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A Tetragonal-Pyramidal Indium(III) Species. The Crystal Structure of Tetraethylammonium Pentachloroindate(III)

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The crystal structure of tetraethylammonium pentachloroindate(III), $((C_2H_5)_4N)_2InCl_5$, has been determined from three-dimensional X-ray data collected by counter methods. The structure has been refined by least-squares techniques to a conventional R factor of 9.5% for the 811 observed reflections. The salt crystallizes in the tetragonal space group P4/n with two formula units in a cell of dimensions $a = 9.374$ (10) Å and $c = 14.137$ (10) Å. The calculated density of 1.48 g/cm³ is close to the measured value of 1.45 g/cm³. The pentacoordinate indium atom in the anion is bonded to five chlorines and has crystallographic fourfold symmetry. The apical In–Cl bond length is 2.415 (12) Å and the four basal bond lengths are 2.456 (7) Å. This anion is the first undistorted example of this geometry in a nontransition element.

Introduction

As with many other main group elements, the stereochemistry of indium(III) has generally been discussed in terms of either four- or six-coordinate species. There is however now considerable evidence that some at least of the addition compounds of the type InX_3L_2 (X = Cl, Br, I; L = monodentate donor) involve five-coordination around the metal.[1,2] Examples of this coordination number in the solid state are comparatively rare outside the transition metal series, and it was therefore of considerable interest to determine the crystal structure of the salt $((C_2H_5)_4N)_2[InCl_5]$. This is one of a series of compounds originally reported by Ekeley and Potratz[3] and formulated by these authors as double salts of the type $InX_3 \cdot CX$, $InX_3 \cdot 2CX$, etc. (X = Cl, Br, I; C = substituted ammonium or sulfonium cation). As the result of studies of the solution properties of anionic indium(III) halide complexes,[4] it was suggested that these species should be regarded as the complex salts $CInX_4$, C_2InX_5, etc., and a recent crystal structure investigation[5] of $(C_2H_5)_4NInCl_4$ has shown that this interpretation is correct. Wharf and Shriver[6] have very recently provided spectroscopic evidence which favors the formulation $((C_2H_5)_4N)_2InCl_5$.

There are at least three possible stereochemical forms for the anion in the salt $((C_2H_5)_4N)_2[InCl_5]$; the monomeric $InCl_5^{2-}$ unit may have trigonal-bipyramidal (D_{3h}) or tetragonal-pyramidal (C_{4v}) symmetry, plus the less likely dimer $In_2Cl_{10}^{4-}$, with two $InCl_6$ units sharing a common edge. The general relationship between the two MX_5 structures has been discussed by Muetterties and Schunn[7] and others. These authors have also reviewed thoroughly the properties of the many five-coordinate species known up to 1966.

The structure of $((C_2H_5)_4N)_2[InCl_5]$ shows that the anion has a C_{4v} structure which is unique among compounds of the nontransition elements. This geometry is compared with that of other five-coordinate species and the In–Cl bond lengths are discussed in terms of other indium–chlorine compounds.

Experimental Section

Tetraethylammonium pentachloroindate was obtained by the method described by Ekeley and Potratz.[3] Single crystals for X-ray work were grown by slowly evaporating a solution of this material in dichloromethane and were then sealed into thin-walled Lindemann glass capillary tubes. An investigation of twinned crystals grown from ethanol solution is in progress.[8]

Weissenberg photographs of the zones $0kl$, $1kl$, $2kl$, $3kl$, and $4kl$ using Cr Kα radiation, together with precession photographs of the zones $hk0$ and hhl using the Mo Kα, showed absences for only $hk0$ with $h + k = 2n + 1$. This combined with the Laue group indicated unambiguously the space group P4/n.

Crystal Data.—$((C_2H_5)_4N)_2[InCl_5]$, formula weight 552.5, is tetragonal, space group P4/n (identified from Laue group and the systematic absences of X-ray reflections). $a = b = 9.374$ Å, $c = 14.137$ Å ($\sigma = 0.01$ Å) (λ 0.7107 Å for Mo Kα radiation). $V = 1242$ Å³, $D_m = 1.45$ ($\sigma = 0.04$) g cm^{-3} (Berman density balance determination), $Z = 2$, $D_x = 1.48$ g cm^{-3}, $F(000) = 568$, and μ(Mo Kα) = 14.85 cm^{-1}.

All data were collected using a cube-shaped crystal of 0.4-mm edge, mounted with its a axis parallel to Φ. Cell dimensions were determined by extrapolation from high-angle reflections measured on a Picker four-circle diffractometer (at 25°); the errors were estimated from the internal consistency obtained.

Reflection intensities for the unique set of data were measured using zirconium-filtered Mo Kα radiation and a scintillation detector with pulse-height analysis. Measurements were made using a 1.1° takeoff angle with a symmetrical θ–2θ scan of 2° width (carried out at a rate of 2°/min). The detector was positioned 23 cm from the crystal and the symmetrically variable aperture device was arranged so that the detector aperture was 5.0 mm high and 4.0 mm wide. Examination of a number of reflection profiles showed isotropic mosaicity which did not warrant cooling the crystal in liquid nitrogen.

Background was estimated in five different directions in reciprocal space, and a curve as a function of θ only satisfactorily described the results obtained. Accordingly each reflection which did not count 1.2 times background was coded as unobserved (denoted by an asterisk in Table II) and assigned a value of half the local background intensity. Of the 936 intensities recorded in the range $0° < 2\theta < 45°$, 125 were unobserved. Four standard reflections were measured every 3 hr and retained a con-

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[1] D. M. Adams, A. J. Carty, P. Carty, and D. G. Tuck, *J. Chem. Soc., A*, 162 (1968).

