70. *The Crystal Structure of* trans-*Dipyridinetetrachlorogermanium*(IV) *and of its Silicon and Titanium Analogues.*

By R. HULME, G. J. LEIGH, and I. R. BEATTIE.

Infrared studies show that the 1 : 2 addition compounds of silicon, titanium, and germanium tetrachlorides with pyridine are structurally similar. They also suggest that co-ordinated pyridine gives an abnormally low C–H stretching intensity. *X*-Ray investigation of *trans*-dipyridine-tetrachlorogermanium(IV) shows its unit cell to contain two molecules. These molecules are centrosymmetric and have *trans*-octahedral form. The germanium–chlorine distance is unambiguously determined from both Fourier and Patterson projections to be 2·27 Å. It follows that the octahedral radius of germanium is 1·28 Å.

A TETRAHEDRAL distribution of bonds about silicon, germanium, and titanium in the quadrivalent state is well established.[1] The covalency maximum of six is found for all three elements in ions of the type $[MF_6]^{2-}$ and for titanium and germanium in the corresponding chloride complexes.[2] Wells [1] has pointed out that octahedrally co-ordinated silicon is found only with the most electronegative elements, the sole other example established crystallographically being the compound with empirical formula SiP_2O_7.[3] Dhar *et al.*[4] claim, however, to have resolved a silicon complex $Si(acac)_3,HCl$ (where Hacac = acetylacetone). Although the hydrogen chloride appears to be an integral part of the molecule, they suggest that this may be an example of six-co-ordinate silicon. More recently Lindqvist [5] has shown that the 1 : 2 adduct of titanium tetrachloride and phosphorus oxychloride contains molecular species of the formula $TiCl_4(POCl_3)_2$: the two molecules of phosphorus oxychloride are in *cis*-relation to each other and not in the expected *trans*-alignment.

Though numerous adducts of Group IV tetrahalides with various donor molecules have been studied, most of these compounds, which are easily hydrolysed solids, have not been fully characterised. Where complex formation has been studied in the gas phase, dissociation is usually extensive or apparently complete. The 1 : 2 addition compounds of silicon, germanium, and titanium tetrachlorides with pyridine have been fairly well characterised,[6] but nothing is known of their stereochemistry. It was suggested that the germanium compound has, surprisingly, a molecular weight in boiling benzene [7] corresponding to a six-co-ordinate species. We have investigated these compounds in the solid state by infrared and *X*-ray techniques.

Infrared Studies.—We were not able to obtain the infrared spectra of these compounds in Nujol mulls or potassium chloride discs owing to the rapid hydrolysis by atmospheric moisture. However, good spectra were obtained on depositing the compounds directly on to the plates of an infrared gas cell. These spectra are recorded in Fig. 1, where those of pyridine and pyridinium chloride are included. The spectra of the pyridine adducts of the tetrahalides, especially those of silicon and germanium, are very similar. The majority of the absorptions due to pyridine occur, but at somewhat lower frequencies, the magnitude of the observed shifts being, in the main, in the order of Ti > Ge > Si. Because these

---

[1] Wells, " Structural Inorganic Chemistry," Oxford, 1945.

[2] Hoard and Williams, *J. Amer. Chem. Soc.*, 1942, **64**, 633; Siegel, *Acta Cryst.*, 1952, **5**, 683; Vincent and Hoard, *J. Amer. Chem. Soc.*, 1942, **64**, 1233; Engel, *Z. Krist.*, 1935, **90**, 341.

[3] Levi and Peyronel, *Z. Krist.*, 1935, **92**, 190.

[4] Dhar, Doran, and Kirschner, *J. Amer. Chem. Soc.*, 1958, **80**, 753.

[5] Lindqvist, Internat. Conf. on Co-ordination Chemistry, London, 1959 (*Chem. Soc. Special Publ.* No. 13).

