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## The Crystal Structures of the Dimethyldicyano Compounds of Silicon, Germanium, Tin and Lead

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The crystal data for the group IV compounds  $(\text{CH}_3)_2\text{M}(\text{CN})_2$  are:

|   | <i>a</i>    | <i>b</i>   | <i>c</i>   | Space group | <i>Z</i> | <i>D</i> <sub>calc</sub> |
|---|-------------|------------|------------|-------------|----------|--------------------------|
| $(\text{CH}_3)_2\text{Si}(\text{CN})_2$ | 13.76 (2) Å | 7.44 (1) Å | 6.45 (1) Å | <i>Pnma</i> | 4        | 1.11 g.cm <sup>-3</sup>  |
| $(\text{CH}_3)_2\text{Ge}(\text{CN})_2$ | 13.64 (2)   | 7.49 (1)   | 6.35 (1)   | <i>Pnma</i> | 4        | 1.58                     |
| $(\text{CH}_3)_2\text{Sn}(\text{CN})_2$ | 9.00 (2)    | 9.74 (2)   | 7.95 (1)   | <i>Fmm2</i> | 4        | 1.92                     |
| $(\text{CH}_3)_2\text{Pb}(\text{CN})_2$ | 9.02 (1)    | 8.37 (2)   | 8.88(1)    | <i>Fmm2</i> | 4        | 2.77                     |

In the Si and Ge compounds, approximately tetrahedral molecules form linear chains through weak acid-base  $\text{N}\cdots\text{M}$  interactions. In the Sn compound, and presumably in the Pb compound, stronger  $\text{N}\cdots\text{M}$  interactions occur such that planar sheets are formed; each normally tetrahedral molecule is distorted to a more nearly octahedral arrangement by the formation of two additional equivalent  $\text{N}\cdots\text{M}$  interactions.

### Introduction

Previous work shows that the trimethylcyano compounds of germanium (Schlemper & Britton, 1966*b*), tin (Schlemper & Britton, 1966*a*), and lead (Chow & Britton, 1971) have intermolecular interactions in the solid state that are more specific than van der Waals interactions. In  $(\text{CH}_3)_3\text{GeCN}$ , discrete molecules interact through a weak donor-acceptor interaction between the lone pair on the nitrogen atom and the germanium atom in the next molecule. In  $(\text{CH}_3)_3\text{SnCN}$  (and probably in  $(\text{CH}_3)_3\text{PbCN}$ ), the structure is similar, but the interaction has proceeded to the point where each cyanide group is halfway between two adjacent trimethyltin groups. It has also been observed, in the series  $(\text{CH}_3)_{3-n}\text{As}(\text{CN})_n$ , that as *n* increases from 1 to 3 the intermolecular  $\text{N}\cdots\text{As}$  interaction increases in strength, as evidenced by the shortening of the  $\text{N}\cdots\text{As}$  distance (Britton, 1967). We report here the structures of  $(\text{CH}_3)_2\text{M}(\text{CN})_2$ , where M is Si, Ge, Sn, and Pb. This series was studied to see to what extent the second cyanide group affects the previously observed interactions, *i.e.* whether it merely strengthens them, as

with arsenic, or whether it leads to sixfold coordination, to some degree, around the metal atom. The structures of  $\text{SnF}_4$  and  $\text{PbF}_4$  (Hoppe & Dahne, 1962) and of  $(\text{CH}_3)_2\text{SnF}_2$  (Schlemper & Hamilton, 1966) suggest a model for tetragonally symmetric sixfold coordination around the metal atom [shown later in Fig. 1(c)].

### Experimental

#### *Preparation and properties*

Dimethyldicyanosilane was prepared by mixing dimethyldichlorosilane with chloroform and placing the solution over  $\text{AgCN}$ . The mixture was shaken occasionally and allowed to stand for two months. The solution was then filtered and the liquid distilled off under a vacuum. The resulting solid was purified by vacuum sublimation. Peaks were observed at 2195 and 2108  $\text{cm}^{-1}$  in the  $\text{C}\equiv\text{N}$  region of the infrared spectrum; these may be compared with values 2179 and 2096  $\text{cm}^{-1}$  reported by McBride & Beachell (1952). The peak at 2195  $\text{cm}^{-1}$  was approximately three times as intense as the one at 2108  $\text{cm}^{-1}$ . When the compound was left exposed to the air, it hydrolyzed rapidly and both peaks decreased

in intensity, to be replaced by one at 2090  $\text{cm}^{-1}$ . Observed melting point was 80–83°C.

Dimethyldicyanogermane was prepared by reacting dimethyldichlorogermane with trimethylcyanosilane at 70°C in *o*-xylene. Single crystals of a size suitable for X-ray investigation were formed when the reaction mixture was cooled to room temperature. The infrared spectrum showed a single peak in the cyanide region at 2195  $\text{cm}^{-1}$ . The crystals melted at 116–118°C. Atmospheric moisture hydrolyzed the compound quickly first to a liquid, and then to a white powder.

Dimethyltin dicyanide was prepared by reacting dimethyltin dichloride with trimethylcyanosilane in *o*-xylene at 70°C. Crystals suitable for X-ray examination precipitated as the reaction proceeded. The melting point, >400°C, the ready hydrolysis in air, and the infrared spectrum all agreed with the results of Lorberth (1965), except that no infrared peak was observed at 1595  $\text{cm}^{-1}$ .

Dimethyllead dichloride was prepared by introducing chlorine gas into an ethyl-acetate solution of tetra-

methyllead at –60°C and warming the solution to –10°C (Grultner & Krause, 1916). Reaction of  $(\text{CH}_3)_2\text{PbCl}_2$  in water with excess silver oxide gave a solution of  $(\text{CH}_3)_2\text{Pb}(\text{OH})_2$ . Hydrogen cyanide gas was passed into the filtered solution of the hydroxide to give a white precipitate of  $(\text{CH}_3)_2\text{Pb}(\text{CN})_2$ . It was not possible to prepare well-formed crystals either by sublimation or by recrystallization from ethanol, chloroform, or benzene; so only X-ray powder photographs were possible. Analytical data suggest that perhaps 10%  $(\text{CH}_3)_2\text{Pb}(\text{OH})_2$  was present as an impurity. (Calc: C, 16.61; H, 2.09; N, 9.68%. Found: C, 15.94; H, 2.29; N, 8.28%.) The C–N stretching frequency is 2152  $\text{cm}^{-1}$  in the infrared spectrum and 2148  $\text{cm}^{-1}$  in the Raman spectrum. The coupling constant  $J(^{207}\text{Pb}-\text{CH}_3)$  is 145 in dimethyl sulfoxide at room temperature, compared with  $J$  values of 85 for  $(\text{CH}_3)_3\text{PbCN}$ , 154.5 for  $(\text{CH}_3)_2\text{PbCl}_2$ , and 83 for  $(\text{CH}_3)_3\text{PbCl}$  (Shier & Drago, 1966). The compound starts to decompose around 130°C and decomposes completely at 270°C without melting.