[2] M. J. Taylor, *ibid.*, 1462 (1967).

[3] J. B. Ekeley and H. A. Potratz, *J. Am. Chem. Soc.*, **58**, 907 (1936).

[4] D. G. Tuck and E. J. Woodhouse, *J. Chem. Soc.*, 6017 (1964).

[5] J. Trotter, F. W. B. Einstein, and D. G. Tuck, submitted for publication.

[6] I. Wharf and D. F. Shriver, *Chem. Commun.*, 526 (1968).

[7] E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966).

[8] J. Trotter and F. W. B. Einstein, unpublished results.

stancy within 1.5% over the entire data collection. Coincidence losses were carefully checked for the most intense reflections and found to be negligible. Lorentz and polarization factors were applied and the structure factors were calculated in the usual way; no correction for absorption was made since transmission factors would vary less than ±10% in F^2 for extreme cases.

Structure Determination

The density and space group requirements can only be met by an ordered arrangement in which one indium and one chlorine atom are on either a $\bar{4}$ site or a fourfold axis. From the unsharpened three-dimensional Patterson function it was possible to assign approximate positions on the fourfold axis to the indium atom and one chlorine atom and the remaining general chlorine atom was located. The nitrogen atoms of the tetraethylammonium groups were initially assumed to be on four of the $\bar{4}$ sites. Block-diagonal least-squares refinement of these atomic positions and of individual isotropic temperature factors was carried out, assuming initial values for the temperature factors of 3.0, 4.0, and 5.0 Å^2, respectively. A value of 0.18 was obtained for the agreement factor R [defined as $\Sigma(||F_o| - |F_c||)/\Sigma|F_o|$] after several cycles of refinement. At this stage, the temperature factor for one of the two pairs of equivalent nitrogen atoms became unreasonably large, indicating it had been incorrectly placed. An electron density Fourier difference map revealed that this atom (N(8); see Figure 1 and Table I) should have been located on the fourfold axis, with the symmetry satisfied by disorder in the orientations of the tetraethylammonium groups centered on this axis. Further least-squares refinement and another Fourier difference map showed that a similar type of disorder was also present in the $(C_2H_5)_4N$ group (N(4)) on the $\bar{4}$ site, although this is not required by the symmetry of the position. The disorder of both of these positions is illustrated in Figure 1 by showing one type of tetraethylammonium position by solid lines and the other type by dashed lines. Throughout the refinement, the structure factor agreement was examined as a function of both $|F_o|$ and sin θ, and appropriate weighting schemes were chosen. The final scheme used was $\sqrt{w} = 1$ if $|F_o| < 25$, and $\sqrt{w} = 25/|F_o|$ if $|F_o| > 25$. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ and the standard deviation of an observation of unit weight was 0.94, confirming that reasonable weights had been assigned. Scattering factors[9] used were those calculated on the TFD model for the indium atoms and were self-consistent-field values for the remainder. Full allowance was made for anomalous scattering by the indium atom;[9] in the listing of structure factors, F_{calcd} is given the sign of the real component and the magnitude of the total value.

R converged to a value of 0.095, with the parameter shifts less than 0.1 standard deviation in the final cycle. A final electron density difference map was computed and showed no anomalous features. The largest peak (1.5 e/Å^3) appeared near the general chlorine atom. There were no other peaks larger than 1.0 e/Å^3. The final atomic positions and their standard deviations are given in Table I, and the observed and calculated structure factors are given in Table II. (Asterisks denote unobserved reflections.)

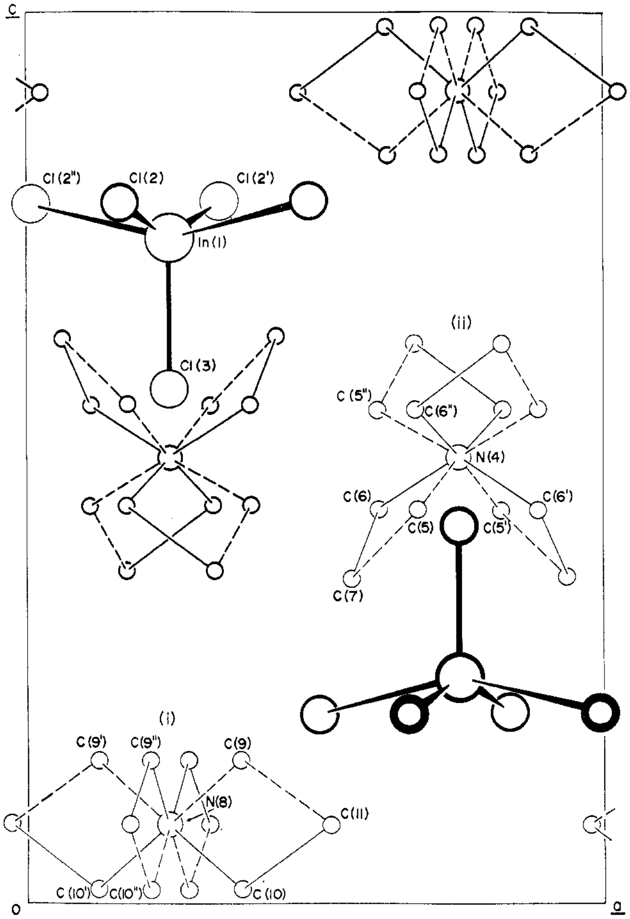

Figure 1.—The crystal structure of $((C_2H_5)_4N)_2[InCl_5]$ projected along the b axis.

