VOCl₃: Crystallization, Crystal Structure, and Structural Relationships: A Joint X-Ray and ³⁵Cl-NQR Investigation*

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Cooling of VOCl₃ below its melting point (196 K) yields an amorphous phase, which transforms into the crystalline state upon further cooling. The crystallization is accompanied by a remarkable change in color from pale yellow to deep orange. A single crystal has been grown from the amorphous phase. VOCl₃ crystallizes in the orthorhombic system, space group $Pnma$, with lattice parameters $a = 4.963(1)$, $b = 9.140(4)$, $c = 11.221(5)$ Å at 133 K; $Z = 4$. The ³⁵Cl-NQR experiments show two signals at approximately 11.4 MHz of intensity 2 : 1, which implies two different crystallographic sites for chlorine atoms, in agreement with the centrosymmetric space group $Pnma$. The crystal structure exhibits isolated tetrahedral molecules VOCl₃ lying on a mirror plane and stacked with their V–O axis along [100] to form trigonal prismatic columns. A close relationship exists with the structure of AsBr₃, in which the lone pair occupies the position corresponding to the oxygen atoms.

Introduction

VOCl₃ is clearly distinguished from the other transition metal oxide trihalides because it is liquid down to 196 K and exists in the form of tetrahedral molecules. Its crystal structure is unknown; also, it is uncertain whether VOCl₃ remains in the monomeric state as does POCl₃ (*1*) or whether it dimerizes like the comparable Cl₃VNCl (*2*) or polymerizes like the other transition metal oxide trihalides (*3*). Cl₃VNCl is very volatile like VOCl₃ and

monomeric in the gaseous state (*4*); in the crystalline state it forms chlorine bridges (*2*).

The metal oxide trihalides besides VOCl₃ are solid at room temperature and polymerized via dichloro- and oxobridges, to build an octahedral coordination for the metal atoms. Among them, TaOCl₃, metastable and amorphous at room temperature, appears to be rather singular.

As will be discussed below, the crystal structure of VOCl₃ is more closely related to those of POCl₃ and of the VA element trihalides. The latter are comparable since the lone pair occupies the place of the oxygen atom. A review of the structures of

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these compounds was given by Galy and Enjalbert (5). The crystal structure of VOCl₃ is briefly mentioned therein.

Crystallization

A droplet of liquid $VOCl_3$ was encapsulated in a Lindemann capillary with a diameter of 0.3 mm, which was placed on a CAD4 Enraf Nonius automatic diffractometer equipped with a nitrogen gas stream low temperature device. The crystal was grown *in situ,* using the device already described by Enjalbert (6). The usual procedures (6) for growth of a crystal from a liquid were dropped after a number of failures. The liquid is usually cooled to approximately 10 K below the melting point ($T_{mp} = 196$ K for $VOCl_3$). For $VOCl_3$ the situation appears to be more complicated: when cooled slowly and continuously down to 196 K it solidifies, giving rise to the formation of a pale yellow amorphous phase, as checked by X-ray diffraction. After a few hours, orange nuclei appear and the whole solid transforms quickly into an orange crystalline phase. It was possible to grow a single crystal of suitable quality; if the liquid was quickly cooled down to 90 K the remarkable deep orange color of the sample immediately appeared, indicating that the amorphous to crystalline phase transition had occurred.

X-Ray Data Collection

The crystallographic data of $VOCl_3$ were directly obtained after crystal growth. They are summarized in Table I. According to the observed extinctions, the possible space groups in the orthorhombic system are *Pn2₁a* and *Pnma*. Pnma was selected, based on the Patterson function and the ³⁵Cl-NQR results.

Information concerning the intensity data collection at 133 K is given in Table I.