Table 1. *Crystal data for  $(\text{CH}_3)_2\text{M}(\text{CN})_2$  where M = Si, Ge, Sn, Pb*

|                          | Si                      | Ge                      | Sn                      | Pb                      |
|--------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| <i>a</i>                 | 13.76 (2) Å             | 13.64 (2) Å             | 9.00 (2) Å              | 9.02 (1) Å              |
| <i>b</i>                 | 7.44 (1)                | 7.49 (1)                | 9.74 (2)                | 8.37 (2)                |
| <i>c</i>                 | 6.45 (1)                | 6.35 (1)                | 7.95 (1)                | 8.88 (1)                |
| Space group              | <i>Pnma</i>             | <i>Pnma</i>             | <i>Fmm2</i>             | <i>Fmm2</i>             |
| <i>Z</i>                 | 4                       | 4                       | 4                       | 4                       |
| Molecular volume         | 165 Å <sup>3</sup>      | 162 Å <sup>3</sup>      | 174 Å <sup>3</sup>      | 168 Å <sup>3</sup>      |
| <i>D</i> <sub>calc</sub> | 1.11 g.cm <sup>-3</sup> | 1.58 g.cm <sup>-3</sup> | 1.92 g.cm <sup>-3</sup> | 2.77 g.cm <sup>-3</sup> |

Table 2. *Positional and thermal\* parameters for  $(\text{CH}_3)_2\text{M}(\text{CN})_2$ †*  
M = Si, Ge, Sn

|   | <i>x</i>     | <i>y</i>      | <i>z</i>     | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ | <i>B</i> ‡ |
|---|--------------|---------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|------------|
| <b><math>(\text{CH}_3)_2\text{Si}(\text{CN})_2</math></b> |              |               |              |              |              |              |              |              |              |            |
| Si  | 0.1504 (3)   | $\frac{1}{4}$ | 0.1909 (9)   | 26 (2)       | 232 (14)     | 229 (17)     | 0            | –1 (6)       | 0            | 3.65 (17)  |
| C(1)  | 0.0952 (10)  | 0.4627 (21)   | 0.2687 (25)  | 70 (10)      | 228 (37)     | 376 (57)     | 22 (14)      | –24 (15)     | –78 (43)     | 5.5 (4)    |
| C(2)  | 0.2821 (15)  | $\frac{1}{4}$ | 0.2640 (37)  | 54 (13)      | 247 (54)     | 327 (92)     | 0            | 9 (20)       | 0            | 5.0 (5)    |
| C(3)  | 0.1587 (15)  | $\frac{1}{4}$ | –0.0972 (43) | 61 (13)      | 134 (49)     | 304 (77)     | 0            | 51 (28)      | 0            | 4.2 (5)    |
| N(1)  | 0.3621 (11)  | $\frac{1}{4}$ | 0.3147 (40)  | 40 (11)      | 423 (62)     | 600 (89)     | 0            | 19 (24)      | 0            | 7.5 (5)    |
| N(2)  | 0.1664 (14)  | $\frac{1}{4}$ | –0.2702 (46) | 63 (14)      | 405 (76)     | 446 (97)     | 0            | 2 (27)       | 0            | 7.1 (6)    |
| <b><math>(\text{CH}_3)_2\text{Ge}(\text{CN})_2</math></b> |              |               |              |              |              |              |              |              |              |            |
| Ge  | 0.1506 (1)   | $\frac{1}{4}$ | 0.1911 (3)   | 45 (1)       | 239 (5)      | 157 (4)      | 0            | 6 (2)        | 0            | 3.74 (6)   |
| C(1)  | 0.0930 (10)  | 0.4720 (24)   | 0.2723 (22)  | 72 (8)       | 326 (40)     | 259 (36)     | 25 (16)      | 15 (14)      | –9 (35)      | 5.6 (3)    |
| C(2)  | 0.2891 (17)  | $\frac{1}{4}$ | 0.2600 (27)  | 74 (13)      | 270 (48)     | 126 (33)     | 0            | 18 (16)      | 0            | 4.5 (4)    |
| C(3)  | 0.1582 (14)  | $\frac{1}{4}$ | –0.1204 (35) | 51 (10)      | 268 (47)     | 310 (56)     | 0            | 27 (24)      | 0            | 4.9 (4)    |
| N(1)  | 0.3695 (13)  | $\frac{1}{4}$ | 0.3006 (34)  | 68 (11)      | 342 (50)     | 312 (50)     | 0            | –1 (21)      | 0            | 5.9 (4)    |
| N(2)  | 0.1640 (16)  | $\frac{1}{4}$ | –0.2939 (33) | 110 (16)     | 416 (60)     | 269 (53)     | 0            | 38 (32)      | 0            | 7.3 (5)    |
| <b><math>(\text{CH}_3)_2\text{Sn}(\text{CN})_2</math></b> |              |               |              |              |              |              |              |              |              |            |
| Sn  | 0            | 0             | 0            | 58 (3)       | 101 (4)      | 116 (8)      | 0            | 0            | 0            | 2.85 (4)   |
| C(1)  | 0.1706 (73)  | 0             | 0.2098 (98)  | –            | –            | –            | –            | –            | –            | 4.5 (10)   |
| C(2)  | 0            | 0.2086 (45)   | –0.0715 (83) | –            | –            | –            | –            | –            | –            | 3.8 (9)    |
| N   | 0.2568 (143) | 0             | 0.3054 (99)  | –            | –            | –            | –            | –            | –            | 6.9 (14)   |

\* Anisotropic temperature factors are of the form  $T = \exp [-(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)]$ . They have been multiplied by 10<sup>4</sup>.

† E.s.d.'s for the final significant values are given in parentheses.

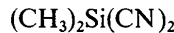
‡ For atoms with anisotropic thermal parameters, *B* is the value from the last least-squares cycle in which that particular atom was treated as isotropic.