TABLE I

ATOMIC POSITIONS AND TEMPERATURE FACTORS, WITH STANDARD ERRORS

Atom	x	y	z	B, Å^2
In(1)	0.2500 (–)	0.2500 (–)	0.7444 (1)	3.2 (1)
Cl(2)	0.1637 (5)	0.4893 (5)	0.7861 (3)	5.5 (1)
Cl(3)	0.2500 (–)	0.2500 (–)	0.5736 (5)	4.5 (1)
N(4)	0.7500 (–)	0.2500 (–)	0.5000 (–)	2.8 (4)
C(5)	0.6810 (26)	0.3710 (26)	0.4397 (17)	2.9 (4)
C(6)	0.6271 (50)	0.1932 (48)	0.4392 (34)	7.7 (1.0)
C(7)	0.5682 (20)	0.3092 (20)	0.3689 (14)	6.0 (4)
N(8)	0.2500 (–)	0.2500 (–)	0.0824 (14)	3.0 (4)
C(9)	0.3742 (28)	0.2775 (29)	0.1510 (17)	3.4 (5)
C(10)	0.3742 (29)	0.2811 (29)	0.0158 (19)	3.6 (5)
C(11)	0.5201 (20)	0.3071 (20)	0.0840 (13)	6.0 (4)

Structure Description and Discussion

The structure is made up of tetragonal-pyramidal pentachloroindate(III) ions and tetraethylammonium ions, packed together in an electrostatically favorable manner. The cations are of two crystallographically independent types, one of which (i) is interleaved with the pentachloroindate(III) ions along the fourfold axis, while the other (ii) occupies sites of $\bar{4}$ symmetry

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(9) "International Critical Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962.

