Chlorine-35 NQR and Structure of Tellurium(IV) Chloride

Keinosuke HAMADA, Hirofumi MORISHITA and Yasuko SANO

Chemical Laboratory, Faculty of Education,
Nagasaki University, Nagasaki

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Abstract

Some molecules of tetrahalides of sulfur, selenium, and tellurium have been indicated to be a trigonal bipyramid with one of the three equatorial positions unoccupied (point group $C_{2v}$) by the vibrational spectra, electron diffraction, or NMR of fluorine. The present paper reports that for the structure of TeCl$_4$ $T_d$ is excluded, but it is not sure whether the structure is $C_{2v}$ or $C_{3v}$ by NQR of TeCl$_4$ obtained.

Experimental

Tellurium(IV) chloride was prepared by the direct union of the elements$^{1,2}$ and measured at room temperature with a superregenerative oscillator. The resonance frequencies were measured with DELICA GRID-DIP meter (HAM-310).

Results and Discussion

The values of NQR frequency of Tellurium(IV) chloride consist of the two groups; $27.0 \pm 0.03$ MHz and $28.0 \pm 0.03$ MHz group. The $27.0$ MHz group contains a few resonance line around $27.0$ MHz and the $28.0$ MHz group, a couple of resonance lines around $28.0$ MHz. The resonance lines in both groups are very close each other and indistinguishable by the above grid-dip meter. Apparently the crystal packing of TeCl$_4$ places chlorines in numerous crystallographically distinct sites, that is, the compound will have neighbouring atoms in slightly differing spatial arrangements and positions, consequently leading to differing electric field gradients and hence separate NQR frequencies. However, about 1 MHz difference of the one group from the other
group is meaningful in determining the molecular structure of TeCl4.

The possible structures for TeCl4 are Td, C3v, and C2v.

For the TeCl4 molecule, electron diffraction3) has indicated a nuclear configuration approximating to a trigonal bipyramid with one of the three equatorial positions unoccupied (C2v). Such a structure is consistent with the observed electric dipole moment4).

For the SeF4 molecule, electron diffraction has been interpreted as indicating C2v symmetry5), and the Raman spectrum of the liquid makes C2v probable6). The fluorine MMR of SF4 appears as two peaks of equal area, concluding that the SF4 molecule is C2v structure7).

Dodd et al.8) have supported the conclusion that the point group of SF4 is C2v, based upon selection rules, states of polarization of Raman lines and infrared band contours.

The 1 MHz difference of NQR frequencies between the one resonance group and the other one means that tellurium(IV) chloride has two kinds of chlorines that are chemically non-equivalent. Accordingly, the highly symmetrical model, Td is excluded. However, the line intensities of both groups could not be measured yet, because of the weak signals. So it cannot be decided from the present NQR experiments whether the point group of TeCl4 is C2v, or C3v with three equatorial chlorines and one axial chlorine.

Now SeC14 and SeCl4 are being researched by NQR, Raman, and IR methods, in order to be compared with the results for TeCl4.

(P. S.) The crystal structure of TeCl4 has recently been determined from X-ray data9). The structure consists of isolated tetramers, Te4Cl16, which have a cubane-like structure with approximate Td symmetry. Every Te atom has three neighbouring terminal Cl atoms with an average distance of 2.511 Å. The coordination of the Te is completed to a distorted octahedron by three bridging chlorine atoms with much longer Te-Cl bond lengths (average 2.929 Å).

It has independently been reported10) that the Cl195 NQR spectrum of TeCl4 shows two groups of three lines, as reported in this Bulletin. That was previously interpreted in terms of a monomer C2v (or C3v) structure. But that is readily compatible with the tetrameric structure described in ref. 9.

3) D. P. Stevenson and V. Schomaker, J. Amer. Chem. Soc., 62, 1267 (1940)
7) G. H. Cady, Chemistry in Canada, Oct., 22 (1965)