Nuclear Quadrupole Resonance Investigation of the Comparative Differences Between Hexachloro-stannate, -tellurate, and -plumbate resulting from Cationic Effects

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N.q.r. frequencies of 14 salts of $SnCl_6^{2-}$, $TeCl_6^{2-}$, and $PbCl_6^{2-}$ have been recorded in an effort to observe possible differences in anion distortion which could result from the ' inert ' pair electrons of Te^{IV}. There is no evidence of stereochemical activity of the Te^{IV} ' inert ' pair as might be indicated by an increase in the number of chlorine resonance frequencies and/or anomalous changes in bond ionicity in any of the compounds studied. $PbCl_6^{2-}$ appears to be more sensitive to the cation than $SnCl_6^{2-}$ but the $TeCl_6^{2-}$ ion is less sensitive. It is concluded that anion sensitivity to the cation is not readily predictable on the basis of the size alone.

THE tellurium atom in $TeCl_6^{2-}$ has seven electron pairs in its valency shell. Vibrational,[1] *X*-ray,[2-4] and n.q.r.[5,6] data gathered for this ion indicate that it assumes O_h symmetry both in the solid state and in solution. Consequently, it is cited as an exception to the valency shell electron-pair repulsion (VSEPR) theory advanced by Gillespie and Nyholm.[7] The VSEPR theory predicts a distorted six-co-ordinate structure for $TeCl_6^{2-}$. The seventh electron pair instead becomes ' stereochemically inert ' (in terms of angular effects) by occupying the a_{1g}* MO located primarily on the tellurium atom.[8,9]

With the exception of vibrational data[1] and a preliminary report of the crystal structure of pyridinium hexachlorotellurate(IV) ($R = 0{\cdot}18$)[3] and vibrational data for $(Ph_2I)_2TeCl_6$,[1] all structural and spectroscopic information known to us deals with compounds in which the cation has cubic or spherical symmetry. As a result the $TeCl_6^{2-}$ ion lies at a cubic crystal lattice site. It is not clear how much this high site symmetry influences the apparent desire of the $TeCl_6^{2-}$ ion to remain rigorously octahedral.[10]

In the present investigation $TeCl_6^{2-}$ salts were prepared in which the counter-ion is of sufficiently low symmetry that the anion site will be very distorted, and the ^{35}Cl n.q.r. spectrum of the anion was recorded. N.q.r. spectroscopy is a useful technique in studies of this kind because inequivalency in the chlorine atoms is readily revealed by the number of signals observed. In addition, the $PbCl_6^{2-}$ salts were examined because, of the main-group element hexahalogenometallates, the $PbCl_6^{2-}$ ion most closely resembles the $TeCl_6^{2-}$ ion in size. These comparisons enable the importance of the size difference of the anions to be evaluated as it relates to the cationic effect. Hereinafter it will be assumed that the cationic effect is any effect that the cation has upon the anion, whether it be an electrostatic contribution to the electric-field gradient or a static polarization of the anion.

EXPERIMENTAL

$SnCl_6^{2-}$ *and* $TeCl_6^{2-}$ *Salts*.—The tin and tellurium compounds were prepared in the following general manner.[11] $SnCl_4,5H_2O$ (5 g) was dissolved in 1M-HCl (15 ml), or TeO_2 (5 g) was dissolved in 12M-HCl (15 ml). A slight excess of the cation chloride salt was dissolved in the minimum of water, and the two solutions were mixed. Crystallization occurred immediately or after slow evaporation. The compounds were carefully recrystallized from dilute HCl and dried (P_2O_5) in a vacuum desiccator. The preparation of K_2TeCl_6 presents a problem because of simultaneous precipitation of KCl. The following procedure was adopted. $TeCl_4$ (10·0 g, 0·037 mol) was dissolved in 1M-HCl (10 ml). KCl (2·0 g, 0·027 mol) was dissolved in H_2O (6 ml). The solutions were mixed and allowed to evaporate very slowly for ten days. Pure crystals of K_2TeCl_6 were collected by use of a glove-bag filled with N_2, and dried (P_2O_5).