TABLE I

CRYSTALLOGRAPHIC DATA AND PARAMETERS OF THE X-RAY DATA COLLECTION

1. Physical and crystallographic data
   Formula: VOCl₃   Molecular weight: 173.2
   Crystal system: orthorhombic   Space group: *Pnma*
   Cell parameters at 133 K:
     $a = 4.963(1)$ Å $V = 509.0(3)$ Å³
     $b = 9.140(4)$ $Z = 4$
     $c = 11.221(5)$
   $\rho_X = 2.261$ g · cm⁻¹
   Absorption factor: $\mu_{(\lambda MoK\alpha)} = 28$ cm⁻¹
   Morphology: cylinder in Lindemann capillary ϕ 0.3 mm, height = 0.5 mm

2. Data collection
   Temperature: 133 K
   Radiation: MoKα
   Monochromator: oriented graphite (002)
   Crystal-detector distance: 207 mm
   Detector window: height = 4 mm, width = 4 mm
   Takeoff angle: 4.0°
   Scan mode: $\theta,2\theta$
   Maximum Bragg angle: $\theta = 30°$
   Scan angle: $0.95 + 0.347 \tan\theta$
   Values determining the scan speed:
     SIGPRE = 0.75, SIGMA = 0.018, VPRE = 10° · min⁻¹, TMAX = 90 sec
   Standard reflections: 4 0 0; 0 4 0; 0 0 2
   Periodicity: 3600 sec

3. Conditions for refinement
   Reflections for the refinement of the cell dimensions: 25
   Recorded reflections: 900
   Independent reflections: 435
   Utilized reflections: 394 with $I \geq 3\sigma(I)$
   Refined parameters: 28
   Reliability factors:
     $R = \Sigma|kF_0 - |F_c||/\Sigma kF_0 = 0.049$
     $R_w = [\Sigma w(kF_0 - |F_c|)^2/\Sigma wk^2F_0^2]^{1/2} = 0.051$
     with $w = 4F_0^2/\sigma^2(F_0^2)$

NQR Spectroscopic Study

Experimental

After distillation under a strictly controlled dry argon atmosphere, a NQR sample was prepared by sealing approximately 1.5 g of product in a 13 mm diameter Pyrex ampoule. All spectra were recorded with sideband suppression, using Zeeman modulation, on a Decca NQR spectrometer (7–90 MHz) for which special coils were made to accommodate the 15 mm diameter samples (7, 8). The temperature dependence of the frequencies was measured in a rf probe especially constructed to fit an "Air Liquide-

SMC" cryostat. Sample temperatures were measured with a copper-constantan thermocouple and these determinations are estimated to be accurate to ± 0.5 K. The initial absolute calibration of the spectrometer marker system was performed with a Schlumberger FB 2603 frequency counter.

The ^{35}Cl resonance frequencies at 77 K are given in Table II. Frequencies are estimated to be within ± 5 kHz. The corresponding ^{37}Cl frequencies were found to be in good agreement with the ratio of quadrupole moments $Q_{35}/Q_{37} = 1.2688$. Values in brackets are the relative intensities of the signals (see Fig. 1) obtained with 10 and 18 sec recording time constants in series.

Results

Cooling down the sample to just below the melting point (ca. 170 K) did not immediately produce any NQR signals; they appear suddenly after a few hours. From direct observation of the sample it is evident that the NQR signals appear as crystals of VOCl₃ form. At lower temperatures the NQR signals appear immediately.

In the temperature range 77–194 K, two signals, ν_1 and ν_2, were recorded for ^{35}Cl resonance frequencies (Table II, Fig. 1). Their relative intensities are in a ratio close to 2 : 1. These frequencies ν_1 and ν_2 dimin-

ish when the temperature increases. They vanish above 194 K which is very close to the melting point of the sample, $T_{mp} = 196$ K. It is worth noticing that the frequency area presently measured is in good agreement with a previous work (11.54 MHz at 83 K). However, in this earlier study, only one chlorine site had been detected (9).

The existence of two signals in the observed intensity ratio implies the existence of two different crystallographic sites for the chlorine atoms, one of which has a double multiplicity indicating the presence of a symmetry element, a mirror plane, within the tetrahedral VOCl₃ molecule. This is consistent with the space group *Pnma*, the alternative one, *Pn2₁a*, requiring three different signals of similar intensity.

The small difference between ν_1 and ν_2, $\Delta\nu = 0.067$ MHz at 77 K, proves that the chlorine atoms are chemically quasi equivalent. The $\Delta\nu$ decreases smoothly with increasing temperature to $\Delta\nu = 0.042$ MHz at 194 K, which is an indication of the libration of the whole molecule without any internal movement.

