$(CH_3)_3CCOOSbCl_4$: Structure Determination by Zeeman Perturbed NQR*

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A single crystal of tetrachloro(0,0-pivaloylato)antimony(V) has been studied at 77 K, by Zeeman perturbed ^{35}Cl NQR, using a FT-NQR pulsed spectrometer. The four lines at zero-field, $\nu_1 = 27.6468$, $\nu_2 = 27.3070$, $\nu_3 = 25.7341$ and $\nu_4 = 25.3438$ MHz yield eight EFG tensors in the magnetic field, related by a twofold symmetry element in the crystal. The corresponding asymmetry parameters are $\eta_1 = 0.134$, $\eta_2 = 0.13$, $\eta_3 = 0.07$, and $\eta_4 = 0.09$. The molecular structure deduced from the relative orientations of the principal Z-axes of the EFG tensors confirms that the higher quadrupole coupling constants are associated with the chlorine atoms in equatorial positions, relative to the plane of the organic ligand, as predicted from NQR powder studies. It is concluded that the crystal structure is monoclinic with two (class m or 2) or four (class $2/m$) molecules per unit cell. The molecular packing is such that the planes formed by equatorial or axial chlorine atoms are approximately at right angles to their symmetry related images.

1. Introduction

Tetrachloro(0,0-pivaloylato)antimony(V) belongs to a group of antimony pentachloride chelate derivatives which have been the object of systematic NQR powder studies [1–3]. The ^{35}Cl resonance frequencies observed fall generally into two distinct groups, and it has been suggested that the two sets of frequencies are associated with chlorine atoms in axial or equatorial positions relative to the plane of the ligand. Since the principal Z-axis of the electric field gradient (EFG) tensor around the chlorine nucleus will almost certainly lie along the Sb–Cl bond, single crystal Zeeman perturbed NQR can give information about the relative orientation of these bonds in the molecule. Furthermore, it can give insight into the crystal structure of the compound, particularly useful in cases such as the present one, where there are no X-ray data available. We present here the results of such a study for $(CH_3)_3CCOOSbCl_4$. They have confirmed the general scheme of molecular structures previously proposed for these chelates [1] and allowed us to predict the molecular arrangement in the lattice.

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2. Experimental

The single crystal was prepared from the powder by zone melting in a glass ampoule, sealed under vacuum. The compound decomposes readily when exposed to the atmosphere and is light sensitive. The growth conditions did not allow a priori knowledge of the crystal's orientation in the laboratory system of coordinates.

Measurements were carried out at 77 K, in a magnetic field of 54.00 Gauss, using a Matec pulsed spectrometer. The one-circle goniometer system used and the details of data accumulation and treatment have been described elsewhere [4].

3. Results and Discussion

When the orientation of the crystal in the laboratory frame is not known a priori, the Zeeman NQR rotation pattern can generally only give information about the relative orientations of the magnetic field and EFG tensor coordinate systems. However, if the crystal has a symmetry element bigger than $\bar{1}$, the rotation patterns of the physically inequivalent sites can yield the orientation of the EFG tensor in the crystal lattice [5]. This is the case here: Figure 1 shows the typical appearance of the rotation patterns obtained. The curves passing through the experimental points are least-squares fits [6]. For each of the ^{35}Cl resonance frequencies measured in

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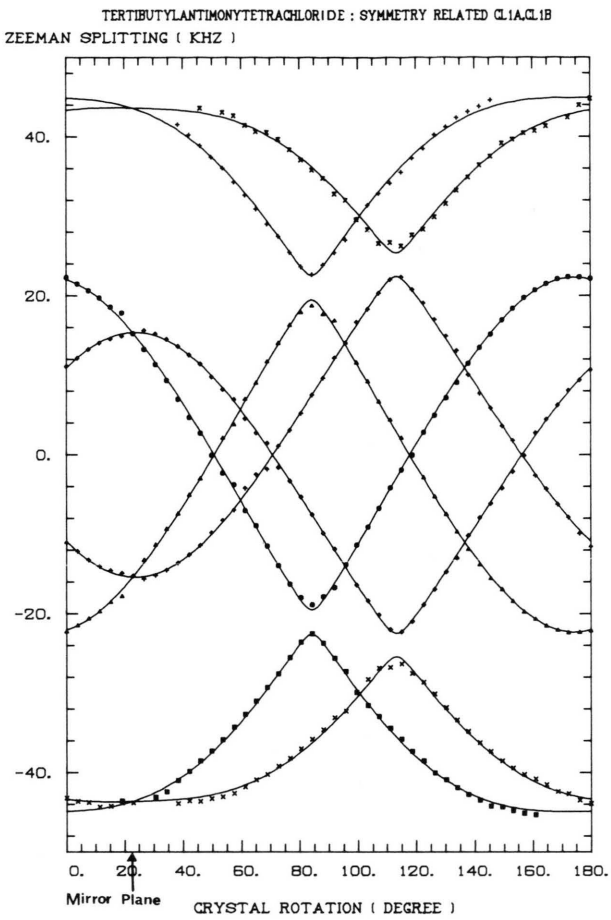

