hence concluded that the two aloins are not derivatives of isomeric anthrones.[7,16]

The most recent empirical formula, $C_{21}H_{24}O_9$, has been proposed by Owen and Simonsen[17] on the basis of analyses and X-ray studies of the methyl ether derivative, $C_{21}H_{17}O_2(OCH_3)_7$. This recent formula is also supported by Gardner[18] on the basis of analyses made in his laboratory by Joseph. He stated that the present evidence is compatible with a structure for the aloins of a β-methylanthracene nucleus with side chain, but it is not certain whether the side chain has six or five carbon atoms with corresponding uncertainty as to the location of one of the carbon atoms.

In our polarographic work it was noted that the aloins are very readily oxidized in alkaline buffers which introduces waves not typical of the aloins. In acetate buffers of pH 4 or 5 the waves are of satisfactory form and suitable for quantitative measurement. The maxima that occur in alkaline media are not suppressed by methyl red and methyl cellulose. The half-wave potentials, Table III, show that the reduction resembles that of a substituted anthrone (Table II). The close similarity of the half-wave potentials of the two compounds suggests that they are position isomers, that have the same structural groups.

It is of practical interest that the wave due to the aloins is shown in extracts of crude aloes or in pharmaceutical products made from aloes. The practical details of the polarographic estimation of the aloins have been published.[19] For both compounds a current of 0.43 microamp. per mg. in 25 ml. was found up to concentration of 10 mg. per 25 ml. with a capillary of $m^{2/3}t^{1/6} = 1.23$.

Acknowledgments.—The financial support of the Wallace Laboratories which made this work possible is gratefully acknowledged. The gift of reference compounds by Dr. Percy Julian is also acknowledged.

Summary

The polarography of the aloins has been compared with that of simple and substituted anthrone. Anthraquinone monoxime and 10-vinylanthranyl acetate have also been examined polarographically.

The close similarity of the polarographic behavior of the aloins to 10-hydroxy-10-methyl anthrone suggests that they are anthrones; the close similarity of the polarograms of the isomeric aloins suggests that they are position isomers with the same structural groups.

PRINCETON, N. J. RECEIVED MARCH 29, 1948

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[16] J. H. Gardner and J. A. Campbell, THIS JOURNAL, **64**, 1378 (1942).

[17] L. N. Owen and J. L. Simonsen, *ibid.*, **64**, 2516 (1942).

[18] J. H. Gardner, *ibid.*, **67**, 2111 (1945).

[19] K. G. Stone and N. H. Furman, *Anal. Chem.*, **19**, 105 (1947).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA AND THE DEPARTMENT OF RESEARCH IN CHEMICAL PHYSICS OF MELLON INSTITUTE]

The Crystal Structure of Ammonium Pentachloroindate Monohydrate[1]

BY HAROLD P. KLUG, ELIZABETH KUMMER AND LEROY ALEXANDER

Introduction

The stereochemistry associated with a 1:5 stoichiometric ratio in crystalline inorganic compounds is of special theoretical interest. Compounds with such a ratio occur rather infrequently, and to date only a few of them have been studied structurally. Already, however, five different structural methods for achieving the 1:5 ratio have been demonstrated, and none of them involves five-fold coördination. Phosphorus pentachloride, PCl_5, has a CsCl-type packing of ionic tetrahedral PCl_4^+ and octahedral PCl_6^- groups.[2] Phosphorus pentabromide, PBr_5, has a different structure consisting of a packing of tetrahedral PBr_4^+ and spherical Br^- ions.[3] Brosset[4] demonstrated the AlF_5 ratio in Tl_2AlF_5 and $K_2AlF_5 \cdot H_2O$ to be achieved through infinite chains of AlF_6 octahedra extending through the crystal. Cs_3CoCl_5 and Rb_3CoCl_5 were investigated by Powell and Wells,[5] and more recently $(NH_4)_3ZnCl_5$ was completely studied by Klug and Alexander.[6] These compounds are packings of the spherical metallic cations, tetrahedral $CoCl_4^=$ or $ZnCl_4^=$ anions, and extra Cl^- ions. Their formulas might be more accurately written in the form $Cs_2CoCl_4 \cdot CsCl$ and $(NH_4)_2ZnCl_4 \cdot NH_4Cl$.