The curves $\nu = f(T)$ can be approximated by the formula

$$\nu = a_1 T^{-1} + a_2 + a_3 T + a_4 T^2$$

the coefficients of which are given in Table II. The mean value of ν_1 and ν_2 close to 11.4 MHz can be compared with the corresponding value for $\text{Cl}^- : \nu = 0$ MHz and $\text{Cl}_2 : \nu = 55$ MHz to estimate the degree of ionization or polarization of the V–Cl bond, which is seen to be rather important.

TABLE II

^{35}Cl NQR FREQUENCIES OF VOCl₃ BETWEEN 77 AND 194 K

^{35}Cl NQR frequencies for VOCl₃ at 77K:
$$\nu_1 = 11.52_0 \text{ MHz [10]}$$
$$\nu_2 = 11.58_7 \text{ MHz [17]}$$

Parameters obtained from least-squares analyses of the experimental NQR frequency vs temperature data:

	ν_1	ν_2	
a_1	-8.02×10^{-1}	1.26×10^{-1}	MHz · K
a_2	1.17×10	1.17×10	MHz
a_3	-1.48×10^{-3}	-1.38×10^{-3}	MHz · K⁻¹
a_4	-2.10×10^{-6}	-3.05×10^{-6}	MHz · K⁻²

Structure Determination and Refinement

Approximate coordinates of the atoms were derived after deconvolution of the Patterson function. From the observation of the [0v0] Harker line, it was clear that a mirror plane was present, perpendicular to the b axis, confirming the centrosymmetric
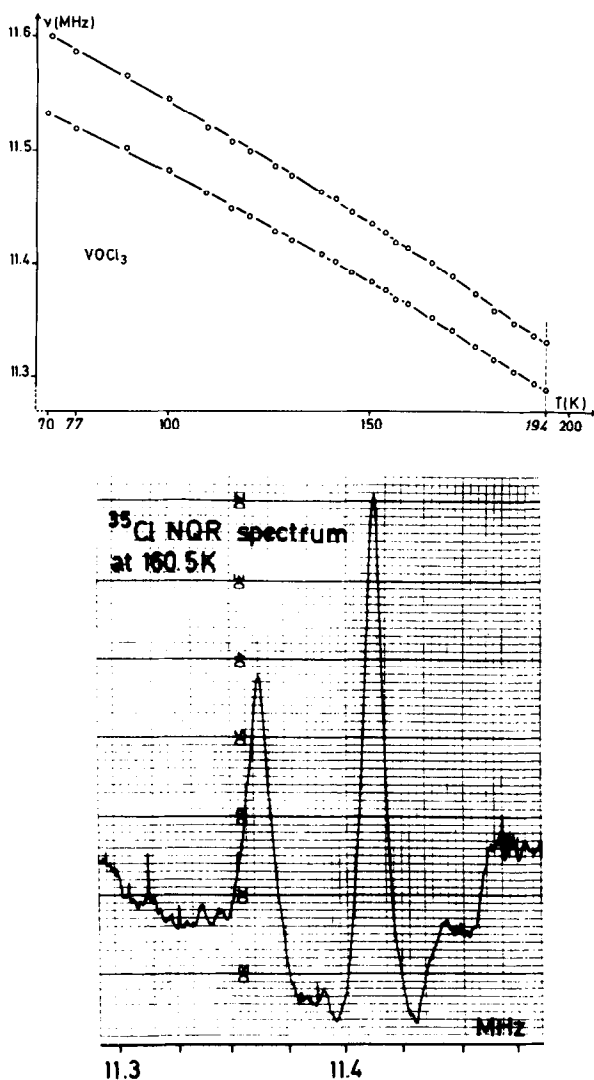
FIG. 1. Temperature dependence of ^{35}Cl-NQR frequencies for VOCl$_3$.

space group *Pnma,* as already indicated by NQR results.

Atomic coordinates and anisotropic thermal parameters were then refined by least squares procedures. Final results corresponding to a reliability index $R = 0.049$ are listed in Table III. All the calculations were performed on a CII Iris 80 computer using various programs: Legros and Aussoleil's CAD4CICT10, Ibers and Doedens'

NUCLS, Zalkin's FOURIER, Busing *et al.*'s ORFFE, and Johnson's ORTEP. The table of the values of F_0 and F_c can be obtained from the authors upon request.

