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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 $(CH_3)_2M(CN)_2$ are:

	a	b	c	Space group	Z	D_{calc}
$(CH_3)_2Si(CN)_2$	13·76 (2) Å	7·44 (1) Å	6·45 (1) Å	*Pnma*	4	1·11 g.cm^{-3}
$(CH_3)_2Ge(CN)_2$	13·64 (2)	7·49 (1)	6·35 (1)	*Pnma*	4	1·58
$(CH_3)_2Sn(CN)_2$	9·00 (2)	9·74 (2)	7·95 (1)	*Fmm*2	4	1·92
$(CH_3)_2Pb(CN)_2$	9·02 (1)	8·37 (2)	8·88(1)	*Fmm*2	4	2·77

In the Si and Ge compounds, approximately tetrahedral molecules form linear chains through weak acid-base N···M interactions. In the Sn compound, and presumably in the Pb compound, stronger N···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 N···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 $(CH_3)_3GeCN$, 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 $(CH_3)_3SnCN$ (and probably in $(CH_3)_3PbCN$), 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 $(CH_3)_{3-n}As(CN)_n$, that as n increases from 1 to 3 the intermolecular N···As interaction increases in strength, as evidenced by the shortening of the N···As distance (Britton, 1967). We report here the structures of $(CH_3)_2M(CN)_2$, 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 SnF_4 and PbF_4 (Hoppe & Dahne, 1962) and of $(CH_3)_2SnF_2$ (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 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 cm^{-1} in the C≡N region of the infrared spectrum; these may be compared with values 2179 and 2096 cm^{-1} reported by McBride & Beachell (1952). The peak at 2195 cm^{-1} was approximately three times as intense as the one at 2108 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 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 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 cm^{-1}.

Dimethyllead dichloride was prepared by introducing chlorine gas into an ethyl-acetate solution of tetramethyllead at −60 °C and warming the solution to −10 °C (Grultner & Krause, 1916). Reaction of $(CH_3)_2PbCl_2$ in water with excess silver oxide gave a solution of $(CH_3)_2Pb(OH)_2$. Hydrogen cyanide gas was passed into the filtered solution of the hydroxide to give a white precipitate of $(CH_3)_2Pb(CN)_2$. 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 % $(CH_3)_2Pb(OH)_2$ 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 cm^{-1} in the infrared spectrum and 2148 cm^{-1} in the Raman spectrum. The coupling constant $J(^{207}Pb{-}CH_3)$ is 145 in dimethyl sulfoxide at room temperature, compared with J values of 85 for $(CH_3)_3PbCN$, 154·5 for $(CH_3)_2PbCl_2$, and 83 for $(CH_3)_3PbCl$ (Shier & Drago, 1966). The compound starts to decompose around 130 °C and decomposes completely at 270 °C without melting.

Table 1. *Crystal data for* $(CH_3)_2M(CN)_2$ *where* M = Si, Ge, Sn, Pb

	Si	Ge	Sn	Pb
a	13·76 (2) Å	13·64 (2) Å	9·00 (2) Å	9·02 (1) Å
b	7·44 (1)	7·49 (1)	9·74 (2)	8·37 (2)
c	6·45 (1)	6·35 (1)	7·95 (1)	8·88 (1)
Space group	*Pnma*	*Pnma*	*Fmm*2	*Fmm*2
Z	4	4	4	4
Molecular volume	165 Å^3	162 Å^3	174 Å^3	168 Å^3
D_{calc}	1·11 g.cm^{-3}	1·58 g.cm^{-3}	1·92 g.cm^{-3}	2·77 g.cm^{-3}

Table 2. *Positional and thermal* parameters for* $(CH_3)_2M(CN)_2$†
M = Si, Ge, Sn

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B‡
$(CH_3)_2Si(CN)_2$										
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)
$(CH_3)_2Ge(CN)_2$										
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)
$(CH_3)_2Sn(CN)_2$										
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 $T=\exp[-(\beta_{11}h^2+\ldots+2\beta_{12}hk+\ldots)]$. They have been multiplied by 10^4.

† 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 *Kα* radiation ($\lambda = 0{\cdot}7107$ Å). Cell dimensions for the Pb compound were assigned from a powder photograph (Cr *Kα* radiation, $\lambda = 2{\cdot}909$ Å) indexed by analogy to the Sn compound. All four compounds are orthorhombic. For the isomorphous Si and Ge compounds, systematic extinctions of $0kl$ for $k+l$ odd and of $hk0$ for h odd indicate the space group to be either *Pnma* or $Pn2_1a$. 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 *F*222, *Fmm*2, 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

$(CH_3)_2Si(CN)_2$

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 $hk0$–$hk6$ using filtered Mo *Kα* 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* $(CH_3)_2M(CN)_2$ *where* M = Si, Ge, Sn

