

Zeeman Effect on ^{35}Cl NQR of $\text{TeCl}_4 \cdot \text{POCl}_3$ (NQR/Zeeman effect/ TeCl_4 -complex)

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Temperature dependence of ^{35}Cl NQR frequencies in $\text{TeCl}_4 \cdot \text{POCl}_3$ giving six NQR lines was observed in the range of 77 K to 400 K. Three of the NQR lines faded out near 285 K and the others could be detected up to 360 K. The Zeeman effect on the resonance lines was examined at 253 K using a single crystal. Each of these lines gave a single zero-splitting pattern and all the asymmetry parameters for these lines were negligibly small. On the basis of the crystal symmetry and the orientations of the Te - Cl and P - Cl bonds, the molecular structure of the title compound was deduced and the assignment of the NQR lines was performed with the aid of a CNDO/2 MO calculation.

The ^{35}Cl NQR spectrum of the donor-acceptor complex, $\text{TeCl}_4 \cdot \text{POCl}_3$ was previously reported by Kravchenko et al.¹⁾ They deduced on the basis of the spectral pattern and the intensity ratio of the resonance lines that the orbitals on the Te atom in the complex is hybridized sp^3d^2 and the complex has D_{3h} -octahedral configuration. The investigations on conductivity, vibrational spectra, and dipole moment in the solution of the 1:2 complexes, $\text{TeCl}_4 \cdot 2\text{D}$ (D = pyridine, tetramethylthiourea, etc.) revealed that the 1:2 complexes should be formulated as $[\text{TeCl}_3 \cdot 2\text{D}]^+ \text{Cl}^-$.^{2,4)}

The crystal of tellurium(IV) chloride is made up of isolated tetramers, $\text{Te}_4\text{Cl}_{16}$, which are formed with the arrangement of alternate TeCl_3^+ and bridged Cl^- ions at the apexes of the distorted cube, and the configuration around the Te atom is distorted-octahedral with three terminal Te - Cl bonds and three Te...Cl bridging bonds.⁵⁾ In the crystal of $\text{TeCl}_4 \cdot \text{AlCl}_3$, TeCl_3^+ and AlCl_4^- ions are bridged with three Cl atoms from the AlCl_4^- ion and infinite chains are formed.^{6,7)} The coordination around the Te atom is also octahedral. The similar structure can be found out in the crystal structure of $\text{TeCl}_4 \cdot \text{SbCl}_5$.⁷⁾ It is, therefore, necessary to take into account the possibility that $\text{TeCl}_4 \cdot \text{POCl}_3$ may have a polymeric structure $[(\text{TeCl}_3 \cdot \text{POCl}_3)^+ \text{Cl}^-]_n$ with bridging Cl atoms in addition to a discrete D_{3h} -octahedral structure.

Knowledge of the directions of the electric field gradient (efg) axes and other NQR parameters is helpful for investigating the molecular structure. The Zeeman effect on the NQR lines of a single crystal serves as a good tool for this purpose.

Experimental

The complex $\text{TeCl}_4 \cdot \text{POCl}_3$ was obtained by dissolving TeCl_4 in hot phosphoryl chloride and cooling the solution. A single crystal was grown by the Bridgeman technique. Then a small excess of POCl_3 was added to the complex to avoid decomposition of the complex. The resonance lines were observed using a superregenerative oscillator. The Zeeman effect was measured by means of the zero-splitting cone method at 253 K. The desired temperature was attained within ± 1 K by controlling the boiling rate from liquid nitrogen. The magnetic field was supplied with a Helmholtz coil with a field strength of about 20 mT.

Results and Discussion

The complex $\text{TeCl}_4 \cdot \text{POCl}_3$ gave a widespread ^{35}Cl NQR spectrum consisting of six resonance lines at 77 K. Temperature dependence of the NQR frequencies are shown in Fig. 1. The resonance lines are termed ν_1, ν_2, \dots , from the lower frequency to the higher. The ν_3, ν_4 , and ν_5 lines faded out near 285 K and the remaining lines near 360 K. The ν_6 line was more intense than the ν_1 and ν_2 lines having, instead, broader line-widths. Although the intensity of the ν_6 line was estimated to be twice that of the ν_1 or ν_2 line previously,¹⁾ the area ratio of the lines seems not to be necessarily the case.