Space groups and unit cells

Unit cells and space groups for the Si, Ge, and Sn compounds were found from oscillation, Weissenberg, and precession photographs using Mo *K*α radiation (λ=0.7107 Å). Cell dimensions for the Pb compound were assigned from a powder photograph (Cr *K*α radiation, λ=2.909 Å) indexed by analogy to the Sn compound. All four compounds are orthorhombic. For the isomorphous Si and Ge compounds, systematic extinctions of 0*k**l* for *k*+*l* odd and of *h**k*0 for *h* odd indicate the space group to be either *Pnma* or *Pn2<sub>1</sub>a*. For the Sn and Pb compounds, the requirement for reflection that *h*, *k*, and *l* be all even or all odd indicates the space group to be *F222*, *Fmm2*, or *Fmmm*. Densities were not measured experimentally because of the high reactivities of the compounds. Values of *Z* were assigned by consideration of the molecular volumes and they were confirmed by the solved structures. Crystal data are summarized in Table 1. Probable errors in cell dimensions from the single-crystal data (Si, Ge, Sn) are

estimated to be one part in 600; error estimates in the powder data stem from a least-squares treatment of the data.

Determination of structures



The sublimed crystals formed flat plates elongated along *c* with a well-developed {100} form. A crystal, cleaved to a cross section of 0.24 × 0.08 mm, was sealed in a glass capillary for intensity measurements. Multiple-film, equi-inclination Weissenberg intensity data were collected for layers *hk*0–*hk*6 using filtered Mo *K*α radiation. Two 20° oscillation photographs were also taken for use in scaling the Weissenberg data. All intensities were estimated by visual comparison with a prepared intensity strip. There were 189 reflections of observable intensity and 40 reflections with intensities too weak to observe in the region of reciprocal space investigated; unobserved reflections were included in the structure determination with intensities equal to

Table 3. Observed and calculated structure factors (× 10) for (CH<sub>3</sub>)<sub>2</sub>M(CN)<sub>2</sub> where M = Si, Ge, Sn

| H K  |     | FO |   | FC  |      | H K |   | FO  |    | FC |   | H K |     | FO |   | FC  |     | H K |   | FO  |      | FC |   |     |     |   |   |     |    |   |   |      |      |   |   |     |     |
|------|-----|----|---|-----|------|-----|---|-----|----|----|---|-----|-----|----|---|-----|-----|-----|---|-----|------|----|---|-----|-----|---|---|-----|----|---|---|------|------|---|---|-----|-----|
| M=Si | L=0 | 10 | 3 | 175 | -170 | 8   | 0 | 464 | 49 | 2  | 2 | 366 | 329 | 5  | 1 | 326 | 326 | 7   | 4 | 137 | -147 | 14 | 1 | 150 | 155 | 7 | 3 | 108 | 89 | 2 | 2 | 1705 | 1523 | 1 | 7 | 455 | 611 |

UNOBSERVED REFLECTIONS INDICATED

half the minimum observable intensity for that scattering angle. Lorentz and polarization corrections were made; no absorption corrections were made ( $\mu = 2.4 \text{ cm}^{-1}$ ).

Refinement began using final parameters of the  $(\text{CH}_3)_2\text{Ge}(\text{CN})_2$  structure (see below). Full-matrix least-squares refinement, with isotropic thermal parameters for the light atoms and anisotropic thermal parameters for Si, gave an  $r$  value of 0.12 and an  $R$  value of 0.16.\* At this point, the Weissenberg layers were rescaled so that the layer-to-layer differences were smoothed out without introducing any new trend with increasing  $l$ . Refinement was then continued with all atoms anisotropic, and data converged to an  $r$  value of 0.073 and an  $R$  value of 0.116. Weights used in the final cycles were  $w = 1.0$  for  $F_o \leq 8.19$  and  $w = (8.19/F_o)^4$  for  $F_o > 8.19$ . Final parameters are given in Table 2. Final structure factors are listed in Table 3.

\*  $r = \sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^4$ ;  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ . The numerator of  $r$  was the function refined. Various calculations were made using local programs or programs supplied by Dr L. W. Finger of the Geology Department, University of Minnesota, and were carried out on the CDC 1604 and 6600 computers of the University Computer Center. Scattering factors used in the calculations were taken from *International Tables for X-ray Crystallography* (1962).

$(\text{CH}_3)_2\text{Ge}(\text{CN})_2$

The habit of this crystal was identical to that of the  $(\text{CH}_3)_2\text{Si}(\text{CN})_2$  crystals. A crystal, cleaved to a needle elongated along  $b$  and of cross section  $0.28 \times 0.28 \text{ mm}$ , was sealed in a glass capillary for intensity measurements. Multiple-film, equi-inclination Weissenberg intensity data were collected using Zr-filtered Mo  $K\alpha$  radiation for layers  $h0l$ – $h7l$ . Precession intensity data were collected for the  $hk0$  and  $0kl$  nets and were used to scale the Weissenberg data. There were 424 reflections of observable intensity in the region of reciprocal space examined, plus 60 reflections with intensities too weak to observe; the latter were omitted from the refinement. Lorentz and polarization corrections were made; absorption corrections were made assuming the crystal to be a cylinder of diameter  $0.28 \text{ mm}$  ( $\mu = 50.7 \text{ cm}^{-1}$ ).

Atomic positions were found from Patterson and Fourier maps. These positions fit space group  $Pnma$  well, and the possibility that the space group was  $Pn2_1a$  was not further considered. A full-matrix least-squares refinement, with light atoms isotropic and the Ge atom anisotropic, converged with  $r = 0.15$  and  $R = 0.17$ . Weissenberg layers were then rescaled to smooth out layer-to-layer fluctuations without introducing any trend with  $k$ . Refinement continued with all atoms