Lindqvist[7] recently determined the structure of $(NH_4)_2FeCl_5 \cdot H_2O$ and found it to contain discrete octahedral $[FeCl_5H_2O]^=$ groups. The water molecule is not distributed randomly among the six corners of the octahedra, but occupies a particular corner of the octahedra that lie on the symmetry planes in the cell. This investigation of $(NH_4)_2InCl_5 \cdot H_2O$ has established it as another ex-

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[1] Presented before the Division of Physical and Inorganic Chemistry, Chicago meeting of the American Chemical Society, April 20, 1948.

[2] Powell, Clark and Wells, *J. Chem. Soc.*, 642 (1942).

[3] Powell and Clark, *Nature*, **146**, 971 (1940).

[4] Brosset, *Z. anorg. allgem. Chem.*, **235**, 139 (1937); "Electrochemical and X-Ray Crystallographic Investigation of Complex Aluminum Fluorides," separate, Stockholm, 1942.

[5] Powell and Wells, *J. Chem. Soc.*, 359 (1935).

[6] Klug and Alexander, THIS JOURNAL, **66**, 1056 (1944).

[7] Lindqvist, *Arkiv Kemi Mineral. Geol.*, **24A**, 1 (1946).

ample of the same structure type, which is known as the Jl_8 type and has been observed earlier in $Cl_2[Rh(NH_3)_5Cl]$.[8]

Experimental

The compound $(NH_4)_2InCl_5 \cdot H_2O$ was readily prepared from stoichiometric quantities of the component salts by crystallization from water solution. Chemical analysis served to confirm its composition and identity. *Anal.* Calcd.: In, 33.15; Cl, 51.22. Found: In, 33.89; Cl, 51.49.

Wallace[9] had described the crystals, reporting them to be rhombic bipyramidal with axial ratios $a:b:c = 0.9668:1:1.4005$, and a sp. gr. of 2.281 at 20°. The chief faces present are the forms {100}, {101}, {120}, and {011}. Crystals selected for the present study were small and almost equidimensional. Laue, rotation, and oscillation photographs in routine fashion confirmed the symmetry and revealed the crystal-chemical constants of its unit cell. These findings are tabulated in Table I.

TABLE I

UNIT CELL DATA FOR $(NH_4)_2InCl_5 \cdot H_2O$

Symmetry: Orthorhombic

Dimensions of cell: $a_0 = 14.10$ Å.
$b_0 = 10.17$ Å. (all ± 0.05 Å.)
$c_0 = 7.16$ Å.

Molecules per cell: 4

Space group: D_{2h}^{16} – *Pnma*

Observed axial ratios:

$(NH_4)_2InCl_5 \cdot H_2O$	1.387:1:0.704
$(NH_4)_2[FeCl_5H_2O]$	1.399:1:0.720

This study was actually begun in 1942, but the war interrupted the work and it was not resumed again until recently. The space group was determined from Laue photographs six years ago, the method so common in this country up to that time. Just about this time the Weissenberg camera became generally available, and the space group has since been independently verified from complete sets of Weissenberg photographs. Consideration of the alternative noncentrosymmetrical space group, C_{2v}^{9}-*Pna*, seemed unnecessary after the indate's isomorphism with $(NH_4)_2[FeCl_5H_2O]$ had been established.

The Weissenberg photographs are also the source of intensity data from several hundred different planes. The intensities, visually estimated with the aid of a calibrated scale of spots and the multiple film technique, were transformed into relative structure factors, F, using Buerger and Klein's tables[10] of Lorentz and polarization factors for the equi-inclination Weissenberg technique. No attempt was made to apply the temperature factor or the absorption factor except that small crystals were used to reduce the effect of the latter.

The final and most important step in the study is the locating of the 8 ammonium groups, 4 indium atoms, 4 water molecules, and 20 chlorine atoms in the cell. For this problem there is a wealth of data, and also a favorable case for the use of the Patterson–Harker technique.[11] The heavy indium atoms should readily be located by this method, and probably the chlorines too, as in the study of $(NH_4)_3ZnCl_5$ in which the zinc and chlorine atoms were all located by the Patterson–Harker vector technique. Actually, however, the close agreement of the axial ratios with those of $(NH_4)_2[FeCl_5H_2O]$, suggesting that the two compounds are isomorphous, was observed almost immediately. In case of isomorphism the parameters of the iron compound might be expected to be a good approximation for those of the indium compound. Accordingly it seemed worthwhile to calculate a few structure factors for the indate using the parameters of the ferrate.

