

- BOEKELHEIDE, V. & LAWSON, J. A. (1970). *J. Amer. Chem. Soc.* **92**, 1558.
- DAVIS, B. R. & BERNAL, I. (1971). *J. Chem. Soc.* In the press.
- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP* Report ORNL-3794, Oak Ridge National Laboratory, Tennessee.
- MITCHELL, R. H. & BOEKELHEIDE, V. (1970). *J. Amer. Chem. Soc.* **92**, 1555.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
- VÖGTLE, F. (1970). *Liebigs Ann.* **735**, 193.
- VÖGTLE, F. & NEUMANN, P. (1970). *Chem. Commun.* p. 1464.

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## The Crystal and Molecular Structure of the 1:1 Compound Formed between Phosphorus Pentachloride and Tellurium Tetrachloride, Cl<sub>9</sub>PTe

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The compound Cl<sub>9</sub>PTe crystallizes in the orthorhombic space group *I2mb* with *Z*=8 and with cell dimensions *a*=12.10, *b*=16.64, *c*=12.52 Å. The structure contains discrete, approximately tetrahedral [PCl<sub>4</sub>]<sup>+</sup> cations, and polymeric chain anions in which each tellurium atom is surrounded by a distorted octahedron of chlorine atoms. The chain consists of octahedra linked by sharing two *cis* vertices. Using visually estimated three-dimensional photographically recorded data the structure was refined to a final *R* of 0.122.

### Introduction

The chemical status of the pentahalotellurate(IV) complex anions is by no means clear, even though several compounds have been prepared which apparently, from the elemental analysis, contain these ions. Tellurium tetrachloride is a tetrameric solid (Buss & Krebs, 1970), containing six coordinate tellurium atoms [3 Te-Cl at 2.32 Å (av) and 3 Te-Cl at 2.93 Å (av)]. Under suitable conditions tellurium tetrachloride reacts readily with chloride ions to form the octahedral [TeCl<sub>6</sub>]<sup>2-</sup> ion. Because of the chemical interest in species containing formal lone pairs of electrons, both the hexachloro- and hexabromotellurate(IV) ions have been structurally characterized by X-ray diffraction (Hazell, 1966; Das & Brown, 1966) and subjected to assorted vibrational spectroscopic assaults (see, for example, Adams & Downs, 1970; Adams & Lloyd, 1971 and references therein). It seems plausible that the addition of chloride ions to TeCl<sub>4</sub> occurs in a stepwise manner and that the species [TeCl<sub>5</sub>]<sup>-</sup> should exist. Ultraviolet and visible spectroscopy in acetonitrile solution gave evidence for a species, possibly [TeCl<sub>5</sub>]<sup>-</sup>, formed when equimolar amounts of TeCl<sub>4</sub> and [TeCl<sub>6</sub>]<sup>2-</sup> are mixed (Beattie & Chudzynska, 1967). Other studies have also provided evidence for [TeX<sub>5</sub>]<sup>-</sup> ions (X=Cl, Br) (Korewa & Smagowski, 1965; Korewa & Szponar, 1965), but since all these solution reactions are carried out in ionizing and potentially coordinating solvents, it may well be that such pentahalo species are sufficiently sol-

vated to influence the coordination geometry. The reported structure (Aynsley & Hazell, 1963) of uronium pentachlorotellurate (IV) is incorrect (Beattie, Chudzynska, Hulme & Aynsley, 1963).

In contrast to the chloro and bromo species the only known fluorocomplex of Te(IV) is the [TeF<sub>5</sub>]<sup>-</sup> ion which exists as discrete square pyramidal anions both in solid KTeF<sub>5</sub> (Edwards & Mouty, 1969; Mastin, Ryan & Asprey, 1970) and in solution from F-19 nuclear magnetic resonance experiments. The structure of β-Me<sub>2</sub>TeI<sub>2</sub> consists of [Me<sub>3</sub>Te]<sup>+</sup> [MeTeI<sub>4</sub>]<sup>-</sup>, the anion of which is square pyramidal with an axial methyl group (Einstein, Trotter & Williston, 1967).