H	K	FO	FC
M=SI			
L=0			
0	2	664	-834
0	4	658	642
0	6	277	-236
2	1	588	-607
2	2	579	542
2	3	216	212
2	4	202	-192
2	5	281	-281
2	6	129	100
4	0	790	-857
4	1	321	286
4	2	316	327
4	3	317	-308
4	4	328	-325
4	5	43*	71
4	6	139	116
4	7	103	-89
6	0	435	362
6	1	292	209
6	2	632	-577
6	3	187	-127
6	4	233	217
6	5	139	129
6	6	158	-137
8	0	206	119
8	1	437	-382
8	2	79	-81
8	3	385	369
8	4	45*	67
8	5	152	-140
8	7	122	124
10	0	263	-251
10	1	180	172
10	2	384	349
10	3	101	-95
10	4	165	-159
10	6	98	109
12	0	95	104
12	1	109	121
12	2	49*	-38
12	3	124	-125
14	0	156	145
14	1	129	-141
14	2	170	-158
16	0	150	-143
L=1			
0	3	149	168
0	5	244	-252
1	2	178	-205
1	3	117	124
2	1	140	144
2	2	331	-320
2	3	170	-163
2	4	90	-91
3	0	360	-333
3	1	19*	-18
3	2	255	264
3	3	25*	46
4	0	464	-347
4	1	232	234
4	2	42	-31
4	3	88	-69
5	0	22*	33
5	1	194	152
5	2	25*	8
5	3	106	-112
6	0	280	220
6	1	50	-54
6	2	66	-63
6	3	170	157
6	4	102	125
7	0	210	193
7	1	84	-83
7	2	147	-143
8	0	29*	-26
8	1	173	-168
8	2	241	232
8	3	128	117
8	4	61	-71
8	6	87	71
9	0	102	-82
9	1	56	-62
10	1	170	162
10	3	175	-170
11	0	62	-74
11	1	85	85
12	2	112	-115
14	1	141	-151
14	3	93	122
L=2			
0	2	228	319
0	4	305	-341
0	6	140	109
1	2	46	46
1	3	131	138
2	3	56	-52
2	4	100	94
2	5	139	146
3	0	66	43
3	1	230	235
3	2	67	51
3	3	159	-160
3	4	30*	-15
3	5	82	74
4	0	462	403
4	1	86	-77
4	2	94	-94
4	3	133	134
4	4	154	163
5	0	94	93
5	1	24*	8
5	2	74	-67
5	3	29*	-37
6	0	142	-113
6	1	158	-145
6	2	288	295
6	3	94	85
6	4	84	-79
6	5	86	-89
7	0	94	-75
7	1	190	-176
7	3	118	107
7	5	82	-72
8	0	130	-76
8	1	208	203
8	2	32*	49
8	3	200	-214
9	0	91	-78
9	1	33*	55
9	2	33*	42
10	0	112	111
10	1	111	-87
10	2	192	-201
11	0	79	83
11	1	106	99
13	1	81	-79
14	0	84	-92
14	2	106	107
L=3			
0	3	131	-112
0	5	156	166
1	2	176	211
1	3	113	-119
1	4	101	-109
2	2	33*	50
2	3	124	106
3	0	384	298
3	1	30*	41
3	2	261	-263
3	3	105	-84
3	4	168	169
4	0	137	93
4	1	128	-93
4	2	67	70
4	3	43*	25
5	0	36*	-15
5	1	203	-170
5	2	40*	-45
5	3	156	133
5	5	97	-102
6	0	190	-155
6	1	40*	53
6	2	43*	60
6	3	115	-105
7	0	313	-252
7	1	44*	67
7	2	205	184
7	4	130	-136
8	0	46*	49
8	2	209	-167
9	0	121	88
9	1	126	118
11	0	153	141
11	1	128	-114
13	0	110	-111
13	2	113	108
L=4			
0	2	25*	13
1	2	140	-180
1	3	155	-168
1	4	110	113
2	2	91	76
2	3	32*	-39
2	4	37*	-18
3	1	276	-299
3	2	80	-81
3	3	208	229
3	5	138	-130
4	0	26*	-31
4	1	27*	-22
4	2	70	-72
4	3	34*	-9
5	0	253	-226
5	1	30*	38
5	2	187	183
5	4	143	-137
5	6	86	80
6	0	32*	-47
6	1	33*	36
6	2	35*	-47
7	0	146	119
7	1	251	204
7	2	67	-72
7	3	148	-137
7	5	102	101
8	0	38*	-8
8	1	38*	-27
9	0	141	121
9	1	121	-112
9	3	79	80
10	0	43*	40
11	0	140	-126
11	1	112	-85
13	1	91	107
L=5			
1	2	64	-89
2	2	91	-99
3	0	118	-114
3	1	24*	-30
3	2	102	105
3	4	65	-68
4	0	118	-98
4	1	69	-62
4	2	30*	37
4	3	59	64
5	0	28*	19
5	1	76	88
5	3	70	-63
6	0	31*	34
6	1	70	70
7	0	135	111
7	2	92	-72
9	1	86	-71
11	0	100	-79
M=GE			
H	L	FO	FC
K=0			
10	0	466	-491
0	2	1498	-1508
0	4	294	243
0	6	157	164
0	8	134	-161
1	2	377	-364
1	3	473	-431
1	4	545	499
1	5	251	240
1	6	267	-236
2	1	787	-724
2	2	366	329
2	3	412	375
2	7	209	-209
3	1	461	-481
3	3	691	705
3	4	139	104
3	5	438	-411
3	7	164	121
4	2	738	761
4	5	136	-144
4	6	193	-185
4	7	158	164
4	8	128	151
5	2	466	457
5	4	567	-570
5	6	295	287
6	0	681	741
6	1	446	444
6	2	399	-390
6	3	251	-220
6	6	194	174
6	8	130	-134
7	1	314	313
7	2	177	-177
7	3	556	-540
7	4	254	235
7	5	312	332
7	6	147	-132
7	7	99	-93
8	0	238	209
8	1	361	-396
8	2	133	-127
8	3	203	193
8	7	125	-145
9	1	159	-148