Table II

Measured and Calculated Structure Factors for $((C_2H_5)_4N)_2[InCl_5]$

K	FO	FC
H= 0, L= 0		
2	1414	-1398
4	1103	1115
6	292	-214
8	516	486
10	244	-237
H= 0, L= 1		
0	13*	-29
1	1296	1246
2	428	396
3	492	-488
4	32*	2
5	547	539
6	230	211
7	167	-215
8	47*	-13
9	357	330
10	55*	55
H= 0, L= 2		
0	922	-1037
1	491	-406
2	168	125
3	331	280
4	606	-587
5	250	-286
6	40*	49
7	257	242
8	321	-270
9	56	-29
10	167	155
H= 0, L= 3		
0	683	-664
1	1423	-1375
2	53	-59
3	691	717
4	87	-82
5	237	-247
6	319	-237
7	196	198
8	48*	-77
9	265	-243
H= 0, L= 4		
0	920	961
1	649	-653
2	613	-595
3	242	176
4	626	601
5	50	66
6	381	-225
7	146	-111
8	408	359
9	52	-27
H= 0, L= 5		
0	877	765
1	1074	1052
2	154	205
3	763	-739
4	126	-108
5	465	451
6	326	311
7	304	-284
8	57	-7
9	265	264
H= 0, L= 6		
0	1120	-1093
1	35	63
2	675	676
3	360	345
4	655	-667
5	163	-185
6	343	308
7	219	194
8	340	-285
9	54*	3
H= 0, L= 7		
0	329	-386
1	563	-581
2	444	-441
3	427	428
4	40*	-40
5	400	-424
6	346	-369
7	370	316
8	52*	94
H= 0, L= 8		
0	373	307
1	18*	-13
2	393	-430
3	322	-323
4	352	343
5	235	224
6	346	-368
7	168	-202
8	247	166
H= 0, L= 9		
0	346	303
1	244	243
2	148	184
3	344	-347
4	78	-93
5	267	325
6	294	280
7	281	-245
8	54*	-25
H= 0, L= 10		
0	334	-216
1	100	117
2	409	427
3	45*	-23
4	220	-206
5	148	-99
6	313	323
7	53*	108
H= 0, L= 11		
0	173	82
1	355	-292
2	134	-146
3	404	390
4	49*	61
5	312	-325
6	140	-124
H= 0, L= 12		
0	301	213
1	156	131
2	425	-433
3	164	-166
4	320	310
5	156	155
6	302	-340
H= 0, L= 13		
0	165	-71
1	161	118
2	187	169
3	227	-225
4	143	-129
5	193	191
H= 0, L= 14		
0	52*	99
1	194	-192
2	135	146
3	175	142
H= 0, L= 15		
0	54*	31
1	183	-162
H= 1, L= 0		
1	1155	-1113
3	80	133
5	648	-634
7	449	473
9	532	-452
H= 1, L= 1		
0	1199	1246
1	653	-500
2	508	-395
3	300	-434
4	710	737
5	225	209
6	416	-441
7	90	-70
8	500	483
9	51*	-18
10	225	-227
H= 1, L= 2		
0	465	-406
1	988	926
2	869	838
3	29*	-13
4	274	-287
5	556	516
6	115	112
7	268	-288
8	95	-77
9	440	379
H= 1, L= 3		
0	1369	-1375
1	29*	-104
2	529	-364
3	464	474
4	472	-396
5	77	98
6	235	219
7	100	78
8	434	-367
9	40	38
H= 1, L= 4		
0	644	-653
1	741	-717
2	563	-559
3	246	193
4	69	-86
5	374	-358
6	74	-57
7	262	246
8	187	-164
9	277	-260
H= 1, L= 5		
0	1046	1052
1	115	-75
2	494	-476
3	406	-390
4	553	539
5	40*	-83
6	434	-439
7	72	-25
8	369	351
9	148	-118
H= 1, L= 6		
0	32*	63
1	674	735
2	492	548
3	677	-702
4	170	-152
5	696	685
6	182	191
7	176	-422
8	76	44
9	256	278
H= 1, L= 7		
0	563	-581
1	357	-349
2	638	676
3	639	720
4	424	-424
5	234	-249
6	349	339
7	184	174
8	300	-225
H= 1, L= 8		
0	37*	-13
1	384	-405
2	410	-441
3	312	327
4	237	258
5	142	-99
6	176	-185
7	197	172
8	61	5
H= 1, L= 9		
0	239	243
1	92	78
2	455	-476
3	181	-260
4	380	380
5	97	-69
6	244	-242
7	52*	-41
8	190	141
H= 1, L= 10		
0	143	117
1	362	369
2	240	325
3	506	-551
4	47*	-34
5	326	313
6	51*	64
7	245	-243
H= 1, L= 11		
0	376	-292
1	100	-97
2	481	555
3	212	249
4	341	-327
5	51*	-78
6	271	287
H= 1, L= 12		
0	211	131
1	385	-362
2	267	-267
3	392	427
4	165	156
5	252	-214
6	169	-128
H= 1, L= 13		
0	212	118
1	141	103
2	250	-371
3	157	-146
4	185	193
5	218	131
H= 1, L= 14		
0	192	-192
1	153	164
2	112	89
3	177	-260
H= 1, L= 15		
0	185	-162
1	55*	-115
H= 2, L= 0		
0	1300	-1395
2	338	436
4	1081	-1033
6	708	705
8	501	-522
H= 2, L= 1		
0	396	396
1	853	-864
2	477	-452
3	336	352
4	97	115
5	1077	-1044
6	110	-117
7	297	331
8	48*	42
9	343	-317
H= 2, L= 2		
0	176	126
1	351	386
2	246	-180
3	220	-211
4	731	702
5	88	-42
6	579	-550
7	79	-93
8	248	228
9	52*	39
H= 2, L= 3		
0	104	-58
1	682	636
2	118	97
3	238	-256
4	35*	17
5	795	731
6	78	-45
7	310	-336
8	51	42
9	288	267
H= 2, L= 4		
0	594	-595
1	72	125
2	675	633
3	192	170
4	540	-504
5	426	420
6	447	436
7	59	-79
8	263	-278
9	53*	86
H= 2, L= 5		
0	162	208
1	750	-773
2	344	-328
3	593	561
4	38*	59
5	625	-609
6	107	38
7	350	371
8	58	42
9	258	-257
H= 2, L= 6		