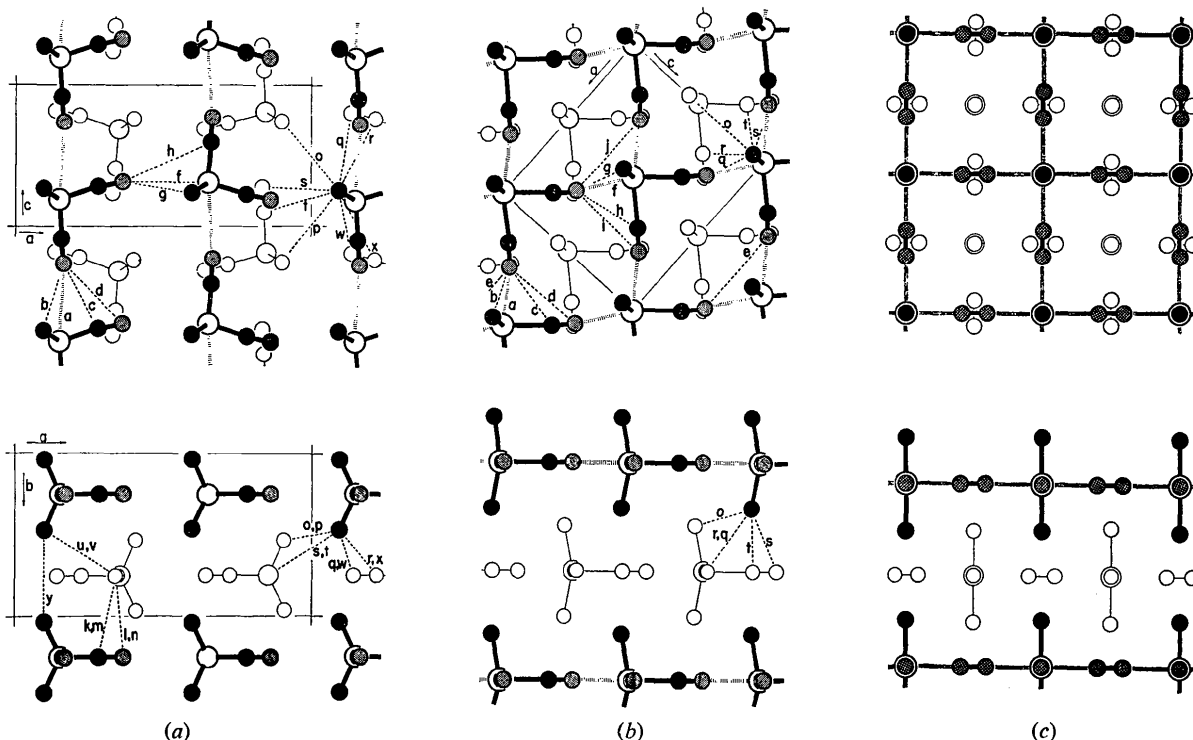


Fig. 1. Structures of (a)  $(\text{CH}_3)_2\text{Si}(\text{CN})_2$  and  $(\text{CH}_3)_2\text{Ge}(\text{CN})_2$ ; (b)  $(\text{CH}_3)_2\text{Sn}(\text{CN})_2$  and  $(\text{CH}_3)_2\text{Pb}(\text{CN})_2$ ; (c) unrealized tetragonal limiting case with disordered CN groups. Metal atoms are open, carbon atoms black, nitrogen shaded, and disordered carbon and nitrogen atoms cross-shaded; hydrogen atoms are not shown. Values of intermolecular distances are given in Table 7. Top view in each case is perpendicular to the plane formed by the interacting molecules. Bottom view is at right angles to this along  $c$  in the first case, along  $[101]$  in the second, and along  $a$  in the third. The different orientations are chosen to emphasize the similarities among the three structures.

anisotropic and it converged with  $r=0.031$  and  $R=0.073$ . Final weights used were  $w=1.0$  for  $F_o \leq 19.1$ ,  $w=(19.1/F_o)^4$  for  $F_o > 19.1$ . Final positional parameters are given in Table 2. Final structure factors are listed in Table 3.

#### $(\text{CH}_3)_2\text{Sn}(\text{CN})_2$

The crystals grew as needles elongated in the  $c$  direction and bounded on the sides by the  $\{100\}$  and  $\{010\}$  forms. A crystal measuring  $0.075 \times 0.105 \times 0.80$  mm was mounted in a glass capillary for intensity measurements. Multiple-film, equi-inclination Weissenberg intensity data were collected for the  $hk0$ – $hk6$  layers along with oscillation–photograph data for scaling the Weissenberg layers, all using unfiltered Mo radiation. There were 161 independent reflections with observable intensities in the region of reciprocal space investigated. Aside from two experimentally inaccessible low-angle reflections, there were no unobserved reflections in this region. The structure was solved from Fourier maps based on the Sn atoms being at the origin, which followed from four molecules being in a face-centered unit cell. The splitting of the peaks corresponding to the methyl–carbon atoms on the Fourier maps clearly indicated that the symmetry was not  $Fmmm$  but  $Fmm2$ , and the structure was finished in the latter space group. Light-atom positions were determined more exactly in successive Fourier maps and then were refined by full-matrix least-squares treatment with the light atoms isotropic and the Sn atom anisotropic. This converged with  $r=0.054$  and  $R=0.105$ . With the Sn atom making the maximum possible contribution to every structure factor, light-atom parameters were necessarily poorly determined; anisotropic refinement of the light atoms was not attempted. The weighting factors used were  $w=1.0$  for  $F_o \leq 32.4$ ,  $w=(32.4/F_o)^4$  for  $F_o > 32.4$ . Final parameters are given in Table 2. Final structure factors are listed in Table 3.

#### $(\text{CH}_3)_2\text{Pb}(\text{CN})_2$

A powder photograph of  $(\text{CH}_3)_2\text{Pb}(\text{CN})_2$  revealed that it could be indexed as being face-centered orthorhombic with the parameters given in Table 1. At first, the pattern appeared to be the body-centered tetragonal one that we expected as the limiting case for this series of structures. But closer examination showed the orthorhombic pattern. A comparison of the intensities (measured on a powder diffractometer using  $\text{Cu } K\alpha$  radiation) with those found in the analogous tin compound led to the assignment of  $a$ ,  $b$ , and  $c$  as given. At first, we were inclined to assign  $a=8.88$ ,  $b=9.02$ , and  $c=8.37$  Å to make the cell dimensions for the tin and lead compounds correspond as closely as possible. However, the intensity of the 202 reflection makes the assignment of  $b$  rather certain, and this is the axis that corresponds to the tetragonal  $c$  axis. Powder data, as well as calculated structure factors based on a  $(\text{CH}_3)_2\text{Pb}(\text{CN})_2$  molecule similar to the Sn analog, are given in Table 4.