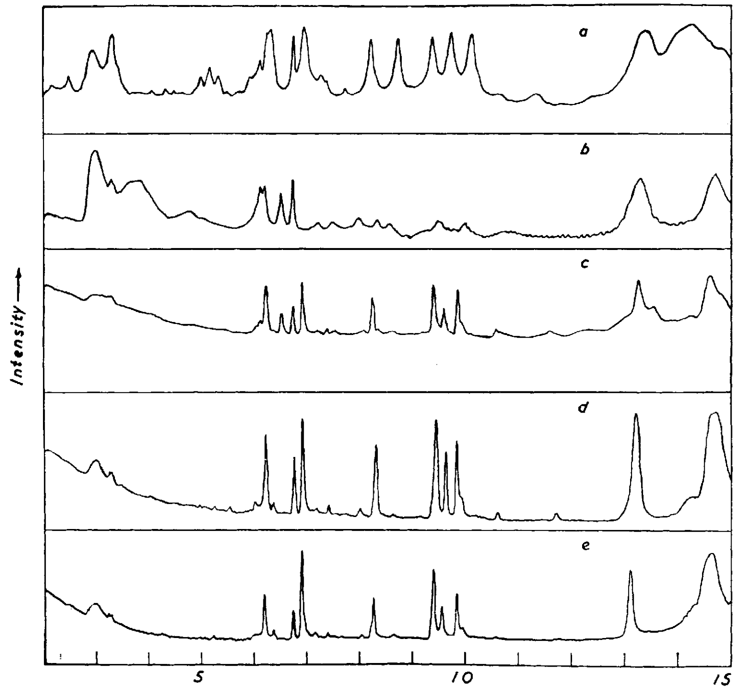
[6] Emeléus and Rao, *J.*, 1958, 4245; Wannagat and Schwarz, *Z. anorg. Chem.*, 1954, **277**, 73; Wannagat and Vielberg, *ibid.*, 1957, **291**, 310.

[7] Abel, *J.*, 1958, 3746.

shifts are relatively small, the conclusion that the internal carbon–carbon and carbon–hydrogen bonding in pyridine has been weakened is not necessarily valid. The relevant spectra are of solids, and crystal fields may cause shifts of the same order as those found. The smallness of the effect also suggests that electronic interaction between the acceptor atom and pyridine is small in all cases.

A somewhat surprising result is the low intensity of the C–H stretching modes which occur at about 3100 cm.$^{-1}$ in the three compounds studied and are of normal intensity for pyridine and pyridinium chloride. This initially led us to suspect a *trans*-alignment of the pyridine rings, as we observed a similar effect in α-dipyridinecobalt(II) chloride, where the two pyridine rings are known [8] to be *trans* to one another. However, as this effect is also found in the 1 : 1 adduct of pyridine and boron trichloride, where such a situation cannot arise, it may merely be an indication that the pyridine is involved in complex-formation. This conclusion is independent of whether we write the boron adduct as $pyBCl_3$ or $[py_2BCl_2]^+BCl_4^-$. The titanium adduct shows small spectral differences from the other two, and these may indicate slight structural differences.

FIG. 1. *Infrared spectra of* (*a*) *pyridine* (*smear on a rock-salt plate*), (*b*) *pyridinium chloride* (*potassium chloride disc*), *and the* 1 : 2 *addition compounds of* (*c*) *titanium,* (*d*) *germanium, and* (*e*) *silicon tetrachlorides with pyridine* (*deposit on a rock-salt plate*).



Note added in proof. Rao [8a] has reported on the 1 : 2 adducts of titanium and zirconium tetrahalides with pyridine. Rao's spectrum for $TiCl_4$,2py is in general accord with ours, and agrees well with our spectra of $SiCl_4$,2py and $GeCl_4$,2py. On the basis of infrared data, Rao assigns a *trans*-configuration to $TiCl_4$,2py, while suggesting that TiF_4,2py and TiI_4,2py are *cis*-.