0	467	476
1	166	174
2	615	-562
3	399	-452
4	710	672
5	192	-182
6	401	-446
7	154	-141
8	337	338
9	55*	6
H= 2, L= 7		
0	432	-441
1	585	577
2	456	520
3	492	-440
4	208	222
5	330	311
6	148	-118
7	182	-225
8	52*	-25
H= 2, L= 8		
0	386	-450
1	206	-190
2	397	413
3	419	433
4	391	-350
5	49*	-5
6	266	272
7	155	166
8	128	-142
H= 2, L= 9		
0	161	184
1	327	-334
2	171	-247
3	404	397
4	89	92
5	304	-240
6	61	-49
7	208	207
H= 2, L= 10		
0	406	427
1	44*	49
2	402	-417
3	77	-106
4	186	163
5	151	-151
6	131	-137
7	54*	18
H= 2, L= 11		
0	183	-146
1	396	365
2	47*	103
3	400	-427
4	50*	-65
5	214	148
6	54*	25
H= 2, L= 12		
0	428	-433
1	158	-152
2	437	430
3	50*	167
4	276	-244
5	54*	-73
H= 2, L= 13		
0	244	169
1	228	-222
2	186	-203
3	257	307
4	66	133
H= 2, L= 14		
0	106	144
1	151	154
2	159	-195
3	132	-110
H= 3, L= 0		
1	2092	2027
3	870	-862
5	956	900
7	183	-240
9	239	206
H= 3, L= 1		
0	463	-488
1	114	117
2	1198	1147
3	183	212
4	720	-709
5	39*	-67
6	574	575
7	115	95
8	96	-176
9	53*	28
H= 3, L= 2		
0	311	280
1	1030	-1053
2	190	-134
3	591	596
4	103	76
5	700	-671
6	43*	-60
7	119	160
8	159	179
9	223	-214
H= 3, L= 3		
0	666	717
1	61	-60
2	830	-786
3	143	-135
4	671	679
5	196	-174
6	395	-376
7	194	-151
8	152	148
9	122	43
H= 3, L= 4		
0	238	176
1	499	539
2	488	-423
3	385	-363
4	308	325
5	923	927
6	115	-92
7	110	-156
8	86	-64
9	176	183
H= 3, L= 5		
0	731	-739
1	351	360
2	817	771
3	38*	9
4	554	-565
5	179	138
6	348	380
7	148	135
8	131	-183
9	55*	-25
H= 3, L= 6		
0	342	345
1	746	-963
2	38*	91
3	805	786
4	114	78
5	707	-761
6	46*	-6
7	334	371
8	151	133
H= 3, L= 7		
0	443	428
1	132	-195
2	453	-430
3	41*	-131
4	253	278
5	45*	-40
6	258	-285
7	50*	-211
8	214	217
H= 3, L= 8		
0	312	-323
1	306	266
2	100	61
3	231	-232
4	202	-223
5	47*	36
6	132	115
7	169	-174
8	179	-170
H= 3, L= 9		
0	324	-347
1	92	130
2	327	283
3	115	31
4	316	-326
5	107	146
6	242	240
7	100	103
H= 3, L= 10		
0	44*	-23
1	296	-247
2	93	105
3	317	331
4	114	-119
5	166	-171
6	53*	9
H= 3, L= 11		
0	403	390
1	106	123
2	313	-271
3	148	-160
4	271	242
5	53*	58
6	180	-182
H= 3, L= 12		
0	163	-164
1	240	188
2	50*	139
3	283	-240
4	53*	-109
5	186	138
H= 3, L= 13		
0	225	-225
1	52*	-69
2	143	100
3	96	121
4	161	-141
H= 3, L= 14		
0	129	142
1	64	-48
2	55*	-49
H= 4, L= 0		
0	1046	1115
2	1195	-1209
4	450	397
6	335	-348
8	308	256
H= 4, L= 1		
0	98	0
1	1191	1172
2	67	34
3	593	-447
4	257	-266
5	475	532
6	143	153
7	140	-201
8	50	-86
9	227	230
H= 4, L= 2		
0	584	-587
1	61	-81
2	787	765
3	184	225
4	132	-156
5	152	-177
6	302	298
7	111	130
8	51*	-80
9	54*	-70
H= 4, L= 3		
0	101	-82
1	1175	-1096
2	402	366
3	243	253
4	87	127
5	265	-262
6	45*	16
7	97	92
8	93	61
9	208	-180
H= 4, L= 4		
0	598	601
1	600	-604
2	851	-963
3	57	-56
4	299	310
5	81	-59
6	348	-376
7	129	-67
8	198	171
H= 4, L= 5		
0	156	-108
1	675	751
2	98	-136
3	389	-427
4	281	-295
5	318	355
6	109	76
7	291	-290
8	142	-126
H= 4, L= 6		
0	648	-667
1	39*	224
2	662	674
3	139	189
4	433	-515
5	116	-93
6	306	353
7	231	219
8	227	-223
H= 4, L= 7		
0	40*	-40
1	356	-391
2	74	54
3	378	414
4	196	203
5	283	-292
6	100	-108
7	235	221
8	170	169
H= 4, L= 8		
0	330	343
1	43*	-26
2	193	-201
3	256	-242
4	320	270
5	196	193
6	190	-199
7	180	-178
H= 4, L= 9		
0	163	-95
1	173	246
2	45*	-91
3	320	-347
4	188	-183
5	279	302
6	52*	74
7	79	-109
H= 4, L= 10		
0	206	-206
1	143	182
2	178	196
3	109	96
4	251	-280
5	52*	-24
6	212	178
H= 4, L= 11		
0	48*	61
1	239	-149
2	50*	25
3	287	309
4	141	127
5	256	-243
H= 4, L= 12		
0	310	310
1	91	62
2	247	-225
3	164	-155
4	282	312
H= 4, L= 13		
0	216	-129
1	155	78
2	54*	134
3	176	-205
H= 5, L= 0		
1	764	-830
3	89	163
5	338	-339
7	385	406
H= 5, L= 1		
0	520	539
1	43	26
2	661	-686
3	159	-105
4	41*	107
5	59	60
6	466	-452
7	50*	-44
8	107	108
H= 5, L= 2		
0	293	-286
1	502	500
2	133	187
3	296	-308
4	199	-191
5	287	292
6	47*	12
7	305	-286
8	58	-83
H= 5, L= 3		
0	235	-247
1	38*	-76
2	377	393