9	2	259	-263
9	3	254	245
9	4	313	304
9	5	145	-150
9	6	153	-158
10	2	257	277
10	6	164	-153
11	1	119	-110
11	2	214	212
11	3	260	221
11	4	267	-274
11	5	142	-153
11	6	143	154
12	0	140	161
12	1	223	250
13	1	121	119
13	3	224	-216
13	5	133	139
14	0	218	221
14	1	156	-179
14	2	139	-145
14	3	118	108
15	2	143	-121
15	4	129	145
16	0	189	-186
16	2	155	121
K=1			
0	3	609	546
0	7	224	-209
1	1	297	-321
1	2	443	-418
1	3	507	465
1	4	488	455
1	5	275	-275
1	6	204	-212
2	1	322	318
2	2	650	614
2	3	192	-181
2	6	222	-215
2	8	154	170
3	1	101	-83
3	2	597	612
3	3	160	155
3	4	667	-698
3	5	104	-105
3	6	337	342
4	0	638	653
4	1	652	663
4	2	305	-328
4	3	262	-274
4	6	147	142
4	7	181	190
5	1	326	326
5	3	541	-537
5	5	310	329
5	7	100	-95
6	0	443	485
6	1	426	-429
6	2	310	-306
6	3	214	215
6	7	159	-159
7	1	140	-119
7	2	408	-421
7	3	171	176
7	4	462	477
7	5	87	-99
7	6	206	-229
8	0	686	-762
8	1	241	-228
8	2	469	461
8	6	112	-120
9	1	165	-162
9	2	166	167
9	3	312	307
9	4	242	-234
9	5	211	-202
9	6	104	129
10	0	135	150
10	1	354	377
10	2	105	-95
10	3	150	-161
10	7	135	135
11	1	145	151
11	2	164	166
11	3	280	-266
11	4	179	-168
11	5	167	170
12	0	376	342
13	2	163	-154
13	3	86	-50
13	4	185	194
14	0	268	-219
14	1	235	-200
14	2	119	136
14	3	154	84
15	1	88	-83
15	3	193	159
K=2			
0	2	828	777
0	6	210	-206
0	8	158	160
1	2	434	394
1	3	511	472
1	4	527	-495
1	5	278	-284
1	6	242	246
2	1	169	151
2	2	469	-421
2	4	110	103
2	5	195	-171
2	6	144	14
2	7	173	215
3	1	455	408
3	2	178	167
3	3	672	-638
3	4	176	-188
3	5	375	382
3	6	77	101
3	7	117	-119
3	8	101	-24
4	0	746	776
4	1	356	-346
4	2	427	-413
4	3	175	184
4	6	193	197
4	7	98	-122
4	8	102	-142
5	2	367	-391
5	4	550	488
5	6	242	-245
6	0	822	-915
6	1	294	-281
6	2	570	553
6	3	130	133
6	6	92	-110
6	8	95	105
7	1	278	-254
7	2	83	101
7	3	476	441
7	4	137	-147
7	5	271	-266
8	0	166	-184
8	1	512	549
8	2	110	116
8	3	277	-295
8	7	100	108
9	1	138	114
9	2	223	203
9	3	193	-186
9	4	233	-233
10	0	492	551
10	2	358	-343
10	6	106	113
11	2	200	-176
11	3	166	-163
11	4	249	229
12	1	306	-278
12	3	130	124
13	1	104	-105
13	3	192	191
14	0	151	-214
14	1	103	109
14	2	125	143
15	2	110	111
15	4	120	-134
K=3			
0	3	336	-325
0	7	187	173
1	2	338	324
1	3	422	-390
1	4	380	-363
1	5	244	234
1	6	195	180
2	1	268	-285
2	2	379	-369
2	3	173	164
2	6	174	181
2	8	113	-138
3	1	92	82
3	2	431	-448
3	3	173	-155
3	4	523	527
3	5	102	107
3	6	266	-265
3	7	95	-37
4	0	534	-548
4	1	406	-433
4	2	308	310
4	3	173	171
4	5	114	101
4	6	120	-99
4	7	139	-154
4	8	125	86
5	1	248	-241
5	5	246	-256
6	0	344	-348
6	1	417	422
6	2	245	223
6	3	236	-214
6	6	87	-65
6	7	130	118
7	2	318	306
7	3	118	-120
7	4	367	-351
7	6	165	168
8	0	599	622
8	1	173	177
8	2	399	-393
9	1	110	120
9	2	147	-123
9	3	223	-226
9	4	170	173
9	5	90	148
9	6	97	-96
10	0	73	-81
10	1	336	-323
10	3	140	144
11	1	124	-116
11	3	208	207
11	4	135	120
11	5	106	-134
12	0	287	-277
12	2	168	173
13	2	118	122
13	4	155	-155
14	0	163	153
14	1	150	155
14	2	89	-91
15	3	99	-129
K=4			
0	2	636	-646
0	6	130	105
1	2	214	-235
1	3	258	-259
1	4	324	299
1	5	160	154
1	6	156	-146
2	1	363	-412
2	2	174	175
2	3	206	203
2	7	133	-133
3	1	282	-241
3	3	419	409
3	4	77	79
3	5	260	-252
4	0	586	-611
4	1	111	130
4	2	390	369
4	6	129	-114
5	2	272	269
5	4	352	-333
5	6	172	172
6	0	425	429
6	1	208	257
6	2	260	-244
6	3	132	-127
6	6	99	102
7	1	174	173
7	2	108	-91
7	3	318	-312
7	4	137	129
7	5	227	197
8	0	124	124
8	1	285	-273
8	2	83	-78
8	3	138	132
9	1	94	-88
9	2	166	-155
9	3	168	149
9	4	201	180
9	5	92	-93
10	0	306	-298
10	2	178	172