Solid compounds apparently containing the [TeX<sub>5</sub>]<sup>-</sup> ion include [Et<sub>4</sub>N][TeCl<sub>5</sub>] (Creighton & Green, 1968) and the mixed haloanion in [Et<sub>4</sub>N][TeCl<sub>2</sub>Br<sub>3</sub>] (Ozin & Vander Voet, 1971). The system PCl<sub>5</sub>-TeCl<sub>4</sub> has been examined in AsCl<sub>3</sub> (Gutmann, 1953) and POCl<sub>3</sub> (Groeneveld, 1956; Groeneveld, 1952; Groeneveld & Zuur, 1953) and evidence for the compounds 2PCl<sub>5</sub>, TeCl<sub>4</sub>; PCl<sub>5</sub>, TeCl<sub>4</sub> and PCl<sub>5</sub>, 2TeCl<sub>4</sub> presented. Beattie has examined the vibrational spectra of the 1:1 compound Cl<sub>9</sub>PTe (Beattie, 1967; Beattie & Chudzynska, 1967) which gave clear cut evidence for the [PCl<sub>4</sub>]<sup>+</sup> ion. The structure of the anion is not clear but the observation of the chlorine isotope splitting pattern of ν<sub>1</sub> of the cation suggests a relatively simple structure.

An examination of the compound Cl<sub>9</sub>PTe was undertaken to establish the structure of the solid and in particular the nature of the anionic species present.

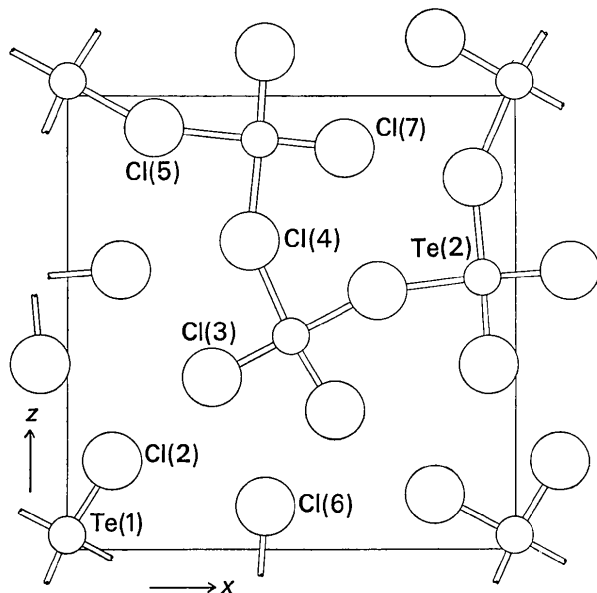


Fig. 1. The atoms lying on the mirror plane at  $y = \frac{1}{2}$  and forming part of the  $[\text{TeCl}_5]^-$  chain anion looking in the  $+y$  direction. Each tellurium atom is surrounded by two more terminal chlorine atoms to complete the distorted octahedral coordination.

## Experimental

### 1. Preparation and crystal growth

Tellurium tetrachloride was prepared by the chlorination of elemental tellurium (Suttle & Smith, 1950). Considerable variability in analysis between different preparations of  $\text{Cl}_9\text{PTe}$  was found (presumably) due to the formation of the 2:1 compound  $\text{Cl}_{14}\text{P}_2\text{Te}$ . The method finally adopted was to take equimolar amounts of phosphorus pentachloride and tellurium tetrachloride, dissolved in warm freshly distilled  $\text{POCl}_3$  and add the  $\text{PCl}_5$  solution to the  $\text{TeCl}_4$  solution. An immediate bright yellow precipitate of  $\text{Cl}_9\text{PTe}$  formed. (Found: Cl, 63.8, 62.7; Te, 25.6%. Calculated for  $\text{Cl}_9\text{PTe}$ : Cl, 66.8; Te, 26.7%. Calculated for  $\text{Cl}_{14}\text{P}_2\text{Te}$ : Cl, 72.4; Te, 18.6%) Crystals of the compound were prepared by sealing in an evacuated glass ampoule a small quantity of  $\text{Cl}_9\text{PTe}$  and phosphoryl chloride. Heating the ampoules at  $100^\circ$  for a few days followed by slow cooling yielded poor quality crystals. Selected crystals of the extremely moisture sensitive compound were mounted in Pyrex capillary tubes in a drybox. Two crystal morphologies were observed, one a plate-like shape and the second approximately octahedral. Single crystals of both types gave identical diffraction patterns. The density was obtained by flotation in the mixed solvent of bromoform-phosphoryl chloride.

