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Nuclear Quadrupole Resonance of α-Dimethyltellurium Dichloride

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Chlorine nuclear quadrupole resonance has been reported on several tellurium compounds such as tellurium tetrachloride¹⁾ and complex salts²⁾. The ionicity of Te–Cl bonds in these compounds differs from each other considerably. It is of interest to compare the ionicity of these compounds with that of an organotellurium compound, α-dimethyltellurium dichloride. It is also interesting to study the Zeeman effect of the single crystal whose structure has been determined by X-ray analysis by Christofferson, Sparks and McCullough.³⁾

Experimental

The material was synthesized by the method of Vernon⁴⁾ from metallic tellurium and methyl iodide as raw material and was recrystallized twice from ethanol solution. Mp 96.6°C (lit.⁴⁾ 92°C). Found: Cl 31.85%. Calcd for $C_2H_6TeCl_2$: Cl 31.57%. X-Ray powder diffraction lines of this sample by X-ray diffractometer were in good agreement with those of literature.³⁾

A single crystal was grown from the melt by slow cooling in the vacuum-sealed cylindrical ampoule and used for the Zeeman measurement. Since this material decomposes gradually by heating, the crystal thus obtained was slightly colored and opaque. The *b*-axis of this monoclinic crystal was found by Laue photographs to lie about 30° from the axis of the ampoule.

Resonance signals were recorded with the usual self-quenching superregenerative oscillator detector.⁵⁾ The Zeeman field was generated by a Helmholtz coil with an intensity of about 20 gauss.

Results and Discussion

Two resonance absorptions were recorded with approximately the same signal to noise ratio, S/N, within the searching range of 40 to 12 MHz, as shown in Table 1.

Table 1. The NQR frequencies of α-dimethyltellurium dichloride at various temperatures

Temp. °K	Freq., MHz Cl_1	S/N	Freq., MHz Cl_2	S/N
77	18.124	4	15.685	2
205	18.028	4	15.463	2
298.3	17.855	4	15.323	3
340.0	17.752	4	15.268	3

Single crystal Zeeman effect study showed two different orientations for each of the two resonance lines. These two sets of orientations seem to arise from two molecules in the unit cell being related to each other by the operation of two-fold axial symmetry as seen from the crystal stucture. The valence angles of Cl–Te–Cl bonds of these molecules observed were 176±3° and are almost equal to 172±0.3° determined by crystal structure analysis.³⁾ The loci of angles of Zero-splitting, θ_0, were searched to find the assymmetry parame-

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1) A. Schmitt and W. Zeil, *Naturforsch.*, **18a**, 428 (1963).

2) D. Nakamura, K. Ito and M. Kubo, *J. Am. Chem. Soc.*, **84**, 163 (1962).

3) G. D. Christofferson, R. A. Sparks and J. D. McCullough, *Acta Cryst.*, **11**, 782 (1958).

4) R. H. Vernon, *J. Chem. Soc.*, **119**, 687 (1921).

5) C. Dean, *Phys. Rev.*, **96**, 1053 (1954).

ter, but it was difficult to obtain a more accurate value of θ_0 than 55±1° owing to an experimental error. The Zeeman effect study has guided us to the assignment of two resonances to each of the two chlorine nuclei in the molecule as shown in Table 2. This conclusion is also supported by the fact that each chlorine atom in the molecule has only one equivalent position in the unit cell and that the frequency difference of the two resonance lines is much larger than that usually expected from the effect of crystalline field.

TABLE 2. THE NQR FREQUENCIES OF Cl ATOMS, THE COVALENCY $(1-i)$ OF Te–Cl BONDS, THE EFFECTIVE CHARGE ρ OF Te ATOMS AND THE BOND LENGTHS OF SEVERAL Te COMPOUNDS

	Freq. MHz	$(1-i)$	ρ	Te–Cl Å
α-$(CH_3)_2TeCl_2$	18.124	0.44	1.18	2.48[c]
	15.685	0.38		2.54[c]
$TeCl_4$[a]	28.166	0.68	1.30	2.27
	27.382	0.40		2.40
$(NH_4)_2TeCl_6$[b]	15.137	0.32	2.08	2.54

a) Ref. 1. b) Ref. 2. c) Ref. 3.

Table 2 shows (1) the NQR frequencies of Cl atoms of several Te compounds, (2) the respective covalency $(1-i)$ of Te–Cl bonds in which i is the ionicity, using Townes and Dailey relation[6] with *s*-hybridization character assumed as 0.15, and (3) the effective charge ρ of Te atom and their bond lengths. The ionicity of Te–Cl bond of α-dimethyltellurium dichloride is larger than that of tellurium tetrachloride by the influence of methyl groups.

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[6] C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **23**, 118 (1955).