10	6	93	-93
11	2	137	126
11	3	138	128
11	4	174	-166
12	1	167	156
12	3	119	-61
13	3	155	-136
14	0	139	134
14	1	133	-103
14	3	128	63
16	0	96	-113
K=5			
0	3	239	254
0	5	72	18
0	7	96	-97
1	2	138	-156
1	3	233	225
1	4	199	183
1	5	137	-133
1	6	105	-89
2	1	90	118
2	2	293	296
2	6	88	-96
2	7	106	25
3	2	236	246
3	4	336	-300
3	6	140	156
4	0	196	225
4	1	276	310
4	2	97	-117
4	3	133	-135
5	1	159	146
5	3	296	-261
5	5	165	166
6	0	215	225
6	1	188	-190
6	2	151	-148
7	2	199	-187
7	3	108	89
7	4	240	220
7	5	87	-55
7	6	125	-112
8	0	284	-305
8	1	81	-86
8	2	216	185
9	1	86	-79
9	2	82	80
9	3	173	153
9	4	123	-113
9	5	110	-105
10	0	90	67
10	1	159	165
10	3	83	-67
11	3	137	-129
12	0	174	156
14	0	92	-111
14	1	111	-95
K=6			
0	2	235	252
1	2	143	134
1	3	166	149
1	4	203	-168
1	5	97	-97
2	1	159	178
2	2	90	-102
2	3	68	-73
3	1	148	124
3	2	55	51
3	3	234	-221
3	5	145	142
4	0	237	249
4	1	125	-119
4	2	139	-146
4	3	66	56
5	2	156	-142
5	4	195	178
5	6	113	-94
6	0	234	-256
6	1	121	-115
6	2	165	158
7	1	78	-89
7	3	119	163
7	5	118	-105
8	1	225	185
8	3	79	-98
10	0	233	185
10	2	129	-115
K=7			
1	2	58	80
1	3	109	-119
1	4	125	-98
1	5	72	76
2	1	57	-77
2	2	94	-98
2	3	66	46
3	2	108	-113
3	4	151	142
4	0	107	-136
4	1	95	-114
4	2	86	82
5	1	78	-68
5	3	128	124
5	5	69	-80
6	0	100	-97
6	1	118	128
6	2	83	63
6	3	64	-67
7	2	77	82
7	4	105	-98
8	0	158	173
8	2	130	-113
10	1	126	-98
M=SN			
L=0			
0	4	1767	1983
0	6	1136	1215
0	8	550	719
0	10	522	492
H	K	FO	FC
2	0	1705	1523
2	2	684	809
2	4	983	1049
2	6	644	738
2	8	518	480
2	10	367	368
4	0	1588	1787
4	2	1298	1279
4	4	1196	1225
4	6	768	827
4	8	534	516
4	10	389	367
6	0	1252	1201
6	2	903	923
6	4	801	904
6	6	629	653
6	8	391	433
6	10	328	316
8	0	774	860
8	2	706	691
8	4	515	660
8	6	425	481
8	8	319	321
8	10	255	231
10	0	475	570
10	2	476	472
10	4	373	452
10	6	329	340
12	0	376	421
12	2	282	361
L=1			
1	3	1300	1369
1	5	1365	1279
1	7	768	688
1	9	556	529
3	1	1743	1532
3	3	1040	1128
3	5	1192	1091
3	7	645	599
3	9	514	472
5	1	1537	1260
5	3	1124	998
5	5	986	922
5	7	556	543
5	9	501	416
7	1	1010	917
7	3	825	754
7	5	670	694
7	7	423	429
9	1	718	651
9	3	659	545
9	5	421	501
L=2			
0	2	898	876
0	4	1015	978
0	6	683	705
0	8	417	470
2	0	2594	2153
2	2	1830	1662
2	4	1362	1431
2	6	1069	958
2	8	600	602
2	10	488	401
4	0	1628	1361
4	2	1245	1043
4	4	1127	999
4	6	751	716
4	8	524	474
6	0	1270	1045
6	2	1037	878
6	4	869	796
6	6	497	579
6	8	363	384
8	0	947	782
8	2	800	665
8	4	596	616
8	6	387	461
10	2	515	494
1	1	1385	1355
1	3	1242	1125
1	5	937	941
L=3			
1	7	655	611
1	9	429	420
3	1	1594	1402
3	3	1437	1189
3	5	1065	950
3	7	732	639
3	9	471	428
5	1	1165	966
5	3	915	831
5	5	640	704
5	7	463	477
7	1	995	774
7	3	689	675
7	5	571	570
7	7	416	395
9	1	710	587
9	3	571	523
9	5	461	440
L=4			
0	2	1055	1299
0	4	1016	1018
0	6	734	752
0	8	585	511
2	0	1038	1101
2	2	1021	1053
2	4	943	856
2	6	614	645
2	8	506	445
4	0	1238	973
4	2	1055	973
4	4	915	774
4	6	627	590
4	8	509	411
6	0	981	832
6	2	922	789
6	4	711	662
6	6	546	508
6	8	402	355
8	0	678	583
8	2	678	574
8	4	534	475
8	6	436	373
10	0	524	424
L=5			
1	3	793	966
1	5	575	684
1	7	556	553
3	1	836	783
3	3	704	749
3	5	551	538
3	7	480	445
5	1	926	787
5	3	779	740
5	5	615	542
5	7	438	439
7	1	648	592
7	3	561	559
7	5	528	419
9	1	380	415
9	3	467	391
L=6			
0	2	758	875
0	4	521	643
0	6	455	511
0	8	316	368
2	0	536	676
2	2	722	774
2	4	511	573
2	6	443	464
2	8	345	339
4	0	729	660
4	2	714	724
4	4	560	549
4	6	478	437
6	0	609	508
6	2	615	565
6	4	487	430
6	6	455	350
8	0	417	416
8	2	425	446
8	4	434	350