X-Ray Studies.—On *X*-ray examination, only one of the prepared crystals was found

---

[8] Dunitz, *Nature*, 1957, **179**, 462; *Acta Cryst.*, 1957, **10**, 307.
[8a] Rao, *Naturwiss.*, 1959, **46**, 556.

to be truly single, and even this had a certain amount of randomly adhering matter. From this crystal it was possible to obtain a few oscillation photographs about one of the principal axes, and a 45-hour multiple-film zero-layer Weissenberg photograph.

From the Weissenberg photograph were found the reciprocal spacings $a^* = 0{\cdot}121_4 \pm 0{\cdot}0005$ and $b^* = 0{\cdot}214_3 \pm 0{\cdot}0010$, which were at 90° to each other. Consideration of non-equatorial reflections on the oscillation photographs led to a value for $c = 7{\cdot}24 \pm 0{\cdot}02$ Å

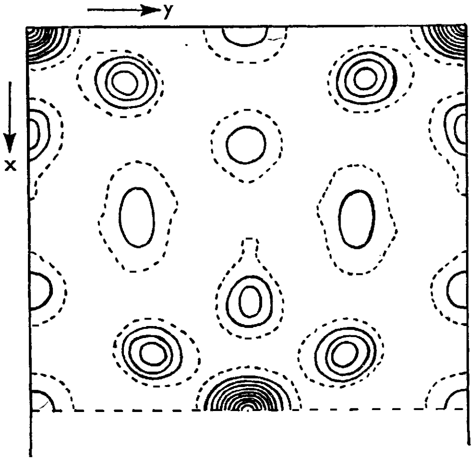


FIG. 2. *Patterson vector map projected on* (001). *Contours at arbitrary equal intervals.*

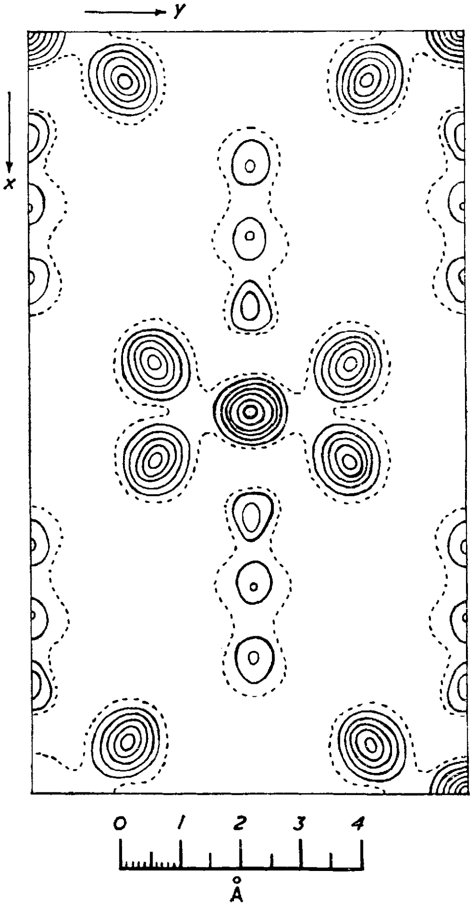


FIG. 3. *Electron-density map projected on* (001). *Broken contour at* 6e/Å^2 *level, and thereafter full contours every* 2e/Å^2 *except round the germanium where twice this interval is used.* $y = 7{\cdot}24$ Å. $z = 13{\cdot}10$ Å.

and an approximate value for the monoclinic angle $\beta = 107° \pm 2°$. The final monoclinic cell dimensions are therefore $a = 13{\cdot}26 \pm 0{\cdot}10$, $b = 7{\cdot}18 \pm 0{\cdot}03$, $c = 7{\cdot}24 \pm 0{\cdot}02$ Å, with $\beta = 107° \pm 2°$. A rough density was obtained from the fact that the crystals slowly sank in iodobenzene (*d* 1·82). For two molecules of $GeCl_4py_2$ per unit cell the calculated density is $1{\cdot}8_8$ g./c.c.

