirically until 2.5 times the standard errors in the rotational constants were nearly equal to their uncertainties. The weights used in the analysis were 4×10^{10}; 1×10^8, 2×10^8, 2×10^8 and 2×10^7 for B_1–B_2, $B_1 + B_2$, A_3, B_3 and C_3, respectively,

TABLE VI. Error Matrix for $OVCl_3$[a].

	k_1[b]	k_2[c]	r(O–V)	r(V–Cl)	δr[d]	∠Cl–V–Cl	l(Cl–Cl)	l(O–Cl)	l(V–Cl)	l(O–V)
k_1	941	386	139	–64	–9	72	173	228	112	95
k_2		1031	–98	47	8	–43	270	218	245	290
r(O–V)			161	–73	–9	89	–23	19	–20	–46
r(V–Cl)				34	4	–38	11	–7	9	21
δr					1	4	2	2	2	3
∠Cl–V–Cl						62	–9	16	–8	–23
l(Cl–Cl)							257	54	65	76
l(O–Cl)								297	53	57
l(V–Cl)									74	68
l(O–V)										288

[a] Units (× 10^{-5}) for the distances are Å, that for the angle is rad and those for the indices are dimensionless. [b] Index of resolution for the long camera region. [c] Index of resolution for the short camera region. [d] $r(V–^{35}Cl)–r(V–^{37}Cl)$.

TABLE VII. Comparison of $OVCl_3$ structures[a].

	r_g[b]	r_0[c]	r_a[d]
O–V	1.570 ± 0.005	1.595 ± 0.005	1.56 ± 0.04
V–Cl	2.142 ± 0.002	2.131 ± 0.001	2.12 ± 0.03
∠Cl–V–Cl	111.3 ± 0.1[e]	111.8 ± 0.2	111.2 ± 2
∠O–V–Cl	107.6 ± 0.1[e]	107.0 ± 0.2	107.7 ± 2

[a] Distances are in Å units and angles are in degrees. [b] Derived from the r_{av} structure. The final result determined in the present study. [c] Ref. 4. Systematic errors due to vibrational effects are not included in the quoted uncertainties. [d] Ref. 5. Derived from a visual electron diffraction study. [e] r_{av} structure.

where a unit weight was assigned to the molecular intensities from $s = 6.3$ to $26.7\,Å^{-1}$ taken at $\pi/10$ intervals. A typical error matrix is shown in Table VI.

The isotopic difference in the angle and the secondary isotopic effect are found to have little influence on the r_{av} structure except on the δr parameter, since the correlation among the r_z parameters is eliminated by the joint use of the electron diffraction intensity. The δr parameter is correlated with $\delta\alpha$ and a change of ± 0.01° in $\delta\alpha$ caused a systematic error of 2.0×10^{-5} Å in δr.

The r_{av} structure listed in Table IV is not significantly different from the $r_\alpha{}^0$ structure derived from the electron diffraction data alone except that the angle parameter is appreciably more accurate. The most probable r_{av} set is shown by S in Figure 5. The r_{av}(V–Cl) is determined almost uniquely by the diffraction data alone, and the most probable r_{av}(O–V) value is improved by use of the relation given by the rotational constants. The isotopic difference δr determined by the present analysis agrees with the preceding estimate.

Comparison of the Structures

The r_g structure derived from the r_{av} structure determined in the present study is compared with the r_0 structure[4] and the earlier structure reported by Palmer[5] in Table VII. Significant differences are observed in the r_g and r_0 distances.

The r_g(V–Cl) distance in $OVCl_3$ is nearly equal to that in VCl_4[26], 2.138 ± 0.002 Å. These molecules seem to be the only vanadium compounds for which precise structures have been determined[27,28]. The V=O bond lengths in various molecules in crystals range from 1.55 to 1.67 Å[28]. The vanadium valence angle (∠Cl–V–Cl) is about 8° larger than the corresponding phosphine valence angle in $OPCl_3$[2], ∠Cl–P–Cl = 103.3 ± 0.2°.

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