The eight even orders of $(h00)$ gave F values in good general agreement with the observed ones, and the agreement was still further improved by a decrease of 0.004 in the parameter of the indium atoms. In a similar fashion the F values for the even orders of $(00l)$ were readily accounted for on the basis of the ferrate parameters with the indium parameter increased by 0.007 from that for iron. A total of 58 F values for various pinacoid and prism planes was calculated without a single unsatisfactory comparison between observed and calculated values. At this point the isomorphism seemed well established, and it was concluded that the next step should be a Bragg projection on (010).

F data were available from 138 planes in the $(h0l)$ zone. The signs of the F's were assumed to be the same as that of the indium contribution, as had been observed to be true in every one of the 58 cases calculated earlier. The summations were carried out by the method of Patterson and Tunell,[12] and yielded a new set of x and z parameters. When these values were used for calculation of the F values for the 138 planes used in the projection, the agreement with the observed F's was improved, but it was observed that the signs of seven of the terms were incorrect. The series was then summed again with the correct signs for all the terms. Using the pinacoid data and addi-

TABLE II

FINAL VALUES OF THE PARAMETERS

Ion or molecule	x	y	z
4 In^{3+} in 4(c)	0.110	(0.250)	0.313
4 Cl_I^- in 4(c)	.000	(.250)	.035
4 Cl_{II}^- in 4(c)	.262	(.250)	.080
4 Cl_{III}^- in 4(c)	.234	(.250)	.581
8 Cl_{IV}^- in 8(d)	.116	.000	.316
4 H_2O in 4(c)	.000	(.250)	.538
8 NH_4^+ in 8(d)	.366	.000	.349

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(8) West, *Z. Krist.*, **91**, 181 (1935).

(9) Wallace, *ibid.*, **49**, 417 (1911).

(10) Buerger and Klein, *J. App. Phys.*, **16**, 408 (1945).

(11) Patterson, *Z. Krist.*, **90**, 517 (1935); Harker, *J. Chem. Phys.*, **4**, 381 (1936).

(12) Patterson and Tunell, *Am. Mineral.*, **27**, 655 (1942).

TABLE III

STRUCTURE FACTOR DATA[13]

hkl	$F_{\text{obs.}} \times 20$	$F_{\text{calcd.}}$	*hkl*	$F_{\text{obs.}} \times 20$	$F_{\text{calcd.}}$	*hkl*	$F_{\text{obs.}} \times 20$	$F_{\text{calcd.}}$	*hkl*	$F_{\text{obs.}} \times 20$	$F_{\text{calcd.}}$
200	0	15	044	20	−24	17·0·2	41	−52	266	70	−73
400	123	−133	064	22	−14	210	148	−182	292	103	70
600	124	−111	084	0	−16	220	0	−1	326	55	−44
800	302	305	0·10·4	18	−6	230	189	162	525	101	−82
10·0·0	162	129	101	31	−46	240	0	12	726	68	33
12·0·0	39	−34	201	122	−209	250	202	−140	10·2·3	112	−51
14·0·0	107	−113	301	60	82	260	0	2	12·2·5	24	14
16·0·0	84	86	401	107	−105	270	137	121	342	183	210
020	149	−205	501	66	66	280	0	6	462	151	−108
040	224	456	601	171	182	290	154	105	552	169	−109
060	176	−160	701	62	60	2·10·0	0	7	682	96	59
080	259	302	801	137	101	2·11·0	89	94	852	38	−52
0·10·0	114	−129	901	113	−95	111	27	44	10·5·2	72	41
0·12·0	220	232	10·0·1	106	−80	122	91	96	12·5·2	82	65
002	73	−79	11·0·1	46	52	143	163	150	14·7·2	66	17
004	32	−30	12·0·1	203	−159	174	135	98	343	72	61
006	83	−88	13·0·1	52	33	175	94	−58	367	32	16
008	170	−185	14·0·1	81	80	137	62	22	396	49	−60
011	116	−173	15·0·1	65	91	241	197	−175	11·3·3	196	92
031	136	156	16·0·1	136	101	341	76	−72	10·3·4	0	−10
051	192	−135	17·0·1	40	−69	451	167	102	436	37	30
071	160	116	102	55	80	561	25	−22	737	53	−30
091	175	−102	202	0	−12	711	46	−50	943	266	169
0·11·1	146	91	302	169	270	811	186	−96	753	169	103
022	104	−93	402	183	283	911	24	−8	11·6·3	37	−42
042	87	−69	502	176	−160	10·7·1	55	79	583	178	−118
062	49	−47	602	99	84	12·2·1	39	73	993	26	5
082	91	−53	702	92	−104	13·5·1	37	8	465	0	−8
0·10·2	0	−36	802	45	−42	15·4·1	66	89	448	96	97
0·12·2	84	−41	902	0	−15	216	65	−75	747	31	−13
013	47	43	10·0·2	67	−69	416	30	−31	11·4·4	168	−115
033	58	−40	11·0·2	163	154	713	137	117	556	135	−100
053	48	35	12·0·2	134	118	914	198	−145	654	0	1
073	35	−29	13·0·2	0	−2	11·1·7	79	−36	667	63	−13
093	37	25	14·0·2	112	116	14·1·2	71	−18	12·3·3	153	36
0·11·3	32	−22	15·0·2	75	−83	226	82	−80	3·12·3	56	−48
024	29	−25	16·0·2	0	8	246	80	86	935	63	2