The oscillation photographs did not record sufficient general reflections to detect any systematic absences, but the Weissenberg photograph showed that *hk*0 reflections were present only if $h + k$ was even. This implies that the projection on to (001) must correspond either to the centrosymmetric plane group *cm*, which has only four-fold general positions, or to the centrosymmetric plane group *cmm*, which has eight-fold general positions. Choice of the plane group *cm* would imply that the two molecules in the unit were unrelated to each other. This is possible but unlikely, and analysis proceeded on the basis of plane group *cmm*. The eight chlorine atoms occupy general positions, but the two germanium atoms must lie in the two-fold special positions, 00 and $\frac{1}{2}\frac{1}{2}$. Likewise, the four pyridine molecules must be accommodated in one or other of the four-fold positions, $(00, \frac{1}{2}\frac{1}{2}) + 0y, 0\bar{y}$ or $x0, \bar{x}0$. The plane group *cmm* can be derived from either of the monoclinic centrosymmetric space groups $C2/m$ (No. 12) or $C2/c$ (No. 15). Because there are only two molecules per unit cell, space group $C2/c$ is impossible and the structure must have the space group $C2/m$.

The intensities of over 100 reflections were estimated visually from the multiple-film Weissenberg photograph. Non-systematically absent reflections were recorded as having intensities less than the minimum intensity observed in their area. The intensities were corrected for geometrical and polarisation effects, but no corrections were made for absorption, extinction, or crystal shape. No allowance was made for the absorption of the Pyrex tubing in which the crystal was placed.

The intensities gave a set of 32 squared structure amplitudes (excluding 12 non-systematically absent reflections) from which it was possible to calculate the Patterson vector map shown in Fig. 2. Because of the strongly scattering germanium atom at the origin and cell centre, the Patterson vector projection on (001) will simulate the true electron-density projection, but will include additional spurious detail. Fig. 2 shows two main peaks, of which the one on the x-axis is to be identified with the pyridine molecule in such a four-fold position, while the other is to be attributed to the chlorine atoms in eight-fold general positions. It follows that the pyridine molecules must lie in the (010) plane and be in *trans*-positions to each other around a six-co-ordinated germanium atom. The remaining, less high peaks, may be satisfactorily explained by this interpretation.

From this postulated structure in projection, it was possible to calculate the sign of each experimentally observed $hk0$ structure amplitude. In so doing, it was noticed that nearly all the signs were determined by the germanium contribution alone. This is equivalent to the allocation of signs to the F values without assuming the position of any of the atoms other than germanium in the molecule. The use of the signs calculated at this stage does not prejudge the existence of the molecule in *cis*- or *trans*-configuration, or even the type of co-ordination around the germanium atom. The resulting projected electron density map on (001), (Fig. 3), obtained by the use of these calculated signs with the observed F values in a Fourier summation, clearly confirms that the molecule is *trans* and six-co-ordinate.

Further, the presence of a mirror plane perpendicular to the y-axis and passing through the germanium atom at the origin, makes possible the determination of the Ge–Cl distance from the y-co-ordinate of the chlorine atom alone, with only the assumption that the octahedral distribution around the germanium atom is not distorted. Fig. 4 shows the molecule in projection on (001) and in side view on (010). In the (001) projection, the distance d_1 (which is $\sqrt{2}$ times the Ge–Cl distance) depends only on the y-co-ordinate of the chlorine atom. This can be found both from the (001) electron-density projection and, without possible ambiguity due to erroneously calculated signs for F values, from the corresponding Patterson vector peaks. The two estimates of d_1 agree well, the value being 3·22 ± 0·03 Å. Solving the right-angled triangle gives 2·27 ± 0·03 Å for the Ge–Cl distance. This is greater than the distance, 2·21 Å, calculated from the sum of the normal (tetrahedral) covalent radii [1] of germanium and chlorine. It is considerably greater than the values ranging from 2·07 to 2·15 Å reported for the Ge–Cl distance in various germanium substituted halides in the vapour state.[9] It is, however, less than 2·35 Å, the