Figure 2 shows the zero-splitting patterns on the ^{35}Cl Zeeman lines in $\text{TeCl}_4 \cdot \text{POCl}_3$ at 253 K. A single Zeeman locus was obtained from each resonance line, suggesting that the crystal is triclinic and all of the equivalent bonds

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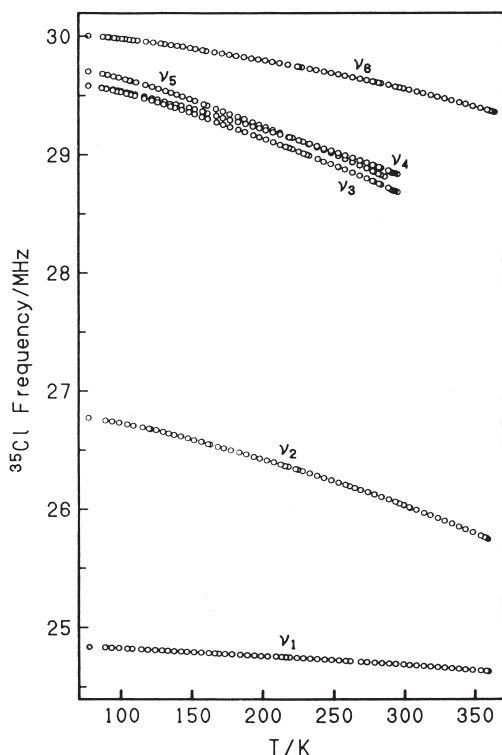


Fig. 1. Temperature dependence of ^{35}Cl NQR frequencies in $\text{TeCl}_4 \cdot \text{POCl}_3$.

are parallel or antiparallel to one another in the crystal. The NQR parameters calculated from the Zeeman loci are listed along with the frequencies in Table 1. The asymmetry parameter (η) for each resonance line is negligibly small. The double bond characters of the Te - Cl and P - Cl bonds, therefore, are insignificant.

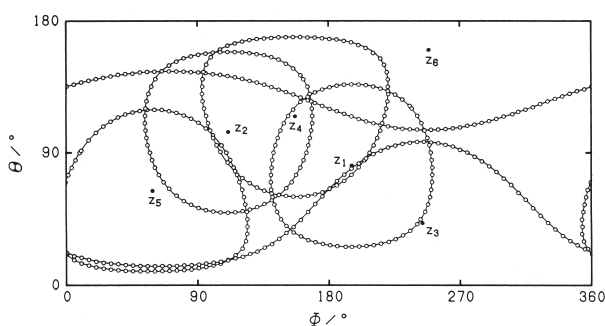


Fig. 2. Zero-splitting patterns of ^{35}Cl lines in $\text{TeCl}_4 \cdot \text{POCl}_3$ at 253 K. z_i indicates the direction of the efg z axis for the i line.

The angles between the M - Cl bonds (M=Te or P) were deduced, assuming that the efg z axis is parallel to the bond direction. The results are shown in Table 2 where the Cl atom contributing to the i line is termed Cl_i . The ν_3 , ν_4 , and ν_5 lines are assigned to the Cl

Table 1. NQR aparameters for $\text{TeCl}_4 \cdot \text{POCl}_3$ at 253 K and NQR frequencies at 77 K.

Line ^{a)}	Frequency (MHz)		e^2Qqh^{-1} (MHz)	Assignment
	77K	253K		
1	24.830	24.717	0.048	Te - Cl
2	26.758	26.219	0.030	Te - Cl
3	29.573	28.893	0.017	P - Cl
4	29.576	29.009	0.039	P - Cl
5	29.696	28.983	0.024	P - Cl
6	29.997	29.672	0.021	Te - Cl

a) The frequencies at 77 K in ref. 1 are 24.282, 26.574, 29.570, 29.754, and 29.994 MHz. The line of 29.570 MHz corresponds to the ν_3 and ν_4 lines.

atoms of the POCl_3 group, because the P - Cl bonds orient nearly at the tetrahedral angle to one another and the remaining lines to the Cl atoms bonded to the Te atom. The angles, $\angle \text{ClPCl}$, are 106.4° on average. These values are in good agreement with the mean values, 106.2° in $\text{SnCl}_4 \cdot 2\text{POCl}_3$,⁸⁾ 106.4° in $\text{SbCl}_5 \cdot \text{POCl}_3$,^{9,10)} and 106.6° in $\text{NbCl}_5 \cdot \text{POCl}_3$.¹⁰⁾

Table 2. Angles (degrees) between the bonds in $\text{TeCl}_4 \cdot \text{POCl}_3$

Bond	Te - Cl ₁	Te - Cl ₂	Te - Cl ₆	P - Cl ₃	P - Cl ₄	P - Cl ₅
Te - Cl ₂	92.88					
	(87.12) ^{a)}					
Te - Cl ₆	93.43	91.26				
	(86.57)	(88.74)				
P - Cl ₃	123.69	128.55	117.81			
	(86.57)	(51.54)	(62.19)			
P - Cl ₄	129.49	44.39	67.75	106.15		
	(50.51)	(135.61)	(112.25)	(52.5)		
P - Cl ₅	54.63	64.13	135.59	106.19	106.83	
	(125.37)	(115.87)	(44.41)			
O - P ^{b)}	122.4	62.5	134.5	112.8	112.2	112.2
	(57.6)	(117.5)	(45.5)			

a) The values in parentheses were supplementary angles.

b) Deduced from the orientations of the P - Cl bonds, assuming that the P - O bond lies on an approximate threefold axis.