UNOBSERVED REFLECTIONS INDICATED *

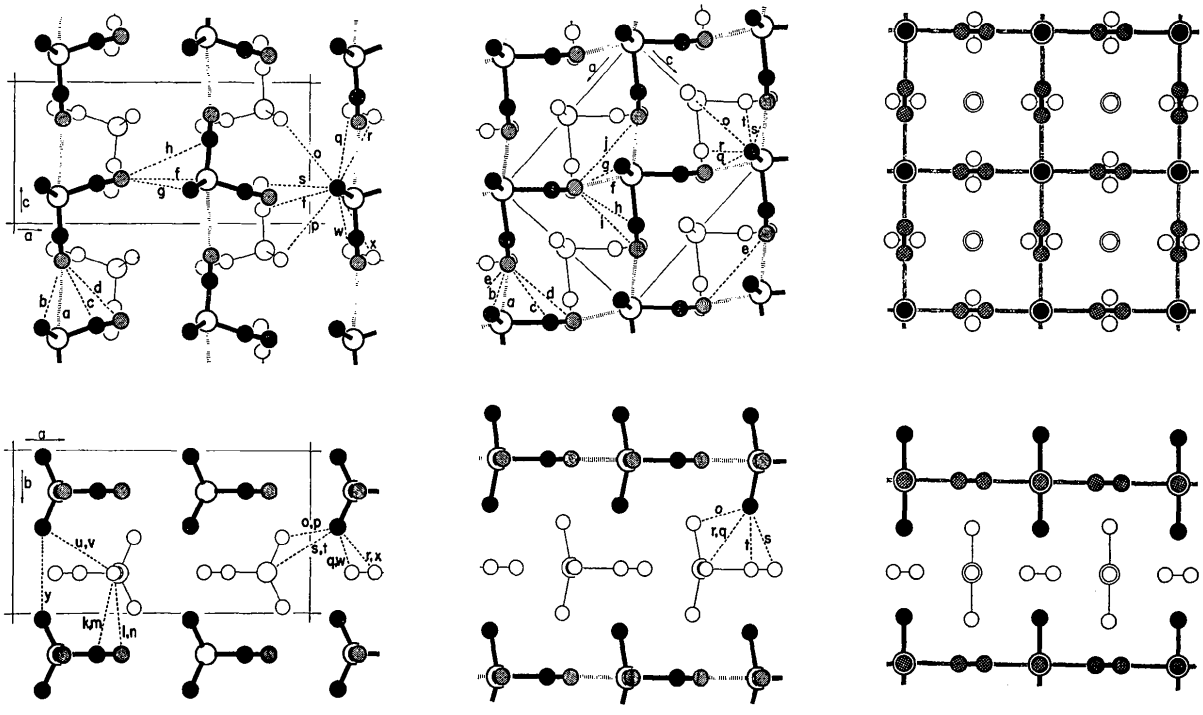
half the minimum observable intensity for that scattering angle. Lorentz and polarization corrections were made; no absorption corrections were made ($\mu=2{\cdot}4$ cm^{-1}).