Fig. 1. ^{35}Cl NQR rotation pattern for the symmetry related sites CL1A and CL1B, $\nu_Q = 27.6468$ MHz and $\eta = 0.134$.

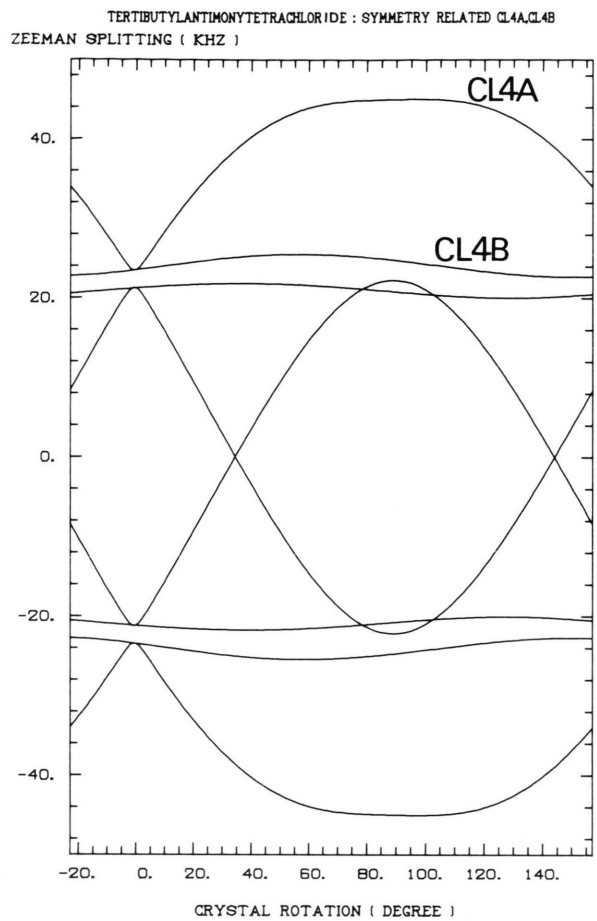

Fig. 2. ^{35}Cl NQR rotation pattern for the symmetry related sites CL4A, CL4B, calculated using the parameters listed in Table 1.

the powder material, two EFG tensors were observed in the magnetic field, showing the presence of either a twofold axis or a mirror plane. We shall assume, from now on, that it is a twofold axis. Furthermore, it is apparent from this figure that all the lines cross at the same point, for a rotation angle $\beta = 23°$. This crossing point corresponds to the angle in the rotation cycle at which the Zeeman field crosses tha plane perpendicular to the twofold axis, and it therefore identifies the position of this plane relative to the laboratory coordinates. All the necessary information to completely determine the orientation of the EFG tensors in the crystal is then available [5].

The quadrupolar data obtained from the theoretical fits [5, 6] of the experimental rotation patterns for the four chemically inequivalent chlorine atoms are listed in Table 1. For the two high-frequency chlorine nuclei, CL1 and CL2, good experimental patterns were obtained for both EFG tensors, to yield reasonably accurate values for the asymmetry parameters. However, for the low-frequency sites, CL3 and CL4, only one of the Zeeman patterns from the symmetry related tensors could be fitted. The reason for the poor experimental results for CL3B and CL4B is apparent from the table, where the values reported for these sites are generated by symmetry rotations from those of CL3A and CL4A, respectively. In both cases, the angle α is close to 90°, so that, relative to these two tensors, the Zeeman field is rotating in a plane perpendicular to the EFG Z-axis. In the experimental conditions

Table 1. Quadrupole parameters from theoretical fittings of the experimental data**.