[9] Pauling and Brockway, *J. Amer. Chem. Soc.*, 1935, **57**, 2684; Dailey, Mays, and Townes, *Phys. Rev.*, 1949, **76**, 136; Anderson, Sheridan, and Gordy, *ibid.*, 1951, **81**, 819; Venkateswarlu, Mockler, and Gordy, *J. Chem. Phys.*, 1953, **21**, 1713.

value obtained[10] for the Ge–Cl distance in Cs_2GeCl_6. From our experiments we conclude that the octahedral radius of germanium is 1·28 ± 0·03 Å, which is somewhat larger than the tetrahedral value of 1·22 Å. The above result in no way depends on determination of the *x*- or *z*-co-ordinates of the chlorine atom, or on the precise extent to which the molecule is tilted about the *y*-axis.

In Fig. 4*a* the projected distance d_1 is seen to be considerably greater than d_2. Further, the pyridine ligand has resolved with three peaks only. It is, therefore, clear that the tilt must be about 60° out of the (001) plane, but always with the pyridine ligand in the (010) plane. It is easy to calculate trigonometrically the angle of tilt from the ratio d_2/d_1 and the sine of the cell angle β. Once the magnitude of tilt is known, the *z*-co-ordinates of each atom in the structure can be estimated. These atomic co-ordinates are listed in Table 1, together with the *x*- and *y*-co-ordinates found from the electron density projection of (001). The Ge–N distance obtained is ~2·02 Å, in agreement with the sum (2·02 Å) of our octahedral germanium radius and the normal covalent radius for nitrogen.

FIG. 4. *Diagrammatic representation of molecule, (a) projected on (001), and (b) projected on (010), to indicate derivation of z-co-ordinates.*

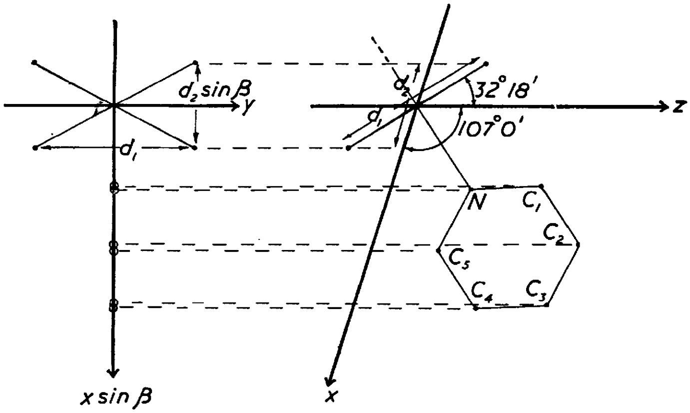


TABLE 1. *Atomic co-ordinates as fractions of cell edges.*

	x	*y*	*z* (estimated)		*x*	*y*	*z* (estimated)
Ge	0	0	0	C_2	0·223	0	0·57
Cl	0·068	0·224	−0·152	C_3	0·320	0	0·52
N	0·135	0	0·22	C_4	0·324	0	0·33
C_1	0·132	0	0·42	C_5	0·233	0	0·18

TABLE 2. *Observed and calculated structure factors (see text).*

Index	F_o	F_c	Index	F_o	F_c	Index	F_o	F_c	Index	F_o	F_c
0 2 0	45	+51	1 1 0	77	+93	1 3 0	8	+19	5 5 0	<7	−1
0 4 0	99	+130	3 1 0	54	+33	3 3 0	21	+14	7 5 0	<7	−5
0 6 0	29	+29	5 1 0	34	+20	5 3 0	50	+38			
0 8 0	38	+37	7 1 0	31	+27	7 3 0	60	+53	2 6 0	<7	−9
			9 1 0	46	+42	9 3 0	54	+55	4 6 0	<7	+18
2 0 0	67	+71	11 1 0	<7	−6				6 6 0	45	+37
4 0 0	37	+21	13 1 0	21	+26	2 4 0	39	+40	8 6 0	39	+34
6 0 0	<5	−9				4 4 0	13	+16			
8 0 0	<6	−14	2 2 0	66	−56	6 4 0	<7	+1	1 7 0	<7	−6
10 0 0	<7	−1	4 2 0	38	+41	8 4 0	<7	−4	3 7 0	<7	+3
12 0 0	28	+28	6 2 0	105	+95				5 7 0	32	+24
14 0 0	25	+36	8 2 0	80	+79	1 5 0	53	+65	7 7 0	39	+37
			10 2 0	31	+32	3 5 0	37	+26			

---

[10] Laubengayer, Bellings, and Newkirk, *J. Amer. Chem. Soc.*, 1940, **62**, 546.