tional prism and pyramid reflections, the parameters obtained from the second summation were further refined to yield the final values listed in Table II.

The maximum limits of error are believed to be ±0.005. These parameters were used for the calculation of structure factors of nearly 600 different reflections for comparison with the experimental data. The satisfactory agreement observed constitutes the final verification of the structure. A part[13] of these results is presented in Table III.

A few planes with simple indices and large intensities appear to have been estimated too low. Also, there is generally a larger relative discrepancy with the calculated value for observed *F*'s below approximately 30, arising from the fact that these represent planes with the faintest intensities measurable and from the necessity of using a factor of 20 to place them on the scale of the calculated *F*'s.

Discussion

The projection on (010) clearly establishes the structure. In Fig. 1 the contour diagram showing the projection of electron density on (010) is reproduced. Since the observed *F*'s were not on an absolute scale, the density values are in arbitrary units, and the contour intervals have no simple relation to the number of electrons per Å.^{2}. For the peak containing indium, contours have been drawn at intervals of 200, while for all other peaks the interval is 100. The atoms contributing to the real peaks are indicated, and the positions of certain symmetry elements in the cell are shown.

A clearer picture of the coördination within the structure is obtained from the schematic view

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[13] In the interest of the conservation of space, data from only 150 planes are presented here as a sample of the kind of agreement obtained. Data from the remaining 400–425 planes are comparable and were submitted as Table III (a) for the use of the referees. These data are available to anyone interested upon request.

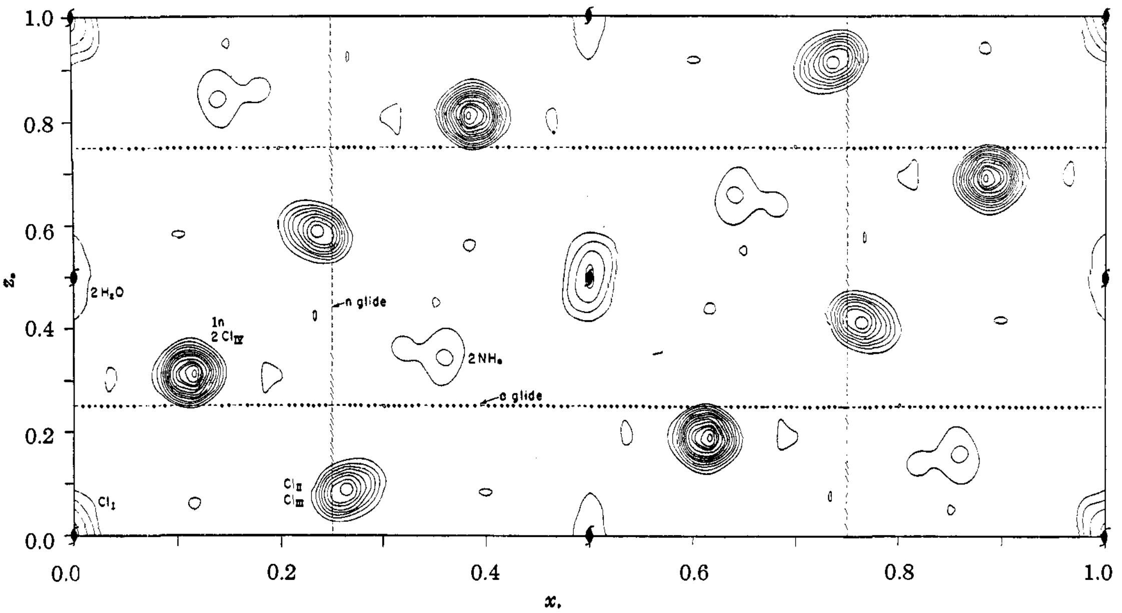

Fig. 1.—$\rho(x, z)$, Bragg Fourier projection of electron density on (010).