Table 4. Powder data for  $(\text{CH}_3)_2\text{Pb}(\text{CN})_2$

| $h$ | $k$ | $l$ | $Q_{\text{obs}}^*$ | $Q_{\text{calc}}$ | $I_{\text{obs}}^\dagger$ | $I_{\text{calc}}^\ddagger$ |
|-----|-----|-----|--------------------|-------------------|--------------------------|----------------------------|
| 1   | 1   | 1   | 0.0394             | 0.0395            | 100                      | 100                        |
| 2   | 0   | 0   | 0.0497             | 0.0495            | 19                       | 14                         |
| 0   | 0   | 2   | 0.0511             | 0.0510            | 18                       | 13                         |
| 0   | 2   | 0   | 0.0574             | 0.0574            | 16                       | 20                         |
| 2   | 0   | 2   | 0.1002             | 0.1003            | 40                       | 21                         |
| 2   | 2   | 0   | —                  | 0.1067            | 7                        | 6                          |
| 0   | 2   | 2   | 0.1079             | 0.1082            | 6                        | 6                          |
| 3   | 1   | 1   | 0.1380             | 0.1381            | 23                       | 15                         |
| 1   | 1   | 3   | 0.1408             | 0.1411            | 20                       | 14                         |
| 1   | 3   | 1   | —                  | 0.1533            | 14                       | 14                         |
| 2   | 2   | 2   | 0.1572             | 0.1574            | 22                       | 16                         |
| 4   | 0   | 0   | 0.1961             | 0.1973            | —                        | 3                          |
| 0   | 0   | 4   | 0.2041             | 0.2033            | —                        | 2                          |
| 0   | 4   | 0   | —                  | 0.2284            | —                        | 3                          |
| 3   | 1   | 3   | 0.2397             | 0.2396            | —                        | 7                          |

\*  $Q=4 \sin^2 \theta/\lambda^2$ .  $Q_{\text{obs}}$  was determined from film data using  $\text{Cr } K\alpha$  radiation.

† Intensities were measured on an XRD-3 powder diffractometer using  $\text{Cu } K\alpha$  radiation.

‡ Calculated using an assumed structure similar to that of  $(\text{CH}_3)_2\text{Sn}(\text{CN})_2$ .

#### Cyanide versus isocyanide

In Table 2 all compounds are reported as cyanides. The possibility that these might be isocyanides was considered and tested for, in each case, by reversing the C and N atoms in the CN group and further refining the structure. Resulting  $r$ ,  $R$ , and  $B$  values (or equivalent  $B$  values for the anisotropic refinements) are given in Table 5. This table shows that the cyanide is clearly preferred to the isocyanide, based on the reliability factors and reasonability of the relative  $B$  values for both the silicon and germanium compounds. Clearly, a mixture of a small amount of isocyanide with a larger amount of cyanide could not be detected in either case. In the tin compound, X-ray evidence is inconclusive; the infrared spectrum is consistent with the cyanide.

Table 5. Comparison of the structures as cyanides versus isocyanides for  $(\text{CH}_3)_2M(\text{CN})_2$ ,  $M=\text{Si, Ge, Sn}$

| Central atom | Parameter          | Cyanide     | Isocyanide  |
|--------------|--------------------|-------------|-------------|
| Si           | $B$ for inner atom | C–5.0 & 4.2 | N–5.9 & 6.5 |
|              | $B$ for outer atom | N–7.5 & 7.1 | C–4.7 & 4.3 |
|              | $r$                | 0.073       | 0.076       |
|              | $R$                | 0.116       | 0.120       |
| Ge           | $B$ for inner atom | C–4.5 & 4.9 | N–7.3 & 7.1 |
|              | $B$ for outer atom | N–5.9 & 7.3 | C–5.0 & 5.4 |
|              | $r$                | 0.031       | 0.043       |
|              | $R$                | 0.073       | 0.082       |
| Sn           | $B$ for inner atom | C–4.5       | N–5.3       |
|              | $B$ for outer atom | N–6.9       | C–6.0       |
|              | $r$                | 0.054       | 0.056       |
|              | $R$                | 0.105       | 0.104       |

#### Results and discussion

The structures are shown in Fig. 1: (a) Si and Ge compounds; (b) Sn compound, and presumably that of the

Pb compound; (c) the idealized tetragonal limiting case. Interatomic distances and angles, compared with those of some related compounds, are given in Table 6. Intermolecular distances are listed in Table 7.

Table 6. Bond lengths and angles in  $(\text{CH}_3)_2\text{M}(\text{CN})_2$ 

| Lengths:           | Compound   | Reference           |
|--------------------|--|---------------------|
| Si-CH <sub>3</sub> | (CH <sub>3</sub> ) <sub>2</sub> Si(CN) <sub>2</sub>  | 1.83 (2) Å <i>a</i> |
| -                  | (CH <sub>3</sub> ) <sub>2,3</sub> SiX <sub>2,1</sub> | 1.85 (avg) <i>b</i> |
| Si-CN              | (CH <sub>3</sub> ) <sub>2</sub> Si(CN) <sub>2</sub>  | 1.87 (2) <i>a</i>   |
| -                  | -  | 1.86 (3) <i>a</i>   |
| Ge-CH <sub>3</sub> | (CH <sub>3</sub> ) <sub>2</sub> Ge(CN) <sub>2</sub>  | 1.91 (2) <i>a</i>   |
| -                  | (CH <sub>3</sub> ) <sub>3</sub> GeCN                 | 1.98 (avg) <i>c</i> |
| Ge-CN              | (CH <sub>3</sub> ) <sub>2</sub> Ge(CN) <sub>2</sub>  | 1.94 (2) <i>a</i>   |
| -                  | -  | 1.98 (2) <i>a</i>   |
| -                  | (CH <sub>3</sub> ) <sub>3</sub> GeCN                 | 1.98 (6) <i>c</i>   |
| Sn-CH <sub>3</sub> | (CH <sub>3</sub> ) <sub>2</sub> SnF <sub>2</sub>     | 2.08 (2) <i>d</i>   |
| -                  | (CH <sub>3</sub> ) <sub>2</sub> Sn(CN) <sub>2</sub>  | 2.11 (5) <i>a</i>   |
| -                  | (CH <sub>3</sub> ) <sub>2</sub> Sn(NCS) <sub>2</sub> | 2.09 (1) <i>e</i>   |
| -                  | -  | 2.14 (3) <i>f</i>   |
| -                  | (CH <sub>3</sub> ) <sub>3</sub> SnCN                 | 2.16 (avg) <i>g</i> |
| -                  | (CH <sub>3</sub> ) <sub>4</sub> Sn                   | 2.18 (3) <i>b</i>   |
| Sn-CN              | (CH <sub>3</sub> ) <sub>2</sub> Sn(CN) <sub>2</sub>  | 2.27 (7) <i>a</i>   |
| C-N                | (CH <sub>3</sub> ) <sub>2</sub> Si(CN) <sub>2</sub>  | 1.15 (2) <i>a</i>   |
| -                  | -  | 1.12 (3) <i>a</i>   |
| -                  | (CH <sub>3</sub> ) <sub>2</sub> Ge(CN) <sub>2</sub>  | 1.13 (2) <i>a</i>   |
| -                  | -  | 1.10 (2) <i>a</i>   |
| -                  | (CH <sub>3</sub> ) <sub>2</sub> Sn(CN) <sub>2</sub>  | 1.09 (12) <i>a</i>  |
| -                  | usual C≡N  | 1.156 <i>h</i>      |