3	294	239
4	42*	-100
5	159	-134
6	369	334
7	50*	47
8	245	-223
H= 5, L= 4		
0	90	66
1	342	-386
2	113	83
3	239	279
4	242	193
5	239	-215
6	89	74
7	242	201
8	54*	-10
H= 5, L= 5		
0	465	481
1	80	-40
2	479	-524
3	171	-143
4	351	386
5	141	91
6	377	-336
7	52*	52
8	211	211
H= 5, L= 6		
0	163	-185
1	548	598
2	92	55
3	399	-399
4	359	-399
5	408	423
6	91	-1
7	286	-286
H= 5, L= 7		
0	399	-424
1	191	-176
2	387	402
3	343	348
4	300	-291
5	145	-137
6	274	245
7	54*	70
H= 5, L= 8		
0	246	224
1	193	-240
2	107	-81
3	274	209
4	323	352
5	234	-198
6	52*	-54
H= 5, L= 9		
0	283	329
1	47*	20
2	200	-234
3	146	-175
4	269	290
5	106	88
6	196	-160
H= 5, L= 10		
0	135	-99
1	279	296
2	63	29
3	320	-322
4	52*	-113
5	232	225
H= 5, L= 11		
0	325	-325
1	142	-120
2	261	264
3	121	114
4	330	-345
H= 5, L= 12		
0	188	155
1	249	-234
2	147	-126
3	284	270
H= 5, L= 13		
0	179	191
1	141	86
H= 6, L= 0		
0	40*	-214
2	785	856
4	518	-565
6	642	579
8	309	-295
H= 6, L= 1		
0	301	211
1	113	-162
2	125	-123
3	408	428
4	182	191
5	390	-351
6	81	-6
7	416	360
8	71	-10
H= 6, L= 2		
0	40*	49
1	227	232
2	268	-276
3	155	-135
4	144	118
5	107	117
6	255	-353
7	87	-36
8	117	139
H= 6, L= 3		
0	287	-237
1	251	288
2	42*	-29
3	381	-320
4	90	-66
5	376	339
6	168	-177
7	352	-284
H= 6, L= 4		
0	188	-225
1	92	-56
2	377	389
3	44*	-32
4	262	-236
5	65	102
6	385	365
7	163	-118
H= 6, L= 5		
0	327	311
1	387	-444
2	50	8
3	418	411
4	116	103
5	328	-313
6	103	67
7	294	289
H= 6, L= 6		
0	332	308
1	346	342
2	42*	-413
3	186	-105
4	416	372
5	50*	65
6	344	-320
7	55*	20
H= 6, L= 7		
0	349	-369
1	294	314
2	133	131
3	361	-318
4	137	-169
5	228	216
6	81	-51
H= 6, L= 8		
0	357	-348
1	238	-259
2	256	244
3	50*	57
4	240	-209
5	99	-116
6	97	121
H= 6, L= 9		
0	253	280
1	186	-235
2	59	-39
3	254	187
4	53*	87
5	222	-194
H= 6, L= 10		
0	315	323
1	84	60
2	243	-229
3	53*	-36
4	226	218
H= 6, L= 11		
0	92	-124
1	317	323
2	87	78
3	232	-228
H= 6, L= 12		
0	308	-340
1	144	-135
H= 7, L= 0		
1	511	510
3	663	-591
5	339	329
7	367	-302
H= 7, L= 1		
0	174	-215
1	120	63
2	504	504
3	224	-163
4	386	-366
5	75	57
6	324	338
7	54*	26
H= 7, L= 2		
0	243	242
1	203	-226
2	137	-130
3	573	510
4	100	111
5	265	-248
6	72	-80
7	218	215
H= 7, L= 3		
0	202	198
1	132	125
2	592	-514
3	128	87
4	335	294
5	50*	46
6	236	-231
H= 7, L= 4		
0	132	-111
1	197	195
2	200	-184
3	435	-415
4	112	78
5	182	202
6	95	-77
H= 7, L= 5		
0	301	-284
1	106	-71
2	375	390
3	138	-138
4	322	-316
5	52*	-37
6	224	238
H= 7, L= 6		
0	238	194
1	368	-382
2	68	66
3	366	348
4	51*	41
5	279	-308
6	98	9
H= 7, L= 7		
0	364	316
1	167	195
2	275	-288
3	51*	-6
4	252	235
5	59	77
H= 7, L= 8		
0	193	-202
1	239	216
2	51*	-11
3	184	-159
4	56*	-59
H= 7, L= 9		
0	285	-249
1	52*	-81
2	196	149
3	54*	-49
4	179	-154
H= 7, L= 10		
0	53*	108
1	228	-240
2	54*	33
H= 8, L= 0		
0	494	486
2	679	-639
4	326	369
6	132	-193
H= 8, L= 1		
0	105	-10
1	331	312
2	108	-6
3	467	-439
4	116	-97
5	53*	116
6	59*	66
H= 8, L= 2		
0	320	-270
1	160	-169
2	299	279
3	59	61
4	179	-186
5	53*	-81
6	55*	113
H= 8, L= 3		
0	88	-77
1	295	-266
2	113	80
3	500	312
4	52*	3
5	65	-134
H= 8, L= 4		
0	393	398
1	103	-70
2	328	-329
3	148	109
4	260	231
5	117	68
H= 8, L= 5		
0	75	-7
1	321	334
2	102	-58
3	308	-325
4	58	-15
5	154	177
H= 8, L= 6		
0	333	-285
1	65	-83
2	274	279
3	90	-90
4	151	-222
H= 8, L= 7		
0	102	96
1	246	-237
2	53*	-14
3	205	237
4	127	104
H= 8, L= 8		
0	226	166
1	56	60
2	169	-167
3	55*	37
H= 8, L= 9		
0	54*	-25
1	132	142
H= 9, L= 0		
1	216	-279
3	250	296
H= 9, L= 1		
0	394	330
1	51*	40
2	122	-153
3	53*	-9
4	158	99
H= 9, L= 2		
0	119	-19
1	104	154
2	61	35
3	193	-205
4	54*	-63
H= 9, L= 3		
0	252	-243
1	87	-86
2	145	199
3	53*	29
4	95	-127
H= 9, L= 4		
0	52*	-27
1	53*	-139
2	53*	-26
3	145	181
H= 9, L= 5		
0	273	266
1	54*	24
2	160	-229
3	60	23
H= 9, L= 6		
0	54*	3
1	167	227
2	137	110
H= 10, L= 0		
0	235	-237
H= 10, L= 1		
0	59*	56
1	55*	-113
H= 10, L= 2		
0	59*	155