### 2. Unit cell

The cell dimensions and space groups were established from Weissenberg and precession photographs.  $\text{Cl}_9\text{PTe}$ , M.W. 477.6; Orthorhombic:

$a = 12.10(2)$ ;  $b = 16.64(2)$ ,  $c = 12.52(2)$  Å;  
 $V = 2520.8$  Å<sup>3</sup>;  
 $D_m = 2.52 \pm 0.03$  (by flotation)  $\text{g.cm}^{-3}$ ;  $D_c = 2.51$   $\text{g.cm}^{-3}$  for  $Z = 8$ .

Linear absorption coefficient  $\mu$ , for  $\text{Cu K}\alpha$  ( $\lambda = 1.5418$  Å) radiation is  $379.6$   $\text{cm}^{-1}$  and for  $\text{Mo K}\alpha$  ( $\lambda = 0.7107$  Å) radiation is  $43.9$   $\text{cm}^{-1}$ .

The systematic absences  $hkl$  for  $h+k+l = 2n+1$  and  $hk0$  for  $h = 2n+1$ ,  $k = 2n+1$  indicated the space group  $I2mb$  (No. 46) or  $Imma$  (No. 74) and the non-centrosymmetric group  $I2mb$  was confirmed by the subsequent analysis. A projection of the unit cell viewed along the  $x$  axis is shown in Fig. 2.

### 3. Intensity data

The crystal used for the data collection was mounted about the  $a$  axis in a Pyrex capillary tube and had the approximate dimensions  $0.8 \times 0.15 \times 0.6$  mm. Data were recorded photographically by the multiple film equiinclination Weissenberg technique for the layers  $0kl$  to  $10kl$  with zirconium-filtered  $\text{Mo K}\alpha$  radiation; intensities were estimated visually by a means of a graduated wedge. 1408 independent reflexions were measured from one octant of reciprocal space of which 93 were considered as unobserved and given an intensity equal to one half the minimum observable. Lorentz and polarization factors were applied but no corrections for dispersion or absorption were made.

## Structure determination

The three-dimensional Patterson function was calculated. No satisfactory solution to the Patterson function could be found with  $Z = 8$  in the centrosymmetric space group  $Imma$ . However, the alternative space group yielded plausible tellurium positions, fully consistent with the large Patterson vectors in which two sets of independent Te atoms in fourfold positions  $4(b)$  were postulated. With scattering factors for neutral tellurium, chlorine and phosphorus atoms from *Inter-*

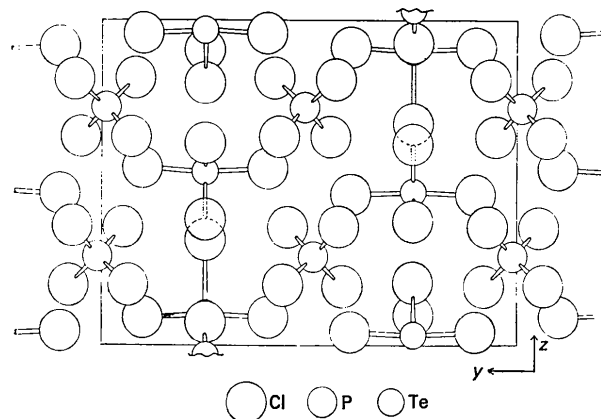


Fig. 2. Projection of the unit-cell contents from  $x = -0.005$  to  $x = 0.500$  viewed in the  $+x$  direction.

*national Tables for X-ray Crystallography* (1962), a structure factor calculation on the tellurium positions ( $R=0.40$ ) and a subsequent electron density synthesis gave strong indications of two chlorine atoms [Cl(1) and Cl(8)]. Repetition of this procedure eventually located all the atoms surrounding the tellurium positions [Cl(1) to Cl(8)]. Full-matrix least-squares refinement of the positional and isotropic thermal parameters of the located atoms [Te(1), Te(2) and Cl(1)–Cl(8)] using unit weights and level to level scale factors reduced the residual to 0.30. An electron density synthesis on the refined parameters gave five peaks defining the position of an approximately tetrahedral  $[\text{PCl}_4]^+$  ion. Further isotropic refinement with all atoms, unit weights and scale factors reduced the residual to 0.154. An empirical weighting scheme was obtained from an analysis of  $|\Delta F|$  vs.  $F_{\text{obs}}$  for various ranges of  $F_o$  [ $W=1/(A+BF_o)$  where  $A$  and  $B$  are constants for a particular range of  $F_o$ .  $F_o=10$  to 40 ( $A=7.7$ ,  $B=0.0256$ ), 40 to 160 ( $A=3.9$ ,  $B=0.0952$ ), 160 to 310 ( $A=-3.75$ ,  $B=0.1515$ ), 310 to 520 ( $A=900$ ,  $B=0.0$ )].  $A$  was set equal to 900 to heavily down-weight the 3 reflexions with  $F_o$  greater than 310 in the final range. Least-squares refinement (62 parameters) using the calculated weights reduced  $R$  to 0.138. Further refinement introducing anisotropic thermal parameters (110 parameters) gave a final  $R$  of 0.122 (excluding unobserved reflexions). This decrease in  $R$  is significant when measured by Hamilton's (1965) test. Examination of the final calculated structure factors revealed a number with large  $\Delta F$  values suggesting a possible error in a chlorine position. A difference Fourier synthesis showed no large positive or negative regions attributable to a misplaced atom. Some negative regions were observed close to the tellurium atoms.