Description of the Structure and Discussions

VOCl$_3$ exhibits a molecular structure with isolated tetrahedral molecules with a

TABLE III

ATOMIC COORDINATES AND THERMAL PARAMETERS FOR VOCl₃

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B_{eq} (Å²)
V	0.1408(4)	$\frac{1}{4}$	0.0456(2)	204(7)	39(2)	42(1)	0	1(3)	0	1.81(6)
Cl(1)	0.2557(6)	$\frac{1}{4}$	−0.1368(2)	336(12)	74(3)	41(2)	0	−5(5)	0	2.6(1)
Cl(2)	0.2732(4)	0.0571(2)	0.1335(2)	361(10)	56(2)	63(2)	9(4)	0(3)	20(2)	2.9(1)
O	−0.1738(15)	$\frac{1}{4}$	0.0508(7)	200(36)	90(9)	93(8)	0	−9(14)	0	3.2(4)

Note. The estimated standard deviation in the last significant figure are given in parentheses. The form of the anisotropic thermal ellipsoid is $\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$. The β values are multiplied by 10^4. $B_{eq} = \frac{4}{3}\Sigma_{ij}(a_i \cdot a_j)\beta_{ij}$.

crystallographic point symmetry C_s. The detailed geometry is shown in Fig. 2. Bond lengths and angles are in excellent agreement with those determined by electron diffraction in the gaseous state (4) (Table IV). The short V–O bond length, 1.562 Å, indicates that the existence of a strong π bonding. The three V–Cl bonds are equal within the standard deviations and lead to the conclusion that they are covalent, as expected for the molecule. Nevertheless, it does not agree completely with the NQR results, suggesting some ionic character of these bonds.

The libration of the molecule, as if it were a rigid body, is shown by NQR and is indirectly confirmed by the shape of the thermal ellipsoids of the various atoms, especially by those for chlorine, which do not indicate a tendency of the molecule to rotate around the V–O axis.

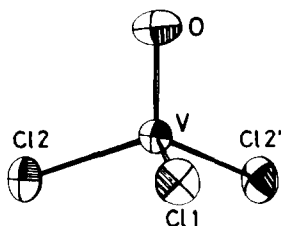Figure 3 is a projection of the molecular packing. It shows that the molecules, lying on the mirror plane, are stacked in columns with V–O bonds parallel to the [100] direction. In the sequence of the columns along the b axis the V–O bonds are alternatively pointing up and down. This packing, which can be described in terms of trigonal prisms sharing their trigonal faces, is illustrated in the right part of Fig. 3.

These rows of trigonal prisms are shifted from one another roughly by $a/2$. As a result, the chlorine atoms of adjacent columns complete these polyhedra as bi-

TABLE IV

BOND LENGTHS (Å) AND ANGLES (°) OF THE VOCl₃ MOLECULE IN BOTH CRYSTALLINE AND GASEOUS STATES. SELECTED INTERATOMIC DISTANCES (Å) IN THE CRYSTAL STRUCTURE

	Solid	Gas
V–O	1.562(7) Å	1.571(4) Å
V–Cl(1)	2.125(3)	2.137(1)
V–Cl(2)	2.124(2)	
O–Cl(1)	2.996(8)	3.010(8)
O–Cl(2)	2.981(6)	
Cl(1)–Cl(2)	3.509(3)	3.522(6)
Cl(2)–Cl(2′)	3.526(4)	
O–V–Cl(1)	107.7(3)°	107.8(0.4)°
O–V–Cl(2)	107.0(2)	
Cl(1)–V–Cl(2)	111.4(1)	111.0(0.1)
Cl(2)–V–Cl(2′)	112.2(1)	

Selected intermolecular distances			
V–Oi	3.402(7) Å	Oi–Cl(2)	3.391(7) Å
Vi–Cl(2′)ii	4.017(3)	Oi–Cl(2′)ii	3.522(5)
		Oi–Cl(1)	3.529(8)