$PbCl_6^{2-}$ *Salts*.—Lead acetate (5 g) was dissolved in concentrated hydrochloric acid (25 ml) and this was filtered into a slight excess of the cation chloride solution dissolved in concentrated hydrochloric acid, and cooled. The yellow precipitate was filtered off. It was redissolved in boiling concentrated hydrochloric acid while chlorine was passed into the solution. Chlorine was passed during cooling, and the crystals were immediately filtered off and dried (NaOH) in a vacuum desiccator.

Analyses.—All compounds were analysed for Te and Sn. Tellurium was determined gravimetrically by converting the salts into TeO_2 according to Vogel's method.[12] Tin was determined gravimetrically as the *N*-benzoylphenylhydroxylamine complex.[13]

N.q.r. Spectra.—The spectra were recorded as described

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[1] D. M. Adams and D. M. Morris, *J. Chem. Soc.* (*A*), 1967, 2067; P. J. Hendra and Z. Jovic, *ibid.*, 1968, 600; J. A. Creighton and J. H. S. Green, *ibid.*, p. 808.

[2] A. C. Hazell, *Acta Chem. Scand.*, 1966, **20**, 165; G. Engel, *Z. Krist.*, 1935, **90**, 341.

[3] E. E. Aynsley and A. C. Hazell, *Chem. and Ind.*, 1963, 611.

[4] V. A. Angoso, H. Onken, and H. Hahn, *Z. anorg. Chem.*, 1964, **328**, 225.

[5] D. Nakamura, K. Ito, and M. Kubo, *J. Amer. Chem. Soc.* 1962, **84**, 163.

[6] T. L. Brown and L. G. Kent, *J. Phys. Chem.*, 1970, **74**, 3572.

[7] R. J. Gillespie and R. S. Nyholm, *Quart. Rev.*, 1957, **11**, 339.

[8] D. S. Urch, *J. Chem. Soc.*, 1964, 5775.

[9] T. B. Brill, Z. Z. Hugus, jun., and A. F. Schreiner, *J. Phys. Chem.*, 1970, **74**, 2999.

[10] Another possible means of distorting the anion could be effected by placing strong electrostatic forces nearby. Compounds of $TeCl_6^{2-}$ having highly charged cations which could distort the $TeCl_6^{2-}$ ion have been prepared (A. Catalina, *Acta Salamanticensia Ser. Cienc.*, 1961, **3**, 77). In every case, however, the cation remains hydrated in the lattice which effectively nullifies its polarizing power.

[11] W. C. Fernelius, *Inorg. Syn.*, 1946, **2**, 188.

[12] A. I. Vogel, ' Quantitative Inorganic Analysis,' John Wiley and Sons, Inc., New York, 1961, p. 509.

[13] A. I. Vogel, ref. 12, p. 506.

previously.[14] The error in frequencies can be *ca.* 0·020 MHz if the wrong line of the resonance multiplet has been chosen as the centre peak. Otherwise it is *ca.* 0·005 MHz. ^{37}Cl signals were observed in several cases to confirm that ^{35}Cl spectra were being recorded. Many salts did not yield signals unless they were carefully recrystallized.

X-*Ray Powder Patterns*.—Powder patterns were obtained by use of a Debye–Scherrer camera and Cu-K_α radiation.

RESULTS

N.q.r. Spectra.—Data for the NH_4^+ [5] and Cs^+ [6] salts of $TeCl_6^{2-}$ have been reported previously and are in reasonable agreement with our frequencies. For the K^+ salt, the possibility of a weak resonance near 15·0 MHz has been mentioned.[5] $(Me_4N)_2TeCl_6$ was previously investigated but no signal was found.[5] Many of the $SnCl_6^{2-}$ frequencies have been reported and are in accordance with ours.[9,15] N.q.r. data for $(NH_4)_2PbCl_6$ and Cs_2PbCl_6 also have been reported.[6,15] Several compounds exhibit some signal asymmetry and this may be due to crystallographic inequivalence of the chlorine atoms. For example, in the pyridinium salts of $SnCl_6^{2-}$ and $TeCl_6^{2-}$ a single frequency is reported even though the line is asymmetric. Two resonances were found in the $PbCl_6^{2-}$ salt. From the known crystal structure [3] of $(pyH)_2TeCl_6$ two crystallographically inequivalent Cl atoms would be expected. If several unresolved signals are present, it is of little consequence to the interpretation of our results particularly when it is observed for all three anions.