## Angles:

|                                     |  |                      |
|-------------------------------------|--|----------------------|
| CH <sub>3</sub> -Si-CH <sub>3</sub> | (CH <sub>3</sub> ) <sub>2</sub> Si(CN) <sub>2</sub>  | 120.2 (10)° <i>a</i> |
| -                                   | (CH <sub>3</sub> ) <sub>3</sub> SiCl <sub>1</sub> Br | 113 (avg) <i>b</i>   |
| CH <sub>3</sub> -Ge-CH <sub>3</sub> | (CH <sub>3</sub> ) <sub>2</sub> Ge(CN) <sub>2</sub>  | 120.9 (8) <i>a</i>   |
| -                                   | (CH <sub>3</sub> ) <sub>3</sub> GeCN                 | 114.8 (avg) <i>c</i> |
| CH <sub>3</sub> -Sn-CH <sub>3</sub> | (CH <sub>3</sub> ) <sub>2</sub> Sn(CN) <sub>2</sub>  | 148.7 (35) <i>a</i>  |
| -                                   | (CH <sub>3</sub> ) <sub>2</sub> Sn(NCS) <sub>2</sub> | 148.9 (9) <i>e</i>   |
| -                                   | -  | 145.9 (14) <i>f</i>  |
| CH <sub>3</sub> -Si-CN              | (CH <sub>3</sub> ) <sub>2</sub> Si(CN) <sub>2</sub>  | 109.5 (5) <i>a</i>   |
| -                                   | -  | 107.4 (5) <i>a</i>   |
| CH <sub>3</sub> -Ge-CN              | (CH <sub>3</sub> ) <sub>2</sub> Ge(CN) <sub>2</sub>  | 109.5 (5) <i>a</i>   |
| -                                   | -  | 106.9 (5) <i>a</i>   |
| -                                   | (CH <sub>3</sub> ) <sub>3</sub> GeCN                 | 103.8 (avg) <i>c</i> |
| CH <sub>3</sub> -Sn-CN              | (CH <sub>3</sub> ) <sub>2</sub> Sn(CN) <sub>2</sub>  | 101.4 (13) <i>a</i>  |
| NC-Si-CN                            | (CH <sub>3</sub> ) <sub>2</sub> Si(CN) <sub>2</sub>  | 101.1 (10) <i>a</i>  |
| NC-Ge-CN                            | (CH <sub>3</sub> ) <sub>2</sub> Ge(CN) <sub>2</sub>  | 100.9 (7) <i>a</i>   |
| NC-Sn-CN                            | (CH <sub>3</sub> ) <sub>2</sub> Sn(CN) <sub>2</sub>  | 85.3 (37) <i>a</i>   |
| SCN-Sn-NCS                          | (CH <sub>3</sub> ) <sub>2</sub> Sn(NCS) <sub>2</sub> | 86.6 (5) <i>e</i>    |
| -                                   | -  | 84.1 (16) <i>f</i>   |
| Si-C-N                              | (CH <sub>3</sub> ) <sub>2</sub> Si(CN) <sub>2</sub>  | 178.1 (22) <i>a</i>  |
| -                                   | -  | 178.1 (22) <i>a</i>  |
| Ge-C-N                              | (CH <sub>3</sub> ) <sub>2</sub> Ge(CN) <sub>2</sub>  | 179.8 (18) <i>a</i>  |
| -                                   | -  | 178.8 (22) <i>a</i>  |
| Sn-C-N                              | (CH <sub>3</sub> ) <sub>2</sub> Sn(CN) <sub>2</sub>  | 177.1 (50) <i>a</i>  |

## Key to references

|          |                                      |
|----------|--------------------------------------|
| <i>a</i> | This work                            |
| <i>b</i> | Sutton (1965)                        |
| <i>c</i> | Schlemper & Britton (1966 <i>b</i> ) |
| <i>d</i> | Schlemper & Hamilton (1966)          |
| <i>e</i> | Forder & Sheldrick (1970)            |
| <i>f</i> | Chow (1970)                          |
| <i>g</i> | Schlemper & Britton (1966 <i>a</i> ) |
| <i>h</i> | Britton (1967)                       |

Discrete, relatively normal molecules are apparent in the structures of the Si and Ge compounds. The CH<sub>3</sub>-M-CH<sub>3</sub> bond angles are larger, and the NC-M-CN

Table 7. Intermolecular distances in  $(\text{CH}_3)_2\text{M}(\text{CN})_2$ 

| Identification*                    | Si                  | Ge         | Sn          |
|------------------------------------|---------------------|------------|-------------|
| N...M                              | <i>a</i> 3.48 (3) Å | 3.28 (2) Å | 2.68 (11) Å |
| N...CH <sub>3</sub>                | <i>b</i> 3.51 (3)   | 3.36 (2)   | 3.14 (8)    |
| N...C                              | <i>c</i> 3.40 (4)   | 3.31 (3)   | 3.28 (12)   |
| N...N                              | <i>d</i> 3.80 (3)   | 3.81 (3)   | 3.98 (1)    |
| N...N                              | <i>e</i> -          | -          | 4.38 (25)   |
| N...M                              | <i>f</i> 3.97 (2)   | 3.84 (2)   | = <i>a</i>  |
| N...CH <sub>3</sub>                | <i>g</i> 3.62 (2)   | 3.50 (2)   | = <i>b</i>  |
| N...C                              | <i>h</i> 4.47 (3)   | 4.43 (2)   | = <i>c</i>  |
| N...N                              | <i>i</i> -          | -          | = <i>d</i>  |
| N...N                              | <i>j</i> -          | -          | = <i>e</i>  |
| N...N                              | <i>k</i> 3.78 (1)   | 3.82 (1)   | -           |
| N...C                              | <i>l</i> 3.79 (1)   | 3.81 (1)   | -           |
| C...N                              | <i>m</i> 3.77 (1)   | 3.80 (1)   | -           |
| C...C                              | <i>n</i> 3.91 (1)   | 3.89 (1)   | -           |
| CH <sub>3</sub> ...CH <sub>3</sub> | <i>o</i> 4.01 (3)   | 3.87 (3)   | 4.05 (1)    |
| CH <sub>3</sub> ...CH <sub>3</sub> | <i>p</i> 4.38 (3)   | 4.31 (3)   | -           |
| CH <sub>3</sub> ...N               | <i>q</i> 4.16 (3)   | 3.98 (2)   | 3.79 (9)    |
| CH <sub>3</sub> ...C               | <i>r</i> 4.20 (2)   | 4.06 (2)   | 3.66 (9)    |
| CH <sub>3</sub> ...N               | <i>s</i> 4.19 (2)   | 4.08 (2)   | = <i>q</i>  |
| CH <sub>3</sub> ...C               | <i>t</i> 4.24 (2)   | 4.12 (2)   | = <i>r</i>  |
| CH <sub>3</sub> ...N               | <i>u</i> 3.92 (2)   | 3.94 (2)   | -           |
| CH <sub>3</sub> ...C               | <i>v</i> 4.10 (2)   | 4.04 (2)   | -           |
| CH <sub>3</sub> ...N               | <i>w</i> 3.67 (3)   | 3.68 (2)   | -           |
| CH <sub>3</sub> ...C               | <i>x</i> 4.24 (3)   | 4.18 (2)   | -           |
| CH <sub>3</sub> ...CH <sub>3</sub> | <i>y</i> 4.16 (4)   | 4.28 (3)   | -           |