FIG. 2. Perspective view of the VOCl₃ molecule.
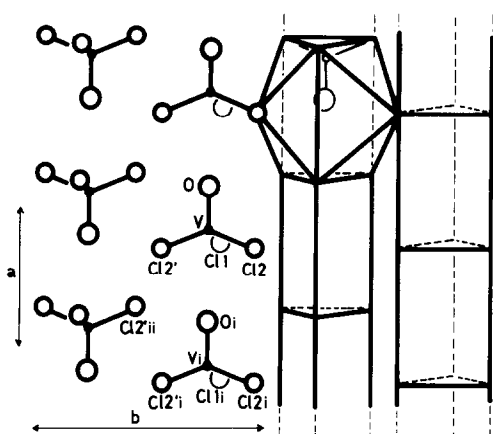
FIG. 3. Perspective view close to the (001) plane of the molecular packing in $VOCl_3$.

FIG. 4. Idealized drawings: (a) $VOCl_3$ onto the plane (100) (space group $Pnma$); (b) $AsBr_3$ onto the plane (001) (space group $P2_12_12_1$). The molecules are represented by the triangle of their halogen atoms and the VO or AsE (E lone pair) groups by small circles.

capped trigonal prisms (see Fig. 3). Their association generates layers parallel to the (001) plane, as indicated on the idealized drawing of the structure projected along the shortest axis a (Fig. 4a).

Using such a description, the VO groups appear to be inserted in bicapped trigonal prisms. Structural relationships can then be established with molecular compounds like POX_3 (X = Cl, Br) and M^*X_3 (M^* = P, As, Sb, Bi; X = F, Cl, Br), a review of which has been given recently by Galy and Enjalbert in this Journal (5).

Finally, $VOCl_3$ does not closely resemble POX_3 which crystallizes in the orthorhombic system (space group $Pnma$) with the YF_3 structure type (10), but crystallizes as the $AsBr_3$ structure type (11) (same system, space group $P2_12_12_1$) (Fig. 4b). In the latter case, the arsenic atoms carrying their lone pair occupy tricapped trigonal prisms. Comparing Fig. 4a and b, it is seen that a small shift of half the Cl–Cl distance of every second layer in $VOCl_3$ does make this structure similar to the $AsBr_3$ structure type.

The crystal structure of $VOCl_3$ thus represents the third structure type of transition metal oxide trihalides known up to now. The two others are $NbOCl_3$ (12) and
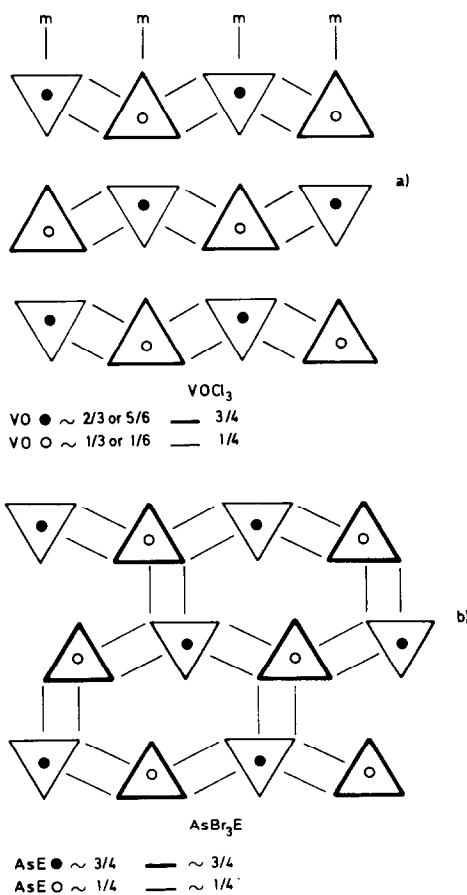
$MoOCl_3$ (13) which are shown in Fig. 5. As a consequence of the tendency of these metal atoms to obtain an octahedral coordination, polymeric structures with bridging chlorine or oxygen atoms are formed.