^{35}Cl N.q.r. frequencies/MHz at 298 K [a]

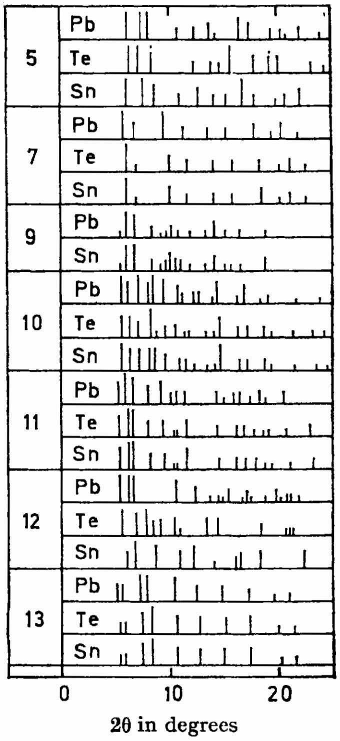
	Cation	$TeCl_6^{2-}$	$SnCl_6^{2-}$	$PbCl_6^{2-}$
1	K^+	15·13(18) 14·99(16)	15·06(25) [b, c]	
2	Rb^+	15·14(7)	15·60(2) [b,c]	
3	Cs^+	15·60(12) [d]	16·05(2) [c,d]	17·71 [d]
4	NH_4^+	14·98(25) [e]	15·45(4) [b,c]	17·05(4) [b,d]
5	$MeNH_3^+$	15·52(12)	15·81(20) [c]	17·50(6)
6	Me_3NH^+		16·63(10) [c]	
7	Me_4N^+	16·29(6)	16·67(5) [c]	18·54(15)
8	$Et_2NH_2^+$	15·91(7)		
9	Et_3NH^+	15·48(6)	14·94(7)	15·39(7)
10	$(pyH)^+$	16·49(7)	17·37(10)	19·44(8) 19·30(4)
11	$(2,6\text{-lutH})^+$	16·54(4)	17·02(4)	18·75(5)
12	$(4\text{-picH})^+$	16·68(10)	17·81(5)	19·87(4) 19·63(8) 18·58(8)
13	$(4\text{-ClpyH})^+$	16·66(8) 16·37(7) 15·56(5) 35·93(15) [g]	17.52(5) 17·32(4) 14·97(4) 35·92(20)	19·71(8) [f] 15·53(4) 35·93(20) [g]
14	$Mg(H_2O)_6^{2+}$	15·55(10)	15·83(6) [c]	

$(pyH)^+$, pyridinium; $(lutH)^+$ = lutidinium; $(picH)^+$ = picolinium

[a] Parenthetical numbers are signal-to-noise ratios. [b] Ref. 15. [c] Ref. 9. [d] Ref. 6. [e] Ref. 5. [f] Very asymmetric. [g] Chlorine atom in the pyridinium ring. ν(^{35}Cl) in 4-chloropyridinium hydrochloride is 35·32(30) MHz at 298 K.

Structural Information.—In order validly to compare $SnCl_6^{2-}$, $PbCl_6^{2-}$, and $TeCl_6^{2-}$ salts having the same cation, they must be isostructural. The Rb^+, Cs^+, and NH_4^+ salts of all three anions are known to have the cubic antifluorite structure with space-group F_{m3m}.[2] K_2SnCl_6 [2] and $(Me_4N)_2SnCl_6$ [16] also have the antifluorite structure. The *X*-ray powder patterns of $(Me_4N)_2TeCl_6$ and $(Me_4N)_2PbCl_6$ are similar to that of the tin salt indicating that all three are isostructural.