\* See Fig. 1. for identification. All distances under 4.50 Å are given.

bond angles are smaller, than tetrahedral, which is what we expect from the relative electronegativities of the CH<sub>3</sub>- and NC- groups. The one unusual feature within the molecules is that the M-CH<sub>3</sub> distances in both compounds (and in the Sn compound too) are shorter than the M-CN distances. Experimental errors are large enough to indicate that the effect may be unreal. But since it occurs in all three compounds, we are inclined to believe it is real. Presumably, the effect is caused by a weakening of the intramolecular M-CN bonds when the intermolecular CN...M bonds are formed.

The packing of the molecules in the Si and Ge compounds is dominated by the CN...M interactions along the *c* direction. Although van der Waals radii for Si and Ge are not normally defined, and perhaps are not definable since no outer-shell unshared electrons exist in these elements, we assume that the van der Waals contact distances for N...P and N...As (3.4 and 3.5 Å, respectively) can also be used as reference points for N...Si and N...Ge distances. By these standards, the N...Si distance of 3.84 (3) Å in (CH<sub>3</sub>)<sub>2</sub>Si(CN)<sub>2</sub> is not remarkable. However, the alignment of the molecules is striking; exactly the same alignment in the Ge analog leads to an N...Ge distance of 3.28 (2) Å, slightly shorter than the expected van der Waals distance and clearly shorter than the corresponding distances in the Si compound and in (CH<sub>3</sub>)<sub>3</sub>GeCN (3.57 Å). The shortening of the distance from (CH<sub>3</sub>)<sub>3</sub>GeCN to (CH<sub>3</sub>)<sub>2</sub>Ge(CN)<sub>2</sub> is virtually identical with the shortening from (CH<sub>3</sub>)AsCN [N...As of

3.18 Å (Camerman & Trotter, 1963)] to  $(\text{CH}_3)\text{As}(\text{CN})_2$  [ $\text{N}\cdots\text{As}$  of 2.94 Å (Schlemper & Britton, 1966b)]. The  $\text{N}\cdots\text{M}$  distances in the Si and Ge compounds are generally longer than in the comparable compounds of P and As because of the greater amount of steric hindrance from the neighboring groups in the former compounds. The increased steric hindrance is twofold: (1) the additional group adds one more repulsive interaction to interfere with the  $\text{N}\cdots\text{M}$  bond; (2) bond angles in group IV compounds are much closer to tetrahedral than in group V compounds, which brings all repulsive neighboring groups close to the nitrogen atom that is trying to form the intermolecular bond.

The second cyanide group in both the Si and Ge compounds also points at the heavy atom in a neighboring molecule, but the distances  $\text{N}\cdots\text{Si}$  [3.97 (2) Å], and  $\text{N}\cdots\text{Ge}$ , [3.84 (2) Å] are about 0.4 Å greater than the estimated van der Waals distances. Despite these longer distances, we still believe that there is an energetically significant interaction here also. Two reasons support this belief: the CN group is aligned towards the Si or Ge atom, and the distance in the Ge compound is less than that in the Si compound. In summary, we regard the 4-coordination of the isolated molecule to be increased to 5-coordination with the formation of the polymeric chains parallel to the *c* axis, with a further tendency toward 6-coordination evident in interactions in the *a* direction.

In the Sn compound, individual molecules can be clearly identified. But angles  $\text{CH}_3\text{-Sn-CH}_3$  [148.7 (35)°] and  $\text{NC-Sn-CN}$  [85.3 (37)°] show that major distortions are caused by interactions with CN groups from neighboring molecules. As mentioned before, the Sn-CN bond length is greater than the Sn-CH<sub>3</sub> bond length, which suggests that intermolecular interaction weakens the primary Sn-CN bond. The  $\text{N}\cdots\text{Sn}$  distance (2.68 Å) is longer than the average Sn-CN distance in  $(\text{CH}_3)_3\text{SnCN}$ , although, perhaps coincidentally, the Sn-CN-Sn total distances are very similar in the two compounds: 6.01 (1) Å in  $(\text{CH}_3)_2\text{Sn}(\text{CN})_2$  and 6.06 (1) Å in  $(\text{CH}_3)_3\text{SnCN}$ . Note that in addition to the greater strength of the intermolecular bonds in the Sn compound, as evidenced by the much smaller length, another distinct difference is evident: the Si and Ge compounds have two unequal interactions, whereas the Sn compound has two equal interactions. We are indebted to Professor R. D. Gillard for the observation that, if we regard an M atom as forming intermolecular bonds to two CN groups, the differences between the Si and Ge situation on one hand, and the Sn situation on the other, is analogous to the difference between the H atoms in unsymmetric and symmetric hydrogen bonds.

The  $\text{Sn}\cdots\text{N}$  interactions lead to the formation of infinite polymeric sheets of molecules perpendicular to the *b* direction. Intermolecular distances within the polymeric sheets follow from the  $\text{Sn}\cdots\text{N}$  interaction and the intramolecular distances. It is interesting that

the short  $\text{CH}_3\cdots\text{N}$  distance of 3.14 Å, which follows perforce from the  $\text{N}\cdots\text{Sn}$  interaction, is shorter than the intramolecular  $\text{C}\cdots\text{C}$  distance of 3.39 Å between the CH<sub>3</sub> and CN carbon atoms.