Structure factors for all the observed and non-systematically absent *hk*0 reflections have been calculated on the basis of the co-ordinates in Table 1. Hartree atomic scattering factors were assumed for germanium, which like those for chlorine, nitrogen, and carbon were taken from " Internationale Tabellen." A temperature factor, $\exp -B \sin^2\theta/\lambda^2$ with $B = 2{\cdot}5$, was applied in each case. The calculated structure factors are listed together with the observed F values in Table 2. The customary reliability factor for all the *hk*0 reflections is 18%.

EXPERIMENTAL

Reagents.—Pyridine was of " AnalaR " quality, stored over potassium hydroxide for several weeks, refluxed with barium oxide, fractionated, and then distilled several times *in vacuo* in an all-glass apparatus with no taps or joints and without access of air; head and tail fractions were rejected. Silicon tetrachloride of technical quality was fractionally distilled and then redistilled several times *in vacuo* as for pyridine. Technical titanium tetrachloride was treated similarly, with no attempt at further purification once the absence of vanadium had been established. Germanium tetrachloride was distilled *in vacuo* as above, but not fractionated.

Extreme purity was not essential, but the absence of moisture was required. A new technique, exemplified below for silicon tetrachloride and pyridine, is applicable to many other systems. The whole of the silicon tetrachloride was first mixed with a little of the pyridine in a separate section of the vacuum-system. The tetrachloride was then distilled from the 1 : 2 addition compound of silicon tetrachloride and pyridine. This removed hydrogen chloride from the tetrachloride, forming a little pyridinium chloride. Pyridine was then distilled on to the complex, any water it contained reacting with the complex to yield silica and hydrogen chloride which again combined with the excess of pyridine. The dry pyridine was then distilled from the residue. This necessitates more care than in the case of the tetrachloride in view of the lower volatility of the pyridine.

Compound Formation.—The complexes were generally formed by allowing the reactants to mix in a vacuum-system in the presence of an excess of the more volatile constituent, which was then pumped away. No analyses were carried out as these compounds have all been studied stoicheiometrically by phase-diagram techniques,[11] and have been characterised by earlier workers.[6,7]

Preparation of X-*Ray Specimen.*—After the compound $(C_5H_5N)_2SiCl_4$ had been melted *in vacuo* in a sealed tube and allowed to resolidify, the tube contained small crystalline aggregates. A similar result occurred with the germanium compound, but in neither case was it possible to obtain single crystals. As both the silicon and the germanium compound are moderately soluble in pyridine, the following technique was used. Germanium tetrachloride with a 20-fold excess of pyridine was sealed in a large Pyrex tube containing open-ended Pyrex thin-walled tubes. The temperature was raised to about 180° and then lowered to room temperature during $\sim$24 hr. In this way a few fairly good, apparently single crystals were obtained in their mother-liquor. The bulk of the mother-liquor was removed and the tubes were then quickly sealed.

Preparation of the Infrared Specimens.—The compounds were carefully sublimed into a normal gas cell made of Pyrex and having rock salt plates attached by means of Araldite adhesive. It was possible to disconnect the cell from the sublimation apparatus by the use of a diaphragm tap.

The authors thank Dr. H. Block for assistance and the D.S.I.R. for a maintenance grant (to G. J. L.).

UNIVERSITY OF LONDON KING'S COLLEGE,
STRAND, LONDON, W.C.2.

[*Received, August* 18*th*, 1959.]

---

[11] Beattie and Leigh, unpublished work.