Table III

Interatomic Distances and Angles, with Standard Errors

Distance, Å		Angle, deg	
I. $InCl_5^{2-}$ Anion			
In(1)–Cl(2) (basal)	2.456 (0.007)	Cl(2)–In(1)–Cl(3)	103.87 (0.30)
In(1)–Cl(3) (apical)	2.415 (0.012)	Cl(2)–In(1)–Cl(2′) (*trans*)	152.26 (0.30)
		Cl(2)–In(1)–Cl(2″) (*cis*)	86.70 (0.30)
II. $(C_2H_5)_4N^+$ Cation i, Centered on Fourfold Axis			
N(8)–C(9)	1.53 (6)	N(8)–C(9)–C(11)	106.7 (3.4)
N(8)–C(10)	1.52 (6)	N(8)–C(10)–C(11)	107.1 (3.4)
C(9)–C(10)	1.91 (7)[a]	C(9)–N(8)–C(9′)	101.7 (3.0)
C(9)–C(11)	1.69 (6)	C(9)–N(8)–C(10″)	113.9 (3.0)
C(10)–C(11)	1.69 (6)	C(10)–N(8)–C(10′)	103.8 (3.2)
		C(10)–N(8)–C(9″)	111.9 (3.2)
III. $(C_2H_5)_4N^+$ Cation ii, Centered on the $\bar{4}$ Site			
N(4)–C(5)	1.56 (5)	N(4)–C(5)–C(7)	111.1 (3.2)
N(4)–C(6)	1.53 (9)	N(4)–C(6)–C(7)	112.2 (6.0)
C(5)–C(6)	1.74 (10)[a]	C(5)–N(4)–C(5″)	107.4 (2.6)
C(5)–C(7)	1.57 (6)	C(5)–N(4)–C(5′)	113.7 (2.6)
C(6)–C(7)	1.57 (10)	C(6)–N(4)–C(6′)	111.8 (5.0)
		C(6)–N(4)–C(6″)	108.3 (5.0)

[a] Nonbonded contacts.

equidistant from four adjacent pentachloroindate(III) ions. Table III shows the important interatomic distances and angles in the structure.

The main interest is obviously in the structure of the pentachloroindate(III) anion, which is the first example of a compound of a main group element with an undistorted tetragonal-pyramidal structure. Muetterties and Schunn[7] have pointed out that in pentacoordinate species with five identical ligands, the differences in the M–X bond lengths are small or undetectable within the experimental error. In the present case, we find that the apical In–Cl bond length of 2.415 Å is different from those at the base of the square pyramid (2.456 Å) (1% level). The indium atom is 0.59 Å above the base of the pyramid, leading to an angle of 103.9° between apical and basal bonds; this is very close to the theoretically required value for a system which minimizes the interatomic Cl–Cl repulsions while retaining C_{4v} symmetry (103.6°, calculated on the basis of a simple inverse-square law of repulsion between ligands).

There are two obvious comparisons that can be made between this structure and those of the corresponding isoelectronic molecules $SnCl_5^-$ and $SbCl_5$. Antimony pentachloride has been studied in the solid state at −30°, at which temperature it has a regular trigonal-bipyramidal structure, with bond lengths of 2.34 Å (apical) and 2.29 Å (equatorial).[10] Earlier Raman and electron diffraction studies[11–13] have shown that this symmetry is maintained in the liquid and gaseous states. The pentachlorostannate anion has the same D_{3h} structure,[14] although the only information refers to a salt with the unusual 3-chloro-1,2,3,4-tetraphenylcyclobutenium cation; the Sn–Cl bond lengths in this compound are all the same within experimental error (2.37 Å). There is no immediately obvious reason for the difference between these two systems and the pentachloroindate(III) structure in terms of bonding interactions. It should be emphasized, however, that the energy difference between the trigonal-bipyramidal and the tetragonal-pyramidal structures is small and that environmental effects may cause one form or the other to be favored (*cf.* ref 7). Thus, for example, there may be symmetry or crystal packing factors in the lattice energy term which favor the tetragonal-pyramidal form in the crystal system studied, and it is always possible that with some other cation the anion might adopt a different stereochemistry. Thus the symmetrical fourfold inversion symmetry of the cations in the $((C_2H_5)_4N)_2[InCl_5]$ may well provide sufficient interionic energy to offset any small differences between the ground states of the D_{3h} and C_{4v} configurations.

In this latter connection, it is worth pointing out that the pentachloroindate(III) anion, in common with many other indium(III) species, readily undergoes rearrangement. For example, the salt $((C_2H_5)_4N)_2[InCl_5]$ is obtained from the reaction of $InCl_3$ with the corresponding tetraalkylammonium halide in ethanol, from which the complex is precipitated almost immediately on mixing the reagents. If one attempts to recrystallize the salt from this solvent under ordinary conditions, the product is $(C_2H_5)_4NInCl_4$ and the starting material is only obtained chemically unchanged if excess $(C_2H_5)_4NCl$ is added to the solution.[15] From dichloromethane solution, on the other hand, $((C_2H_5)_4N)_2[InCl_5]$ recrystallizes without change. Similar examples have been reported previously for other indium(III) complexes.[16] It is clear therefore that the factors involved in the preference of one stereochemistry over another involve a number of factors which are not fully understood.

One further series of five-coordinate compounds which should be discussed in relation to the present work is that of the group V species $(C_6H_5)_5P$, $(C_6H_5)_5As$, and $(C_6H_5)_5Sb$.[7] The first two of these have the trigonal-bipyramidal structure, while the stereochemistry of the $(C_6H_5)_5Sb$ has been described in terms of a distorted tetragonal-pyramidal arrangement of phenyl groups around the antimony. This then is the only compound outside the transition metal series which resembles the $InCl_5^{2-}$ anion stereochemically. The comparison is less useful than one could wish because of the distortion, which has been ascribed to the bulky phenyl groups,[17] although it is not easy to see why this effect should occur with antimony and not with the other elements of this group.