along [010] presented in Fig. 2. Indium is surrounded by five chlorine atoms and a water molecule at the corners of a distorted octahedron. In this diagram octahedra located on the symmetry plane at $y = 0.25$ are delineated with full lines, while those on the plane at $y = 0.75$ are given with dashed lines. The various chlorine atoms of one octahedron are designated with Roman numerals. Each chlorine IV stands for two such chlorines at equal distances above and below the symmetry plane. The NH_4^+ ions are surrounded by a distorted cube of six chlorine atoms and two water molecules. At the NH_4^+ positions in the diagram there are actually two NH_4^+ groups separated from each other by half the length of the *b* axis. There are also four chlorine IV atoms at a slightly greater average distance surrounding each NH_4^+ ion. The structure is thus a packing of NH_4^+ ions and $[InCl_5H_2O]^=$ ions, and the formula of the salt should be written $(NH_4)_2[InCl_5H_2O]$. This would seem to indicate, at the crystallization point, a fair concentration of $[InCl_5H_2O]^=$ ions in an aqueous solution containing In^{3+} ions and a high concentration of chloride ions.

With the parameters for the structure determined it is now possible to calculate the interatomic and interionic distances within the structure. Values listed in Table IV are believed to be good to within ±0.05 Å.

For comparison with the average observed In–Cl distance, 2.58 Å., there appears to be only one experimentally determined value, the one reported by Stevenson and Schomaker,[14] 2.46 Å., from electron diffraction studies of gaseous indium trichloride, $InCl_3$ (this value is actually a correction of H. Brode's work). There is good evidence that gaseous indium trichloride is a dimer with an ethane-like structure. In any case, the In–Cl distance in it will be expected to be somewhat smaller than in the present compound, because the coördination is tetrahedral instead of octahedral, and, further, the chlorine atoms may be pulled in closer to the indium atom than normal for tetrahedral coördination because they are surrounded on only one side by positive atoms. One can, however, predict the approximate bond distance to be expected, assuming either pure ionic or pure covalent bonds. For octahedral coordination with ionic bonds the predicted In–Cl distance should be about 2.67 Å., while for covalent bonds it would be approximately 2.64 Å. Actually, in this compound the distance would be expected to be shorter than predicted because the chlorine atoms will be pulled in more strongly by

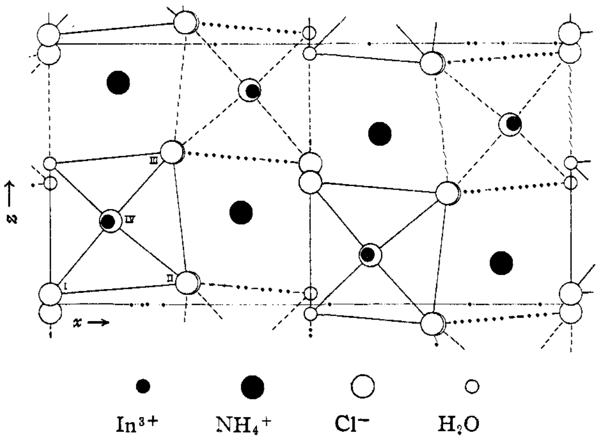

Fig. 2.—Schematic diagram of the structure viewed along [010].

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[14] Stevenson and Schomaker, THIS JOURNAL, 64, 2514 (1942).

TABLE IV

INTERATOMIC DISTANCES IN $(NH_4)_2[InCl_5H_2O]$

$\mathrm{In{-}Cl_{I}}$	2.52 Å.	$\mathrm{Cl_{I}{-}Cl_{II}}$	3.70 Å.	$\mathrm{2(NH_4{-}Cl_{I})}$	3.27 Å. 3.43
$\mathrm{In{-}Cl_{II}}$	2.71	$\mathrm{Cl_{II}{-}Cl_{III}}$	3.61		
$\mathrm{In{-}Cl_{III}}$	2.60	$\mathrm{2(Cl_{I}{-}Cl_{IV})}$	3.62	$\mathrm{2(NH_4{-}Cl_{II})}$	3.51 3.52
$\mathrm{2(In{-}Cl_{IV})}$	2.54	$\mathrm{2(Cl_{II}{-}Cl_{IV})}$	3.68		
Average	2.58	$\mathrm{2(Cl_{III}{-}Cl_{IV})}$	3.58	$\mathrm{2(NH_4{-}Cl_{III})}$	3.56 3.48
		Average	3.63		
$\mathrm{In{-}H_2O}$	2.23			Average	3.46
		$\mathrm{2(NH_4{-}H_2O)}$	4.21 3.87		
$\mathrm{H_2O{-}Cl_{I}}$	3.60			$\mathrm{4(NH_4{-}Cl_{IV})}$	3.35 3.53 3.72 3.82
$\mathrm{H_2O{-}Cl_{III}}$	3.32				
$\mathrm{2(H_2O{-}Cl_{IV})}$	3.42	Average	4.04		
Average	3.44			Average	3.61