The fade-out of the ν_3 , ν_4 , and ν_5 lines is expected for the Cl atoms of POCl_3 as a consequence of reorientation of the PCl_3 moiety around the P - O bond. The temperatures of the fade-out are near 180 K in $\text{SnCl}_4 \cdot 2\text{POCl}_3$ and near 260 K in $\text{SbCl}_5 \cdot \text{POCl}_3$.¹¹⁾ The higher fade-out temperature in $\text{SbCl}_5 \cdot \text{POCl}_3$ was ascribed to the intramolecular partial donor-acceptor bonding between the P atom and the Cl atom bonded to the Sb atom.¹¹⁾ The

fade-out temperature in $\text{TeCl}_4 \cdot \text{POCl}_3$ is higher by about 20 K than in the complex of SbCl_5 . A similar interaction appears to exist in the crystal of $\text{TeCl}_4 \cdot \text{POCl}_3$. The temperature coefficient of the ν_1 line is less negative than those of the other lines. It is therefore presumed that the Cl_1 atom in $\text{TeCl}_4 \cdot \text{POCl}_3$ may likewise participate in hindering the reorientation of the POCl_3 moiety.

Figure 3(a) shows the $\text{TeCl}_4 \cdot \text{POCl}_3$ octahedral structure of $\text{TeCl}_4 \cdot \text{POCl}_3$ previously proposed.¹⁾ The Cl-Te-Cl bond angles close to 90° appear to satisfy this structure. However, such an asymmetrical atomic arrangement should distort the octahedron, and hence the two Te-Cl bonds situated in the trans position to each other should no longer be colinear. In such a case, the ν_6 line should give two Zeeman loci close to each other, corresponding to the bond directions. Therefore, the $\text{TeCl}_4 \cdot \text{POCl}_3$ octahedral model is not reconciled with the results of the Zeeman effect.

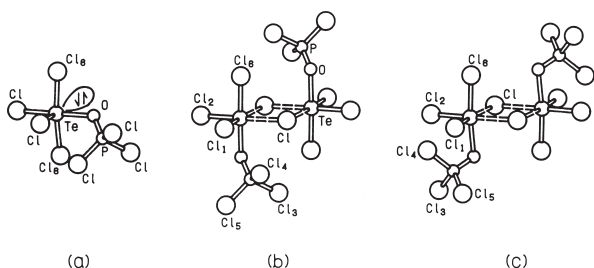


Fig. 3. Assumed molecular structures of $\text{TeCl}_4 \cdot \text{POCl}_3$.

When the structure of $\text{TeCl}_4 \cdot \text{POCl}_3$ is formulated as $[(\text{TeCl}_3 \cdot \text{POCl}_3)^+ \text{Cl}^-]_n$, it comes into question what value of n satisfies the requirement that the $\text{TeCl}_3 \cdot \text{POCl}_3$ fragments orient in the same or opposite directions to each other in the crystal. In the case of $n=1$, the atomic arrangement around the Te atom should be trigonal-pyramidal with a lone pair since the Te^+ ion has five electrons in the valence shell. The results of the Zeeman effect requires that two Te-Cl bonds lie in the equatorial plane. However, any of the Cl-Te-Cl angles are too small compared with an ideal bond angle (120°) in the equatorial plane, even though any cause, like repulsion between the lone pair and the bonding pairs, considerably decreases the bond angles.

In the case of $n=2$, the molecule is presented as a dimer with two bridging Cl atoms. Two plausible structures with an inversion center are shown in (b) and (c) of Fig. 3, considering steric repulsion and supplemental

angles between the bonds. The structure (c) closely resembles that of $[\text{TiCl}_4 \cdot \text{POCl}_3]_2$.¹²⁾ If the bridging bonds are symmetrical with the equal $\text{Te} \dots \text{Cl}$ distances, the NQR spectrum should consist of slightly separated lines and a line fairly separated from them because it is expected that the two terminal Te-Cl bonds trans to the bridging Cl atoms are alike in bond character and the Cl atom trans to the POCl_3 group is different in character from them.

In the case of $2 < n < \infty$, a $2n$ -membered ring composed of the Te and bridging Cl atoms is formed. This ring cannot be composed without the $\text{TeCl}_3 \cdot \text{POCl}_3$ fragments different in orientation from others. This does not satisfy the requirement that the crystal is triclinic.