$(pyH)_2TeCl_6$ is monoclinic [3] and its powder pattern is similar to those of $(pyH)_2SnCl_6$ and $(pyH)_2PbCl_6$. The $(2,4\text{-lutH})^+$ and $(4\text{-ClpyH})^+$ salts of three anions are isostructural, based on their powder patterns. However, there is no intensity and spacing resemblance among the $(4\text{-picH})^+$ salts of $SnCl_6^{2-}$, $TeCl_6^{2-}$, and $PbCl_6^{2-}$ and they probably have different structures. The $MeNH_3^+$ salt of $SnCl_6^{2-}$ is isostructural with $PbCl_6^{2-}$ but not $TeCl_6^{2-}$. $(Et_3NH)_2TeCl_6$ could not be dried sufficiently to obtain a powder pattern, but the $SnCl_6^{2-}$ and $PbCl_6^{2-}$ salts are apparently isostructural. These data are summarized in the Figure.



Positions and intensities of major peaks in the *X*-ray powder patterns of $SnCl_6^{2-}$, $PbCl_6^{2-}$, and $TeCl_6^{2-}$ salts. For numbers, see Table

DISCUSSION

Gillespie pointed out [17] that there is little room on the surface of the $TeCl_6^{2-}$ ion for an extra pair of electrons based on the Cl–Cl contact distances which are nearly twice the van der Waals radius of Cl. The van der Waals radii argument assumes that the Cl atoms are spherical,[18] which is doubtful in an MCl_6^{2-} salt, so that some *p* character could mix with the $5s^2$ electrons if the $TeCl_6^{2-}$ ion undergoes a static distortion due to the lattice symmetry. A decrease in ionic character (increase in n.q.r. frequency) as well as inequivalence in the chlorine atoms would be expected if the 'inert' pair becomes stereochemically active.[17] According to the Table, none of the $TeCl_6^{2-}$ compounds behaves

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[14] T. B. Brill and G. G. Long, *J. Phys. Chem.*, 1971, **75**, 1989.

[15] D. Nakamura, *Bull. Chem. Soc. Japan*, 1963, **36**, 1162.

[16] R. W. G. Wyckoff and R. B. Corey, *Amer. J. Sci.*, 1929, **18**, 437.

[17] R. J. Gillespie, *J. Chem. Educ.*, 1970, **47**, 18.

[18] H. A. Bent, *Fortschr. Chem. Forsch.*, 1970, **14**, 1.

anomalously compared with $SnCl_6^{2-}$ and it is reasonable to assume that the electrons occupying the a_{1g} * MO of the Te^{IV} remain ' stereochemically inert ' regardless of the site symmetry.

The results in the Table show that the $TeCl_6^{2-}$ ion is less sensitive to cationic effects than is $SnCl_6^{2-}$. This seems to be abnormal because the $TeCl_6^{2-}$ ion is larger than the $SnCl_6^{2-}$ ion (Sn–Cl = *ca.* 2·41 Å, Te–Cl = *ca.* 2·50 Å).[2] For this reason the $PbCl_6^{2-}$ ion, which is about the same size as $TeCl_6^{2-}$ (Pb–Cl = *ca.* 2·50 Å),[2] was examined. As expected $PbCl_6^{2-}$ is much more sensitive to the cation than $SnCl_6^{2-}$ and suggests that the sensitivity of an MCl_6^{2-} ion to the cation is not predictable simply on the basis of its size.

The $(4\text{-ClpyH})^+$ salts are interesting from the standpoint of n.q.r. spectroscopy. Particularly in the case of tin and lead, there is an unusually large splitting in the signals arising from the anion. Splittings of this magnitude do not normally arise from crystallographic inequivalence in the chlorine atoms and a complete crystal-structure analysis of the $SnCl_6^{2-}$ salt has been made [19] in order to reveal the source of the effect.

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[19] R. Gearhart, W. A. Welsh, T. B. Brill, and R. H. Wood, following paper.