The final positional and thermal parameters are recorded in Tables 1 and 2, and in Table 3 we detail the intramolecular distances and angles. Bond lengths around the tellurium atoms are shown in Fig. 3. Observed and calculated structure factors are listed in Table 4. No corrections were applied to the calculated bond lengths due to thermal motion of the atoms.

Nearly all the calculations were performed on the S.R.C. Atlas computer, Harwell using the X-RAY 63 system of crystallographic programs devised by J. M. Stewart.

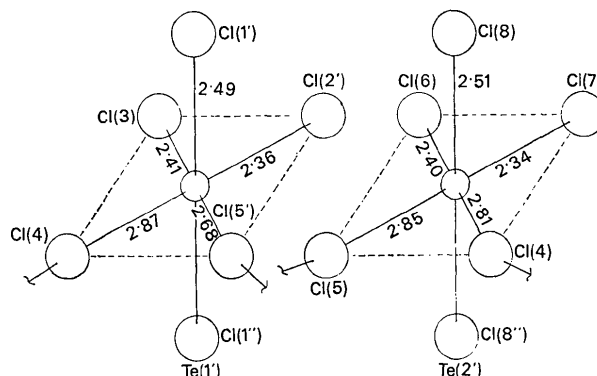


Fig. 3. Bond lengths around the tellurium atoms.

Table 1. Final positional parameters with standard deviations in parentheses

Values, except those denoted with an asterisk, are multiplied by  $10^5$ .

	$x/a$	$y/b$	$z/c$
Te(1)	0*	$\frac{1}{4}$ *	3165 (20)
Te(2)	92825 (37)	$\frac{1}{4}$ *	59750 (21)
Cl(1)	-527 (164)	10075 (43)	4120 (75)
Cl(2)	9900 (136)	$\frac{1}{4}$ *	19393 (103)
Cl(3)	32332 (148)	$\frac{1}{4}$ *	37981 (132)
Cl(4)	40698 (145)	$\frac{1}{4}$ *	67903 (95)
Cl(5)	19442 (150)	$\frac{1}{4}$ *	92901 (144)
Cl(6)	44079 (228)	$\frac{1}{4}$ *	9391 (92)
Cl(7)	62054 (159)	$\frac{1}{4}$ *	88417 (160)
Cl(8)	43181 (169)	9931 (48)	91379 (80)
P	21158 (91)	1040 (49)	27018 (82)
Cl(9)	29451 (128)	8069 (59)	18025 (107)
Cl(10)	11431 (123)	7186 (62)	36112 (100)
Cl(11)	30921 (130)	5164 (73)	63875 (96)
Cl(12)	12892 (121)	6318 (84)	81526 (94)

Table 2. Anisotropic temperature factors ( $\times 10^5$ ) with standard deviations in parentheses

$$T = \exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

Atoms located on the mirror (Te(1), Te(2), Cl(2)–Cl(7)) have  $\beta_{12}$  and  $\beta_{23}$  constrained to be zero due to atom site symmetry (Levy, 1956).