The indium–chloride bond length in $InCl_5^{2-}$ is compared with other known values in Table IV. The values found for the three anions show the lengthening to be expected both as a function of increasing charge and of increasing coordination number. In view of the experimental errors in each determination, no discussion of the differences in the In–Cl bond lengths can be undertaken at present.

TABLE IV

METAL–CHLORINE BOND LENGTHS IN SOME INDIUM(III) AND TIN(IV) COMPLEXES

Species	Coordn no.	Bond length, Å	Ref
$InCl_4^-$	4	2.33	*a*
In_2Cl_6	4	2.46 (av)	*b*
$InCl_5^{2-}$	5	2.42 (apical)	*c*
		2.46 (basal)	
$InCl_5 \cdot H_2O^{2-}$	6	2.58 (av)	*d*
$SnCl_4$	4	2.33	*e*
$SnCl_5^-$	5	2.37	*f*
$(CH_3)_2SnCl_3^-$	5	2.35 (equatorial)	*g*
		2.54 (axial)	
$SnCl_6^{2-}$	6	2.43 (av)	*e*

[a] See ref 5. [b] "Interatomic Distances," Special Publication No. 11, The Chemical Society, London, 1958, p M30. [c] Present work. [d] H. P. Klug, E. Kummer, and L. A. Alexander, *J. Am. Chem. Soc.*, **70**, 3064 (1948). [e] See footnote *b*, p M41. [f] See ref 14. [g] F. W. B. Einstein and B. R. Penfold, *Chem. Commun.*, 780 (1966).

The tetraethylammonium ions in the present structure are of two types, i and ii, both of some stereochemical interest. Each type shows disorder in that the ions are distributed between two alternative configurations; in each case these configurations differ significantly only in the positions of the methylene carbon atoms. For type i, which lies on the fourfold axis, crystallographic considerations require that both

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configurations should be equally occupied; this is consistent with our observation that the refined temperature parameters for the alternative methylene sites are very nearly equal. For type ii, which lies on the $\bar{4}$ site, there is evidence from the thermal parameters that the two configurations may not be equally occupied. In the absence of crystal forces, type ii represents a more energetically favorable state for the tetraethylammonium ion than type i, in that the average distance between methyl groups is the greater.

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The Crystal Structure of Aluminum Hydride[1]

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X-Ray and neutron powder diffraction data for aluminum hydride, AlH_3, and aluminum deuteride, AlD_3, were used to solve this structure. Both compounds crystallize in the trigonal space group $R\bar{3}c$ with six molecules in a hexagonal unit cell of dimensions $a = 4.449$ Å and $c = 11.804$ Å for the hydride and $a = 4.431$ Å and $c = 11.774$ Å for the deuteride. Least-squares refinement of this three-parameter problem using seven unique AlD_3 neutron powder diffraction peaks gave a final R_1 of 0.026. The refined parameters gave $R_1 = 0.040$ for 29 AlH_3 X-ray powder diffraction peaks. Columns of Al atoms and spirals of H atoms are parallel with the c axis and are packed so that the Al has octahedral coordination symmetry. The final Al···H distance of 1.72 Å, the participation of each Al in six bridges, and the equivalence of all Al···H distances suggest that 3c–2e bonding occurs. The closest Al–Al distance is 3.24 Å. The alternating planes of Al and H atoms, perpendicular to the c axis, result in a stable structure which is a three-dimensional network of Al···H···Al bridges and is consistent with the observed high density of the crystal.

The existence of four aluminum hydrides has been reported in the literature. AlH is a short-lived species produced by an electrical discharge between electrodes[2] and has been used to provide a measurement of the Al–H bond length (1.648 Å). The preparation of a polymerized hydride $(AlH_3)_n$ has been claimed by Stecher and Wiberg,[3] but Finholt, Bond, and Schlesinger[4] reported that method to be difficult, giving a somewhat impure product. Their preparation used $LiAlH_4$ and $AlCl_3$ in ether to give a pure product but one from which the ether could not be removed without causing decomposition. Some recent work here at Dow has resulted in five crystalline forms of nonsolvated aluminum hydride.[5] One of these, designated as pattern 1433 in our files, has been reported by two other groups of workers—Rice and Chizinsky,[6] who precipitated it from pentane, and Appel and Frankel,[7] who produced it by bombarding an ultrapure aluminum target with hydrogen ions. However, the X-ray data taken by this second group were of too poor a quality to make the identification unique. In particular, the least-squares fit to a hexagonal unit cell seems to indicate the possibility that their product corresponds to our pattern 1451. Finally, Breisacher and Siegel[8] prepared gaseous AlH_3 and its dimer in a flow system by evaporating aluminum from a hot tungsten filament into hydrogen at low pressure. In a similar experiment, using a static system, the product was trapped out at −195°.[9]

Aluminum does not form a low molecular weight hydride analogous to the simple dimeric hydrides of boron and gallium, and there has been speculation[3,10,11] on the molecular structure of $(AlH_3)_n$ since its first preparation, with all of the proposed structures suggesting that hydrogen bridging is required. Some extended Hückel calculations done by Kato, *et al.*,[12] using a symmetry of C_{3v} and a bond distance of 1.65 Å for AlH_3, lead to an interpretation of the bonding in the structure as having partial ionic character which might be represented as $Al^{+\delta}\cdots H^{-\delta}$. Infrared spectroscopy studies[13] led Roszinski, *et al.*, to describe $(AlH_3)_n$ as having a branched and cross-linked structure with

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