Refinement began using final parameters of the $(CH_3)_2Ge(CN)_2$ 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 $w=1{\cdot}0$ for $F_o \le 8{\cdot}19$ and $w=(8{\cdot}19/F_o)^4$ for $F_o > 8{\cdot}19$. Final parameters are given in Table 2. Final structure factors are listed in Table 3.

$(CH_3)_2Ge(CN)_2$

The habit of this crystal was identical to that of the $(CH_3)_2Si(CN)_2$ crystals. A crystal, cleaved to a needle elongated along **b** and of cross section 0·28 × 0·28 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 mm ($\mu=50{\cdot}7$ 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 $r=0{\cdot}15$ and $R=0{\cdot}17$. Weissenberg layers were then rescaled to smooth out layer-to-layer fluctuations without introducing any trend with k. Refinement continued with all atoms



(a) (b) (c)

Fig. 1. Structures of (a) $(CH_3)_2Si(CN)_2$ and $(CH_3)_2Ge(CN)_2$; (b) $(CH_3)_2Sn(CN)_2$ and $(CH_3)_2Pb(CN)_2$; (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.

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* $r=\sum w(|F_o|^2-|F_c|^2)^2/\sum w|F_o|^4$; $R=\sum||F_o|-|F_c||/\sum|F_o|$. 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).

anisotropic and it converged with $r=0{\cdot}031$ and $R=0{\cdot}073$. Final weights used were $w=1{\cdot}0$ for $F_o \le 19{\cdot}1$, $w=(19{\cdot}1/F_o)^4$ for $F_o > 19{\cdot}1$. Final positional parameters are given in Table 2. Final structure factors are listed in Table 3.

$(CH_3)_2Sn(CN)_2$

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 × 0·105 × 0·80 mm was mounted in a glass capillary for intensity measurements. Multiple-film, equi-inclination Weissenberg intensity data were collected for the *hk*0–*hk*6 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 *Fmm*2, 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 $r=0{\cdot}054$ and $R=0{\cdot}105$. 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 $w=1{\cdot}0$ for $F_o \le 32{\cdot}4$, $w=(32{\cdot}4/F_o)^4$ for $F_o > 32{\cdot}4$. Final parameters are given in Table 2. Final structure factors are listed in Table 3.

$(CH_3)_2Pb(CN)_2$

A powder photograph of $(CH_3)_2Pb(CN)_2$ 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 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 $a=8{\cdot}88$, $b=9{\cdot}02$, and $c=8{\cdot}37$ 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 $(CH_3)_2Pb(CN)_2$ molecule similar to the Sn analog, are given in Table 4.

Table 4. *Powder data for* $(CH_3)_2Pb(CN)_2$

h	*k*	*l*	Q_{obs}*	Q_{calc}	I_{obs}†	I_{calc}‡
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_{obs} was determined from film data using Cr $K\alpha$ radiation.

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

‡ Calculated using an assumed structure similar to that of $(CH_3)_2Sn(CN)_2$.

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 exidence is inconclusive; the infrared spectrum is consistent with the cyanide.