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Te(1)	432 (24)	206 (07)	401 (14)	—	21 (16)	—
Te(2)	417 (28)	237 (08)	444 (17)	—	20 (17)	—
Cl(1)	1026 (108)	201 (21)	787 (62)	-68 (52)	-8 (77)	-50 (29)
Cl(2)	643 (134)	328 (43)	582 (78)	—	-84 (71)	—
Cl(3)	367 (131)	514 (63)	968 (108)	—	-318 (87)	—
Cl(4)	754 (147)	467 (61)	547 (71)	—	49 (70)	—
Cl(5)	397 (131)	493 (62)	964 (121)	—	2 (94)	—
Cl(6)	1853 (229)	311 (41)	378 (64)	—	-37 (94)	—
Cl(7)	447 (155)	462 (59)	1146 (149)	—	-159 (102)	—
Cl(8)	1016 (118)	240 (24)	780 (66)	28 (58)	-53 (82)	15 (31)
P	476 (88)	241 (26)	674 (64)	23 (32)	-50 (47)	-4 (35)
Cl(9)	851 (114)	342 (32)	1205 (99)	0 (48)	414 (88)	75 (46)
Cl(10)	856 (121)	365 (35)	1070 (87)	78 (47)	363 (77)	-72 (44)
Cl(11)	874 (132)	504 (45)	974 (84)	-183 (61)	302 (78)	96 (51)
Cl(12)	692 (114)	647 (55)	971 (84)	157 (59)	188 (79)	-230 (53)

Table 3. *Intramolecular bond lengths and angles with standard deviations in parentheses*

The bridging chlorine atoms are indicated by \*.  
The eightfold equivalent positions of the space group  $I2mb$  are  $x, y, z$ ;  $x, \bar{y}, \bar{z}$ ;  $x, \frac{1}{2} - y, z$ ;  $x, \frac{1}{2} + y, \bar{z}$  together with the corresponding  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$  positions.

The singly primed atoms (') refer to atoms generated from the atoms in Table 1 by the symmetry operation  $\frac{1}{2} + x, y, \frac{1}{2} - z$ . Cl(1') and Cl(1'') as well as Cl(8) and Cl(8'') are related by the mirror plane at  $y = \frac{1}{4}$  ( $x, \frac{1}{2} - y, z$ ).

Te(1')-Cl(1')	2.49 (1) Å
Te(1')-Cl(2')	2.36 (1)
Te(1')-Cl(3)	2.41 (2)
Te(1')-Cl(4)*	2.87 (1)
Te(1')-Cl(5)*	2.68 (2)
Te(2')-Cl(4)*	2.81 (1)
Te(2')-Cl(5)*	2.85 (2)
Te(2')-Cl(6)	2.40 (1)
Te(2')-Cl(7)	2.34 (2)
Te(2')-Cl(8)	2.51 (1)
P-Cl(9)	1.91 (2)
P-Cl(10)	1.93 (2)
P-Cl(11)	1.94 (2)
P-Cl(12)	1.91 (2)
Te(1')-Cl(4)*-Te(2')	151.6 (5)°
Te(1')-Cl(5)*-Te(2)	158.0 (1)
Cl(1')-Te(1')-Cl(1'')	173.7 (7)
Cl(1')-Te(1')-Cl(2')	88.4 (5)
Cl(1')-Te(1')-Cl(3)	87.4 (5)
Cl(1')-Te(1')-Cl(4)	92.0 (5)
Cl(1')-Te(1')-Cl(5')	92.6 (5)
Cl(2')-Te(1')-Cl(3)	93.1 (5)
Cl(2')-Te(1')-Cl(4)	172.6 (4)
Cl(2')-Te(1')-Cl(5)	88.1 (5)
Cl(3)-Te(1')-Cl(4)	94.3 (2)
Cl(3)-Te(1')-Cl(5')	178.8 (3)
Cl(4)-Te(1')-Cl(5')	84.5 (4)
Cl(4)-Te(2')-Cl(5)	91.4 (4)
Cl(4)-Te(2')-Cl(6)	178.4 (4)
Cl(4)-Te(2')-Cl(7)	89.6 (5)
Cl(4)-Te(2')-Cl(8)	93.3 (3)
Cl(5)-Te(2')-Cl(6)	86.9 (4)
Cl(5)-Te(2')-Cl(7)	178.9 (6)
Cl(5)-Te(2')-Cl(8)	90.6 (4)
Cl(6)-Te(2')-Cl(7)	92.0 (6)
Cl(6)-Te(2')-Cl(8)	86.7 (4)
Cl(7)-Te(2')-Cl(8)	89.3 (5)
Cl(8)-Te(2')-Cl(8'')	173.2 (5)
Cl(9)-P-Cl(10)	110.1 (8)
Cl(9)-P-Cl(11)	110.7 (8)
Cl(9)-P-Cl(12)	109.7 (8)
Cl(10)-P-Cl(11)	107.8 (7)
Cl(10)-P-Cl(12)	110.5 (7)
Cl(11)-P-Cl(12)	107.9 (8)