At first thought an infinite chain ($n = \infty$) appears to be a satisfactory structure. If the bent bridging bonds connect the $\text{TeCl}_3 \cdot \text{POCl}_3$ fragments, a satisfactory structure cannot be obtained. This is seen by performing the following operations on the structure (b) or (c) of Fig. 3. First, the Cl_1 atom and the bridging Cl atom trans to the Cl_1 atom in one of the $\text{TeCl}_3 \cdot \text{POCl}_3$ fragments are inverted through the Te atom, and secondly, another fragment is rotated by 180° around its Te-Cl bond. The chain is completed by connecting the dimeric unit thus formed. However, the moved atoms, Cl_1 and Cl_2 , overlap each other.

If the bridging bonds are symmetric and the bridging Cl atom lies on the inversion center, the infinite zig-zag chain can be completed. The crystal composed of such chains is no longer triclinic because a two-fold screw axis exists within the chains, and, in addition, two of the terminal Te-Cl bonds are equivalent. The molecular structure satisfying the results of Zeeman effect, therefore, is restricted to the dimers.

Another problem is determining which Cl atom contributes to which resonance line. Unfortunately, this problem cannot be solved only on the basis of the results of the Zeeman effect. With the aid of CNDO/2 MO calculations,¹³⁾ the assignment of the NQR lines to particular Cl atoms was tried for two types of the dimers. The orientations of the TeCl_3 and POCl_3 moieties were deduced on the basis of the angles between the bonds. Taking into account the supplementary angles between the Te-Cl and P-Cl bonds, two typical configurations arise from the relative orientations of the TeCl_3 and POCl_3 moieties, as shown in Fig. 3.

The bond lengths (in pm) and bond angles (in degree)

were assumed by reference to those of the related compounds^{5,8,14,15} as follows;

Te - Cl=236, Te - O=234, P - O=146, P - Cl=195,

Te...Cl=277 and 287;

Cl₂TeO=173, TeClTe=98, TeOP=137, Cl₁TeO=92.6.

The Cl₁ atom is situated in the position trans to the short Te...Cl bonds. The CNDO/2 parameters were calculated by a previously described method.^{16,17} The field gradients were calculated using the method described by Kaplansky and Whitehead.¹⁸ As a rule, semi-empirical MO calculations tend to give higher NQR frequencies than the observed ones. The highest-frequency lines for the models (b) and (c) were 36.27 and 36.50 MHz, respectively. The frequencies shown in Fig. 4 are normalized in such a way that in each model the calculated highest frequency accords with the observed highest one at 77 K.

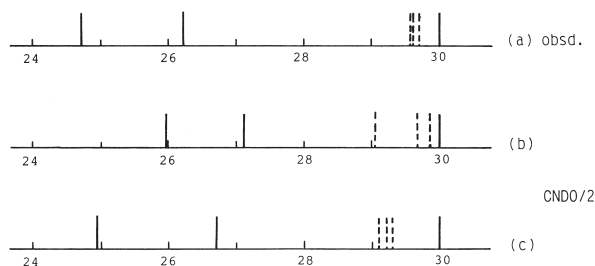


Fig. 4. Observed and calculated ³⁵Cl NQR spectra of [TeCl₄·POCl₃]₂. The bold lines correspond to the NQR lines of the Cl atoms bonded to the Te atom and the dashed lines to the lines of the Cl atoms bonded to the P atom. The calculated spectra of (b) and (c) correspond to the structures of (b) and (c) in Fig. 3.

The MO calculations on the two types of the dimers with the asymmetrical bridging bonds reproduce qualitatively the observed spectrum with respect to the Cl atoms of the Te-Cl bonds. One cannot say on the basis of the calculated spectra which of the structures (b) and (c) is plausible because of the assumed molecular geometry, though the whole spectrum for the structure (c) resembles the observed one in pattern. It is, however, clear that the NQR frequencies of the Cl atoms depend on the coordination positions of the Cl atoms with respect to the Te - Cl bonds. The ν_6 line is assigned to the Cl atom trans to the POCl₃ molecule, and the ν_1 and ν_2 lines are assigned to the Cl atoms trans to the shorter and longer Te...Cl bonds, respectively. As seen from the difference in frequency between ν_1 and ν_2 , more charges flow from the bridging atom to the Cl₁ atom than to the Cl₂ atom.

The resonance of the bridging Cl atom was not observed because the frequency was too low: the frequency was calculated to be nearly 6 MHz.

The ³⁵Cl frequencies in free POCl₃¹⁹ and the corresponding frequencies in TeCl₄·POCl₃ average 28.97 MHz and 29.62 MHz at 77 K, respectively. On complexing, the charge transferred from the Cl atoms of POCl₃ to the Te atom is estimated to be -0.04e. The corresponding charges in SnCl₄·POCl₃ and SbCl₅·POCl₃ were estimated to be -0.08e and -0.10e, respectively.¹¹ Therefore, the acceptor ability of TeCl₄ is fairly inferior to those of SnCl₄ and SbCl₅.

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