Table 5. *Comparison of the structures as cyanides versus isocyanides for* $(CH_3)_2M(CN)_2$, $M=$ 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* $(CH_3)_2M(CN)_2$

Lengths:	Compound		Reference
Si–CH_3	$(CH_3)_2Si(CN)_2$	1·83 (2) Å	*a*
–	$(CH_3)_{2,3}SiX_{2,1}$	1·85 (avg)	*b*
Si–CN	$(CH_3)_2Si(CN)_2$	1·87 (2)	*a*
–	–	1·86 (3)	*a*
Ge–CH_3	$(CH_3)_2Ge(CN)_2$	1·91 (2)	*a*
–	$(CH_3)_3GeCN$	1·98 (avg)	*c*
Ge–CN	$(CH_3)_2Ge(CN)_2$	1·94 (2)	*a*
–	–	1·98 (2)	*a*
–	$(CH_3)_3GeCN$	1·98 (6)	*c*
Sn–CH_3	$(CH_3)_2SnF_2$	2·08 (2)	*d*
–	$(CH_3)_2Sn(CN)_2$	2·11 (5)	*a*
–	$(CH_3)_2Sn(NCS)_2$	2·09 (1)	*e*
–	–	2·14 (3)	*f*
–	$(CH_3)_3SnCN$	2·16 (avg)	*g*
–	$(CH_3)_4Sn$	2·18 (3)	*b*
Sn–CN	$(CH_3)_2Sn(CN)_2$	2·27 (7)	*a*
C–N	$(CH_3)_2Si(CN)_2$	1·15 (2)	*a*
–	–	1·12 (3)	*a*
–	$(CH_3)_2Ge(CN)_2$	1·13 (2)	*a*
–	–	1·10 (2)	*a*
–	$(CH_3)_2Sn(CN)_2$	1·09 (12)	*a*
–	usual $C\equiv N$	1·156	*h*
Angles:			
CH_3–Si–CH_3	$(CH_3)_2Si(CN)_2$	120·2 (10)°	*a*
–	$(CH_3)_3SiCl,Br$	113 (avg)	*b*
CH_3–Ge–CH_3	$(CH_3)_2Ge(CN)_2$	120·9 (8)	*a*
–	$(CH_3)_3GeCN$	114·8 (avg)	*c*
CH_3–Sn–CH_3	$(CH_3)_2Sn(CN)_2$	148·7 (35)	*a*
–	$(CH_3)_2Sn(NCS)_2$	148·9 (9)	*e*
–	–	145·9 (14)	*f*
CH_3–Si–CN	$(CH_3)_2Si(CN)_2$	109·5 (5)	*a*
–	–	107·4 (5)	*a*
CH_3–Ge–CN	$(CH_3)_2Ge(CN)_2$	109·5 (5)	*a*
–	–	106·9 (5)	*a*
–	$(CH_3)_3GeCN$	103·8 (avg)	*c*
CH_3–Sn–CN	$(CH_3)_2Sn(CN)_2$	101·4 (13)	*a*
NC–Si–CN	$(CH_3)_2Si(CN)_2$	101·1 (10)	*a*
NC–Ge–CN	$(CH_3)_2Ge(CN)_2$	100·9 (7)	*a*
NC–Sn–CN	$(CH_3)_2Sn(CN)_2$	85·3 (37)	*a*
SCN–Sn–NCS	$(CH_3)_2Sn(NCS)_2$	86·6 (5)	*e*
–	–	84·1 (16)	*f*
Si–C–N	$(CH_3)_2Si(CN)_2$	178·1 (22)	*a*
–	–	178·1 (22)	*a*
Ge–C–N	$(CH_3)_2Ge(CN)_2$	179·8 (18)	*a*
–	–	178·8 (22)	*a*
Sn–C–N	$(CH_3)_2Sn(CN)_2$	177·1 (50)	*a*

Key to references

a	This work
b	Sutton (1965)
c	Schlemper & Britton (1966*b*)
d	Schlemper & Hamilton (1966)
e	Forder & Sheldrick (1970)
f	Chow (1970)
g	Schlemper & Britton (1966*a*)
h	Britton (1967)

Table 7. *Intermolecular distances in* $(CH_3)_2M(CN)_2$

	Identification*	Si	Ge	Sn
$N\cdots M$	*a*	3·48 (3) Å	3·28 (2) Å	2·68 (11) Å
$N\cdots CH_3$	*b*	3·51 (3)	3·36 (2)	3·14 (8)
$N\cdots C$	*c*	3·40 (4)	3·31 (3)	3·28 (12)
$N\cdots N$	*d*	3·80 (3)	3·81 (3)	3·98 (1)
$N\cdots N$	*e*	–	–	4·38 (25)
$N\cdots M$	*f*	3·97 (2)	3·84 (2)	=*a*
$N\cdots CH_3$	*g*	3·62 (2)	3·50 (2)	=*b*
$N\cdots C$	*h*	4·47 (3)	4·43 (2)	=*c*
$N\cdots N$	*i*	–	–	=*d*
$N\cdots N$	*j*	–	–	=*e*
$N\cdots N$	*k*	3·78 (1)	3·82 (1)	–
$N\cdots C$	*l*	3·79 (1)	3·81 (1)	–
$C\cdots N$	*m*	3·77 (1)	3·80 (1)	–
$C\cdots C$	*n*	3·91 (1)	3·89 (1)	–
$CH_3\cdots CH_3$	*o*	4·01 (3)	3·87 (3)	4·05 (1)
$CH_3\cdots CH_3$	*p*	4·38 (3)	4·31 (3)	–
$CH_3\cdots N$	*q*	4·16 (3)	3·98 (2)	3·79 (9)
$CH_3\cdots C$	*r*	4·20 (2)	4·06 (2)	3·66 (9)
$CH_3\cdots N$	*s*	4·19 (2)	4·08 (2)	=*q*
$CH_3\cdots C$	*t*	4·24 (2)	4·12 (2)	=*r*
$CH_3\cdots N$	*u*	3·92 (2)	3·94 (2)	–
$CH_3\cdots C$	*v*	4·10 (2)	4·04 (2)	–
$CH_3\cdots N$	*w*	3·67 (3)	3·68 (2)	–
$CH_3\cdots C$	*x*	4·24 (3)	4·18 (2)	–
$CH_3\cdots CH_3$	*y*	4·16 (4)	4·28 (3)	–