Layers pack with the methyl groups in one layer nestled among the methyl groups in the next layer. The short distances are  $\text{CH}_3\cdots\text{CH}_3$ , 4.06 Å, and  $\text{CH}_3\cdots\text{C}$  (in CN), 3.67 Å. It is worth considering what the distances and packing would be if the  $\text{Sn-CN}\cdots\text{Sn}$  bridges were statistically centric as they are in  $(\text{CH}_3)_3\text{SnCN}$ . The structure [Fig. 1(c)] would be body-centered tetragonal and exactly analogous to  $\text{SnF}_4$  and  $(\text{CH}_3)_2\text{SnF}_2$ . If we assume the  $\text{Sn}\cdots\text{CN}\cdots\text{Sn}$  distance to be 6.06 Å as in  $(\text{CH}_3)_3\text{SnCN}$ , the intermolecular interlayer  $\text{CH}_3\cdots\text{CH}_3$  distance would be at least 4.30 Å, which is longer than the 4.06 Å found in the actual structure, or the 4.20 Å found in  $(\text{CH}_3)_2\text{SnF}_2$ . Interlayer spacing would then be determined by  $\text{CH}_3\cdots\text{CN}$  contacts. If we assume the  $\text{CH}_3\cdots\text{CN}$  distance to be 3.80 Å [sum of the usual van der Waals radius for CH<sub>3</sub> (2.0 Å) and the equatorial radius of the CN<sup>-</sup> ion (1.78 Å)], and if we take the Sn-CH<sub>3</sub> distance to be 2.08 Å as in  $(\text{CH}_3)_2\text{SnF}_2$ , the interlayer distance would be 4.37 Å. This would lead to a molecular volume of 161 Å<sup>3</sup> compared to the 174 Å<sup>3</sup> found in the actual structure. This result (that the predicted molecular volume would be significantly less for the regular octahedral structure with disordered CN groups) says that the distortion from octahedral that is actually found is not a consequence of crystal packing effects but of requiring a real instability in the octahedral arrangement relative to the distorted tetrahedral arrangement. This is surprising in view of the regular trigonal pyramidal structure of  $(\text{CH}_3)_3\text{SnCN}$ . It also suggests the possibility of phase transition to the octahedral form at higher pressures.

The orthorhombic unit cell for the Pb compound strongly suggests the CN groups are still ordered, and that the structure is similar to that of the Sn compound although it is much more nearly tetragonal than the latter. The Pb-CN-Pb distance is 6.33 Å compared to the corresponding distance of 6.27 Å in  $(\text{CH}_3)_3\text{PbCN}$ . Arguments similar to those for the Sn compound, about the relative efficiency of the ordered *versus* disordered structures, also apply to the Pb compound.

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## Crystal Structure of Hexaurea Salts of Trivalent Metals. I. $\text{Ti}(\text{Urea})_6(\text{ClO}_4)_3$ at Room Temperature

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On the basis of 642 independent intensities collected by film techniques the room temperature structure of  $\text{Ti}(\text{urea})_6(\text{ClO}_4)_3$  was refined in the space group  $R\bar{3}c$  to give a final  $R$  of 0.122, omitting unobserved reflections. Hexagonal cell dimensions are  $a = 18.132$  (5),  $c = 14.149$  (5) Å. The structure consists of a two-dimensional close-packed arrangement of  $\text{Ti}(\text{urea})_6^{3+}$  units in columns parallel to the  $c$  axis. In the columnar interstices the perchlorate ions are arranged in spiral fashion. The structure is loosely linked by an extensive net of H bonds and van der Waals contacts and is closely analogous to that of the iodide salt (Davis & Wood, 1970). The geometry of the  $\text{Ti}(\text{urea})_6^{3+}$  ion is formally octahedral with a superimposed trigonal distortion consisting of a twist about the threefold axis. Partial occupancy of two different sites is found for two of the four perchlorate oxygen atoms, but the geometry of the perchlorate ion remains essentially tetrahedral.

### Introduction

During magnetic studies of transition metal coordination compounds it became desirable to investigate the properties of the  $\text{Ti}^{3+}$  ( $d^1$ ) ion in a highly symmetrical environment, of close to regular octahedral stereochemistry. Accordingly, the hexaurea complex  $\text{Ti}(\text{urea})_6(\text{ClO}_4)_3$  was selected as a suitable system in which to determine and correlate magnetic properties and structure. Independent work on the corresponding iodide salt became available after our structure was established (Linek, Siskova & Jensovsky, 1966; Linek, 1968; Davis & Wood, 1970) and it confirmed the structural details of the  $\text{Ti}(\text{urea})_6^{3+}$  ion. Fowles, Lester & Wood (1969) have also described  $\text{Ti}^{3+}$  in octahedral coordination in  $(\text{TiBr}_3)_2 \cdot 3\text{C}_4\text{H}_{10}\text{O}_2$ .

### Experimental preliminaries

In solution, the compound under study quickly oxidizes in air, so preparations were carried out in an atmosphere of nitrogen. The method, adapted from Barbieri (1915), is described by Wadley (1970). Microanalyses for carbon, hydrogen, and nitrogen, and analysis of titanium confirmed the purity of the product. (Found:

C, 10.34; H, 3.47; N, 23.56; Ti, 6.65%; required for  $\text{Ti}(\text{urea})_6(\text{ClO}_4)_3$ : C, 10.20; H, 3.42; N, 23.45; Ti, 6.78%.)

The crystals were deep blue, elongated hexagonal prisms of sizes ranging up to 3 mm diameter and 10 mm long. Many were simply hollow shells, with spaces almost from one end of the crystal to the other. The crystals, when dry, were quite stable to the atmosphere.

As expected, the temperature dependence of the paramagnetic susceptibility is in accord with an octahedrally coordinated titanium atom (Wadley, 1970). The titanium atom may be bonded with the six urea ligands *via* either the oxygen or nitrogen atom, although oxygen may be favoured by analogy with  $\text{Ti}(\text{H}_2\text{O})_6^{3+}$  and from infrared assignments (Cotton & Wilkinson, 1962; Nakamoto, 1963). Many urea complexes are known to form a continuous urea framework with counter ions distributed in channels or voids of a suitable size, and a model consistent with this distribution may be favoured.

Crystals for X-ray data collection, about 0.2 mm diameter and 0.3 mm long, were cut from solid elongated prisms and examined under a polarizing microscope for cracks or other imperfections. After 60–70 hours of irradiation in the X-ray beam, the crystals