$NbOCl_3$ crystallizes in the tetragonal system (space group $P4_2/mnm$, parameters a = 10.87 Å and c = 3.96 Å) (12). In the structure dimeric units the $Nb_2O_2Cl_6$ formed by two octahedra sharing a Cl–Cl edge are polymerized by oxygen bridges giving rise to infinite ribbons (Fig. 5a). This structure type includes $NbOBr_3$, $WOCl_3$, $WOBr_3$,
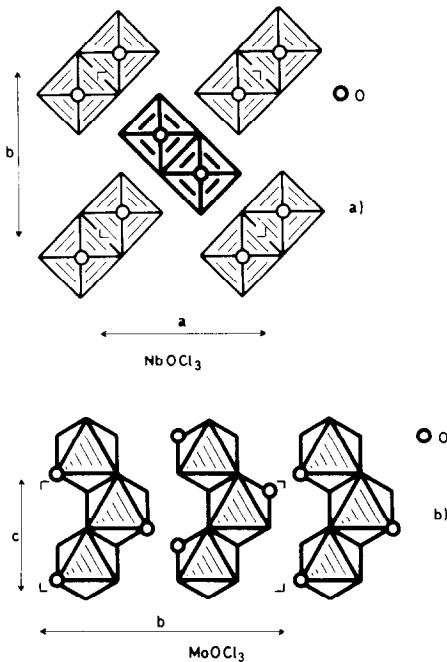
FIG. 5. Idealized drawings of the structures of NbOCl₃ (a) and MoOCl₃ (b). The metal atoms Nb and Mo are inserted in the drawn octahedra and oxygen atoms indicated by small circles.

TcOBr₃, MoOBr₃, and one of the polymorphs of MoOCl₃ (3).

The crystal structure of the second form of MoOCl₃ belongs to the monoclinic system (space group $P2_1/c$, cell parameters $a = 5.74$ Å, $b = 13.51$ Å, $c = 6.03$ Å, $\beta = 92.9°$) (13). The anions are hexagonally close packed, the molybdenum atoms occupying the octahedra, thus producing an infinite zigzag chain, the oxygen atom and one chlorine atom being in terminal positions (Fig. 5b). This structure is similar to those of TcCl₄, TcOCl₃, and ReOBr₃ (3).

When compared with the crystal structure of VOCl₃, the higher coordination number of the octahedral metal atom in these oxide trihalides leads to a more dense packing. This is shown by the smaller volume of 117.0 Å³ for NbOCl₃ compared to 127.3 Å³ for one formula unit of VOCl₃. Phase transitions under high pressure usually result in denser structures with higher coordination numbers for the atoms involved. Therefore, a high pressure phase transition for VOCl₃ may be postulated. As proposed in Fig. 6, this transition could yield a NbOCl₃ structure type by a relatively short translation of the chlorine atoms in the (100) plane (indicated by arrows in Fig. 6). The V–O bonds in the trigonal prismatic columns of solid VOCl₃ already positioned in the right direction, will then assume the infinite . . . –V–O–V– . . . bridging.
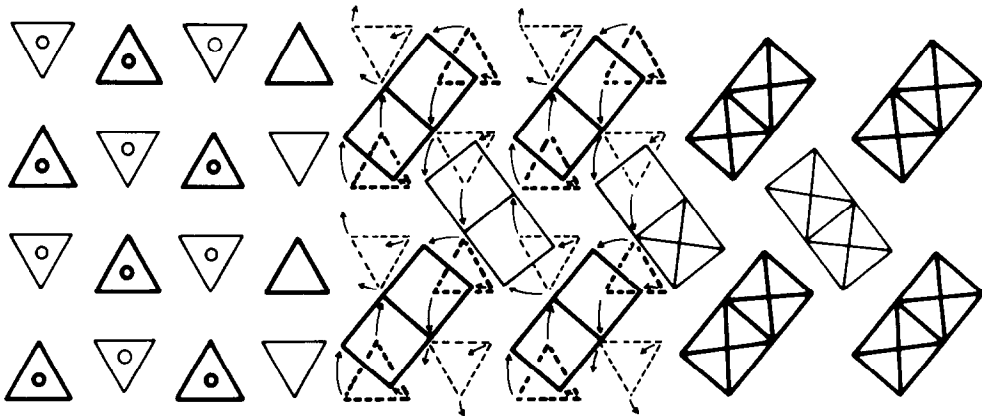

FIG. 6. A proposal for the mechanism of a possible phase transition of VOCl₃ into NbOCl₃ structure type under pressure.

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