### Discussion of the structure

The structure consists of tetrahedral  $[\text{PCl}_4]^+$  cations and polymeric infinite chain anions of composition  $[\text{TeCl}_5]_n^-$ . The analysis imposes no crystallographic symmetry on the cation but inspection of Table 3 shows the ion to have approximately tetrahedral symmetry. Numerous examples of the  $[\text{PCl}_4]^+$  ion are found in the literature and recent examples include  $[\text{PCl}_4][\text{FeCl}_4]$  (Kistenmacher & Stucky, 1968),  $[\text{PCl}_4]_2[\text{Ti}_2\text{Cl}_{10}]$  (Kis-

tenmacher & Stucky, 1971) and  $[\text{PCl}_4][\text{MCl}_6]$ ,  $\text{M} = \text{Nb}$  and  $\text{Ta}$  (Preiss, 1971). Our bond lengths and angles are consistent with these earlier studies.

The anion structure contains approximately octahedrally coordinated tellurium atoms, with two mutually *cis* chlorine atoms being shared by two tellurium atoms. The remaining four terminal chlorine atoms show, as expected, a range of bond lengths (2.34 to 2.51 Å) and are shorter than the Cl (bridging)-Te bonds (2.68 to 2.87 Å). The angles around the central tellurium atoms show small distortions (84.5 to 94.3°) from the idealized 90° angles and the Te(1)-Cl-Te(2) angles for the two bridging chlorine atoms are 151.6 and 158.0°.

The isoelectronic species  $[\text{SbCl}_5]^{2-}$  and  $[\text{TeCl}_5]^-$  show markedly different structures and emphasize the danger of arguing by analogy. The antimony compound contains a discrete square pyramidal anion in the ammonium salt (Webster & Keats, 1971). Bis-piperidinium pentabromobismuthate(III) (McPherson & Meyers, 1968) contains a chain anion with bridging bromine atoms that is similar to the anion in this study. Interestingly bis-piperidinium pentabromoantimonate(III) was reported to be isomorphous with the bismuth compound.

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### References

- ADAMS, C. J. & DOWNS, A. J. (1970). *Chem. Commun.* p. 1699.
- ADAMS, D. M. & LLOYD, M. H. (1971). *J. Chem. Soc. (A)*, p. 878.
- AYNSLEY, E. E. & HAZELL, A. C. (1963). *Chem. & Ind.* p. 611.
- BEATTIE, I. R. (1967). *Chem. in Britain*, 3, 347.
- BEATTIE, I. R. & CHUDZYNSKA, H. (1967). *J. Chem. Soc. (A)*, p. 984.
- BEATTIE, I. R., CHUDZYNSKA, H., HULME, R. & AYNSLEY, E. E. (1963). *Chem. & Ind.* p. 1842.
- BUSS, B. & KREBS, B. (1970). *Angew. Chem.* 9, 463. (Int. Ed.)
- CREIGHTON, J. A. & GREEN, J. H. S. (1968). *J. Chem. Soc. (A)*, p. 808.
- DAS, A. K. & BROWN, I. D. (1966). *Canad. J. Chem.* 44, 939.
- EDWARDS, A. J. & MOUTY, M. A. (1969). *J. Chem. Soc. (A)*, p. 703.
- EINSTEIN, F., TROTTER, J. & WILLISTON, C. (1967). *J. Chem. Soc. (A)*, p. 2018.
- GROENEVELD, W. L. (1952). *Rec. trav. Chim.* 71, 1152.
- GROENEVELD, W. L. (1956). *Rec. trav. Chim.* 75, 594.
- GROENEVELD, W. L. & ZUUR, A. P. (1953). *Rec. trav. Chim.* 72, 617.
- GUTMANN, V. (1953). *Mh. Chem.* 84, 1191.
- HAMILTON, W. C. (1965). *Acta Cryst.* 18, 502.
- HAZELL, A. C. (1966). *Acta Chem. Scand.* 20, 165.
- International Tables for X-ray Crystallography* (1962). Vol. III, Birmingham: Kynoch Press.
- KISTENMACHER, T. J. & STUCKY, G. D. (1968). *Inorg. Chem.* 7, 2150.