Site	$\nu(^{35}Cl)$ / MHz	η	$e^2 \Phi_{zz} Q h^{-1}$ / MHz	α	β_0	γ
CL1A	27.6468	0.134 ± 0.006	55.129 ± 0.015	− 29.09	0.21	86.34
CL1B				− 4.30	151.20	−11.00
CL2A	27.3070	0.13 ± 0.02	54.461 ± 0.050	75.18	19.29	81.55
CL2B				− 3.40	76.00	12.30
CL3A	25.7341	0.07 ± 0.03	51.426 ± 0.043	− 8.40	96.30	−31.00
CL3B				− 96.23*	179.54*	60.38*
CL4A	25.3438	0.09 ± 0.02	50.619 ± 0.027	− 5.70	89.30	−39.30
CL4B				− 92.88*	76.02*	154.60*

* Calculated from the measured values of the symmetry-related A sites.
** The magnetic field rotation axis was found to be tilted by the angle $\delta = 40.8°$ from the monoclinic axis. Angles are expressed in degrees.

Table 2. Direction cosines of the principal axes of the EFG tensors in the crystal coordinate system X_C, Y_C, Z_C.

Site	EFG tensor axis	X_C	Y_C	Z_C
CL1A	X_E	−.4854	−.5222	−.7012
	Y_E	.0274	.7925	−.6093
	Z_E	.8738	−.3150	−.3704
CL1B	X_E	.4854	.5222	−.7012
	Y_E	−.0274	−.7925	−.6093
	Z_E	−.8738	.3150	−.3704
CL2A	X_E	.9511	−.0.310	−.3074
	Y_E	.1927	−.7183	.6685
	Z_E	.2415	.6951	.6772
CL2B	X_E	−.9511	.0310	−.3074
	Y_E	−.1927	.7183	.6685
	Z_E	−.2415	−.6951	.6772
CL3A	X_E	.8602	−.3180	−.3986
	Y_E	−.4982	−.6906	−.5243
	Z_E	−.1086	.6496	−.7525
CL3B	X_E	−.8602	.3180	−.3986
	Y_E	.4982	.6906	−.5243
	Z_E	.1086	−.6496	−.7525
CL4A	X_E	−.7730	.4662	.4302
	Y_E	.6343	.5550	.5382
	Z_E	−.0122	−.6889	.7247
CL4B	X_E	.7730	−.4662	.4302
	Y_E	−.6343	−.5550	.5382
	Z_E	.0122	.6889	.7247

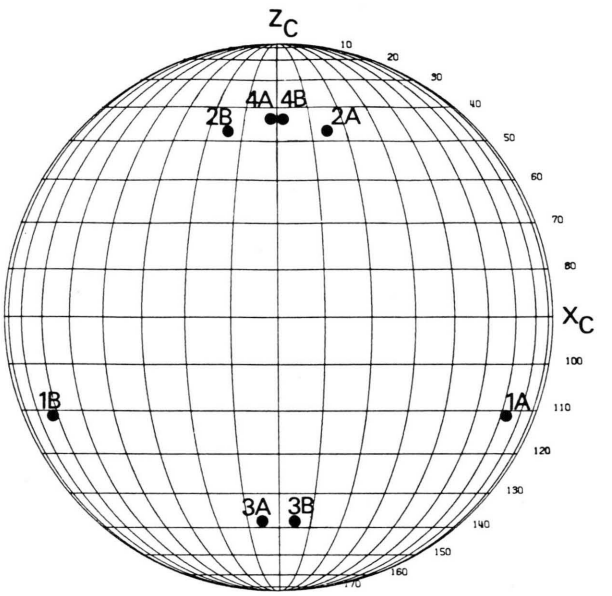

Fig. 3. Directions of the principal Z-axes for the eight EFG tensors in the assumed crystalline model.

used [4], this means that this axis is almost parallel to the direction of the rf-field, resulting in line intensities virtually equal to zero [7] for many orientations of the magnetic field. A typical rotation pattern for this kind of situation is represented in virtually undetected, while probably masking the exact position of the CL4A lines for certain orientations of the magnetic field during the rotation cycle.