* See Fig. 1. for identification. All distances under 4·50 Å are given.

Discrete, relatively normal molecules are apparent in the structures of the Si and Ge compounds. The CH_3–M–CH_3 bond angles are larger, and the NC–M–CN bond angles are smaller, than tetrahedral, which is what we expect from the relative electronegativities of the CH_3– and NC– groups. The one unusual feature within the molecules is that the M–CH_3 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 $CN\cdots M$ bonds are formed.

The packing of the molecules in the Si and Ge compounds is dominated by the $CN\cdots M$ 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 $N\cdots P$ and $N\cdots As$ (3·4 and 3·5 Å, respectively) can also be used as reference points for $N\cdots Si$ and $N\cdots Ge$ distances. By these standards, the $N\cdots Si$ distance of 3·84 (3) Å in $(CH_3)_2Si(CN)_2$ is not remarkable. However, the alignment of the molecules is striking; exactly the same alignment in the Ge analog leads to an $N\cdots Ge$ 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 $(CH_3)_3GeCN$ (3·57 Å). The shortening of the distance from $(CH_3)_3GeCN$ to $(CH_3)_2Ge(CN)_2$ is virtually identical with the shortening from $(CH_3)AsCN$ [$N\cdots As$ of

3·18 Å (Camerman & Trotter, 1963)] to $(CH_3)As(CN)_2$ [N···As of 2·94 Å (Schlemper & Britton, 1966*b*)]. The N···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 N···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 N···Si [3·97 (2) Å], and N···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 CH_3–Sn–CH_3 [148·7 (35)°] and 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_3 bond length, which suggests that intermolecular interaction weakens the primary Sn–CN bond. The N···Sn distance (2·68 Å) is longer than the average Sn–CN distance in $(CH_3)_3SnCN$, although, perhaps coincidentally, the Sn–CN–Sn total distances are very similar in the two compounds: 6·01 (1) Å in $(CH_3)_2Sn(CN)_2$ and 6·06 (1) Å in $(CH_3)_3SnCN$. 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 Sn···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 Sn···N interaction and the intramolecular distances. It is interesting that the short CH_3···N distance of 3·14 Å, which follows perforce from the N···Sn interaction, is shorter than the intramolecular C···C distance of 3·39 Å between the CH_3 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 CH_3···CH_3, 4·06 Å, and CH_3···C (in CN), 3·67 Å. It is worth considering what the distances and packing would be if the Sn–CN···Sn bridges were statistically centric as they are in $(CH_3)_3SnCN$. The structure [Fig. 1(*c*)] would be body-centered tetragonal and exactly analogous to SnF_4 and $(CH_3)_2SnF_2$. If we assume the Sn···CN···Sn distance to be 6·06 Å as in $(CH_3)_3SnCN$, the intermolecular interlayer CH_3···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 $(CH_3)_2SnF_2$. Interlayer spacing would then be determined by CH_3···CN contacts. If we assume the CH_3···CN distance to be 3·80 Å [sum of the usual van der Waals radius for CH_3 (2·0 Å) and the equatorial radius of the CN^- ion (1·78 Å)], and if we take the Sn–CH_3 distance to be 2·08 Å as in $(CH_3)_2SnF_2$, the interlayer distance would be 4·37 Å. This would lead to a molecular volume of 161 Å^3 compared to the 174 Å^3 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 $(CH_3)_3SnCN$. 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 $(CH_3)_3PbCN$. 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. Ti(Urea)$_6$(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 Ti(urea)$_6$(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 Ti(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 Ti(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 Ti^{3+} (d^1) ion in a highly symmetrical environment, of close to regular octahedral stereochemistry. Accordingly, the hexaurea complex Ti(urea)$_6$(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 Ti(urea)$_6^{3+}$ ion. Fowles, Lester & Wood (1969) have also described Ti^{3+} in octahedral coordination in (TiBr$_3$)$_2$.3C$_4$H$_{10}$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 Ti(urea)$_6$(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 Ti(H$_2$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