the indium than by the NH_4^+ ions, and the bond radii hold accurately only where each kind of atom is octahedrally coördinated by the opposite kind. The observed value, 2.58 Å., is thus a reasonable one, and the bond is doubtless partly ionic and partly covalent.

Lindqvist's average non-bonded Cl–Cl distance in the ferrate was 3.39 Å. The value of 3.63 Å. observed is about what would be expected as a result of the exchange of the larger In^{3+} ion (radius = 0.81 – 0.92 Å.) for Fe^{3+} (radius = 0.67 Å.). Similarly the Fe–H_2O distance in the ferrate was 2.08 Å. in comparison with 2.23 Å. for In–H_2O.

There are more data available for comparison of the NH_4–Cl distances. This distance is 3.35 Å. in low ammonium chloride. In the somewhat more similar compound, $(NH_4)_2ZnCl_4 \cdot NH_4Cl$,[6] there are two kinds of ammonium ions from the standpoint of the coördination about them. Eight of them are surrounded by six chlorine atoms at the corners of a trigonal prism (average distance, 3.44 Å.), with three additional chlorine atoms at a little greater distance (average, 3.63 Å.). The remaining four ammonium groups are surrounded by eight chlorine atoms at the corners of an irregular polygon with the distances varying from 3.14 to 3.68 Å., average, 3.32 Å. Thus the observed average NH_4–Cl distances of 3.46 and 3.61 Å. in the indate are about as expected.

Summary

A complete structure determination of the salt $(NH_4)_2InCl_5 \cdot H_2O$ has been carried out by single crystal X-ray diffraction methods in order to study the stereochemistry of its 1:5 stoichiometry. The structure is orthorhombic with a_0 = 14.10 Å., b_0 = 10.17 Å., c_0 = 7.16 Å. and is an example of the $J1_8$ structure type, of which $Cl_2[Rh(NH_3)_5Cl]$ and $(NH_4)_2[FeCl_5H_2O]$ are already known. The structure is a packing of spherical NH_4^+ ions and octahedral $[InCl_5H_2O]^=$ ions. The water molecule occupies a definite corner of the octahedron, which is distorted because of the unequal sizes of Cl^- and H_2O. The NH_4^+ ions are surrounded by a distorted cube of six chlorine atoms and two water molecules. The sixteen parameters fixing the positions of the atoms in the cell have been determined, and the various interatomic distances calculated. The formula of the salt should be written $(NH_4)_2[InCl_5H_2O]$.

PITTSBURGH 13, PA. RECEIVED MAY 24, 1948

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Polysilmethylene Compounds and their Siloxy Derivatives

BY BEN A. BLUESTEIN

The thermal and hydrolytic stability of methyl groups attached directly to silicon has been well established in the now commercially important "silicones." However, the siloxane bonds present in silicones are susceptible to thermal and to catalytic rearrangements.[1] Since the substitution of a methylene group for an oxygen atom of a siloxane would eliminate the possibility of these rearrangements, it seemed of interest to study the chemical and physical properties of compounds containing silicon–methylene–silicon linkages.

Compounds containing disilmethylene groups, [$\equiv$Si–CH_2–Si$\equiv$] were first prepared by Patnode and Schiessler[2] who obtained hexachlorodisilmethylene as a product of the reaction between methylene chloride and silicon–copper. Rochow[3] has disclosed the possibility of preparing polymers containing silmethylene groups but gives no details. Sommer, *et al.*,[4] have recently reported the

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[1] Patnode and Wilcock, THIS JOURNAL, **68**, 356 (1946).

[2] Patnode and Schiessler, U. S. Patent 2,381,000, 2,381,002.

[3] Rochow, "Introduction to the Chemistry of the Silicones," John Wiley and Sons, Inc., New York, N. Y., 1946, p. 46.

[4] Sommer, Goldberg, Gold and Whitmore, THIS JOURNAL, **69**, 980 (1947).