Table 2 lists the direction cosines of the principal axes of the EFG tensors in the crystal-fixed coordinate system, and Table 3 gives the relative orientations of Sb−Cl bonds, assuming that they coincide with the Z-axes of the EFG tensors, as is generally the case. From this table and Fig. 3 it is clear that the A sites form one molecule while the B set belongs to its symmetry related image. The resulting molecular structure, represented in Fig. 4, is in agreement with the slight distortion from octahedral arrangement around the antimony atom found in X-ray studies of similar compounds [2]. The angles

Table 3. Relative orientations of the principal Z-axes of the EFG tensors and the angles between them and the monoclinic axis Z_C *.

EFG tensor	CL1A	CL1B	CL2A	CL2B	CL3A	CL3B	CL4A	CL4B
CL1A	111.74							
CL1B	136.51	− 111.74						
CL2A	105.00	104.06	−47.38					
CL2B	104.06	105.00	94.75	47.38				
CL3A	91.19	54.67	94.84	159.21	− 138.81			
CL3B	54.67	91.19	159.21	94.84	97.62	138.81		
CL4A	93.56	118.34	90.51	13.45	172.53	84.31	43.56	
CL4B	118.34	93.56	13.45	90.51	95.69	172.53	92.90	− 43.56

* The diagonal values (i, i) represent the angles between the EFG tensors' Z-axes and the Z_C axis.

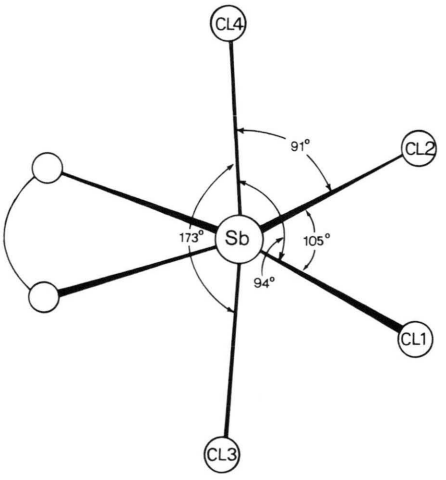

Fig. 4. Molecular structure of $(CH_3)_3CCOOSbCl_4$ from the Zeeman NQR study.

between the Z-directions of the CL1 and CL2 EFG tensors and the normal to the plane containing the axial chlorines (CL3, CL4) were calculated to be 35.5 and 39.5°, respectively, confirming that the Sb−Cl bounds in equatorial positions form a angle bigger than 90° and indicating a small deviation of the axial plane from the bisector of the angle between those bonds. The plane of the axial chlorine atoms forms an angle of 92.5° with that of the equatorial sites.

The molecular structure represented in Fig. 4 and the results on Table 1 show that chlorine nuclei in equatorial positions yield higher quadrupole resonance frequencies than those in axial positions, as had been suggested from the NQR powder studies and is in agreement with the relative lengthes of the equatorial and axial Sb−Cl bonds from X-ray data on similar chelates [1].

We have assumed throughout this discussion that the splitting observed in the rotation patterns is the result of symmetry-related EFG tenors. Another possible origin could be the existence of two differently oriented crystallites in the sample. However, in such cases one of the crystallites is generally more abundant than the other, so that one set of lines would be consistently weaker than the other throughout the rotation cycle. This was certainly not the case in our experiment. Furthermore, several attempts were made at preparing the single crystal, some without success. In the latter, the Zeeman perturbed NQR spectra contained too many lines to be resolved and were obviously not single crystal spectra. We therefore conclude that the crystal structure must be monoclinic, with point symmetry 2, m or $2/m$, depending on whether the molecules are related by a twofold axis, a mirror plane, or both. The molecular packing is such that the axial and equatorial planes within each molecule are inclined at roughly 45° to the monoclinic axis and at approximately right angles to their symmetry related images.

One would have hoped to be able to draw some conclusions on the nature of the molecular bonding from the asymmetry parameter data. However, at least for the axial sites, the smallness of η as well as the error involved prevent any serious analysis. For the equatorial positions, we found that the Y-components of the EFG tensors are virtually parallel to each other and parallel to the Z-components of those in axial positions, suggesting that they may lie along the chlorine p-orbitals perpendicular to the

plane of the ligand, while the X-components were found to lie very close to this plane. This implies that the origin of the asymmetry parameter cannot be simply ascribed to delocalization in a π-system having a nodal plane which contains the antimony atom and the carboxylate group.

Acknowledgements

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