(3) If the properties of the streaks or diffusions vary with order of diffraction, they indicate displacements of the atoms from lattice sites. For example, in Cu_4FeNi_3 (Daniel & Lipson, 1943, 1944) the intensities of the side bands accompanying the main reflexions increase with order.

(4) If the properties of the streaks or diffusions, with respect to the reflexions they accompany or replace, are constant, then some form of imperfection not involving atomic displacements is indicated. $AuCu_3$ provides an example of this; all the unit cells of the reciprocal lattice contain the same distribution of scattered intensity, if the natural fall-off with angle is allowed for.

(5) If *all* the reflexions appear in the same degree of diffuseness, they are probably due to smallness of crystallite dimension, as given by rules (1) and (2); if, however, *some* of the reflexions remain sharp, the imperfections must be such that the atoms scatter in the same relative phases for the sharp reflexions, but not for the diffuse reflexions.

(6) Streaks joining spots usually imply submicroscopic twinning on planes perpendicular to the streaks. It is not necessary to postulate that the structure can assume all possible orientations between the two twins.

These rules are not adequate to explain all observed phenomena of the sort described, and should be regarded only as guiding principles. They do not, in themselves, account for all the details in the diffraction pattern of $AuCu_3$; since this pattern contains disks oriented in three different directions, rule (2) cannot apply. Problems of this sort must be treated individually, and there are several, such as that of ice (Owston, 1949), which still defy solution.

We wish to thank Mr W. Hughes, who constructed the apparatus and who showed great patience in drilling the template for the $AuCu_3$ gratings, and Mr C. W. Bunn who provided the photograph for Fig. 5. We also wish to acknowledge a maintenance grant for one of us (R. M. H.) from the British Iron and Steel Research Association, and a grant from the Department of Scientific and Industrial Research towards the cost of construction of the apparatus.

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The Structure of Mercuric Amidochloride, $HgNH_2Cl$

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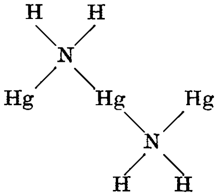
The structure of $HgNH_2Cl$ consists of infinite chains of alternating Hg and NH_2^+ with linear bonds about Hg and tetrahedral bonds about N. The unit cell is orthorhombic with $a = 5{\cdot}167$, $b = 4{\cdot}357$, $c = 6{\cdot}690$ A., and with Hg at 0, 0, 0 and 0, 0, $\frac{1}{2}$. The probable space group is C_{2v}^1–$P2mm$, and the Hg–N bond distance is $2{\cdot}05 \pm 0{\cdot}02$ A.

As a result of a study (Arora, Lipscomb & Sneed, 1951) of the products of reactions between ammonia and mercury (I) compounds, several samples of $HgNH_2Cl$ were prepared. The analysis of the crystal structure from the powder diagram has been carried out by the method employed in a study of Millon's base (Lipscomb, 1951). The mercury atoms have been located with certainty, and indications of the positions of the light atoms have been obtained. In addition, the results, described below, clarify some of the aspects of the crystal chemistry of the series $Hg_2NCl.H_2O$, $HgNH_2Cl$ and $Hg(NH_3)_2Cl_2$.

The sample, placed in a pyrex capillary about 0·1 mm. in diameter, was photographed with Cu $K\alpha$ radiation in a cylindrical camera of 5·73 cm. radius. The intensities were estimated visually, in part by comparison with standards but with no corrections for absorption. Because initial attempts to index the pattern on cubic, tetragonal or hexagonal lattices failed, a radial distribution function was prepared (Waser & Schomaker, 1945). The curve indicated a single, resolved maximum, somewhat sensitive to the artificial temperature factor, at about 3 A., which was interpreted as an indication of the Hg–N–Hg configuration with a bond angle of about $109\frac{1}{2}$° at the nitrogen atom. The infusible, insoluble nature of the compound led then to the suggestion of infinite, probably planar, Hg–N–Hg chains of the type



packed parallel to one another, and led further to the orthorhombic cell with $a=5\cdot167$, $b=4\cdot357$, $c=6\cdot690$ A. Assumption of two $HgNH_2Cl$ in this unit cell results in a calculated density of 5·56 g.cm.$^{-3}$ in satisfactory agreement with the observed density of 5·70 g.cm.$^{-3}$. The mercury atoms, placed at $0,0,0$ and $0,0,\frac{1}{2}$, are 3·345 A. apart and indicate a bond distance Hg–N $=2\cdot05\pm0\cdot02$A. if tetrahedral angles about nitrogen are assumed. This value is in satisfactory agreement with the value of 2·07 A. determined from Millon's base, and is somewhat less precise because the back reflections obtained in the present study showed considerable broadening.

Further specification of the structure is based on the somewhat stringent steric specifications. Construction of a model suggested that the infinite chains of alternate mercury and nitrogen atoms lie in or near (I) the bc plane or (II) the ac plane. Only these two possibilities appear to allow space for the Cl^- ions which are then infinite zigzag chains extending along c and lying between the HgN chains. Now, assuming that the hydrogen atoms are attached to nitrogen atoms to form $Hg(NH_2^+)Hg(NH_2^+)$ chains, with four tetrahedral bonds about nitrogen, it would seem most logical to place the Cl^- ions near the NH_2^+ groups to which hydrogen bonds could be formed. The two possible structures are then

$$\text{I}\quad (C_{2v}^{1}\text{–}Pm2m)\begin{cases}2\,\text{Hg at } 0,0,0;\ 0,0,\tfrac{1}{2},\\ 2\,\text{N at } 0,0\cdot27,\tfrac{1}{4};\ 0,0\cdot73,\tfrac{3}{4},\\ 2\,\text{Cl at } \tfrac{1}{2},0\cdot30,\tfrac{3}{4};\ \tfrac{1}{2},0\cdot70,\tfrac{1}{4},\end{cases}$$

and

$$\text{II}\quad (C_{2v}^{1}\text{–}P2mm)\begin{cases}2\,\text{Hg at } 0,0,0;\ 0,0,\tfrac{1}{2},\\ 2\,\text{N at } 0\cdot23,0,\tfrac{1}{4};\ 0\cdot77,0,\tfrac{3}{4},\\ 2\,\text{Cl at } 0\cdot32,\tfrac{1}{2},\tfrac{3}{4};\ 0\cdot68,\tfrac{1}{2},\tfrac{1}{4}.\end{cases}$$

The parameters in each of these structures were determined by requiring that the N...Cl distance be 3·2 A., and that the Cl...Cl distance be 3·8 A.

The calculations of intensities for these two structures are shown in Table 1. It is believed that the observations are sufficiently good to decide that structure II

Table 1. *Crystal data for* $HgNH_2Cl$

hkl	d_c	I_c		d_o	I_o
		I	II		
100	5·167	76	87	5·167	86
010	4·357	50	44	4·373	60
002	3·345	87	91	3·331	90
110	3·332				
111	2·982	6	6	2·982	5
102	2·808	51	46	3·811	43
012	2·653	39	43	2·659	38
200	2·584	23	11	2·583	7
112	2·360	44	42	2·364	45
210	2·222	15	21	2·219	24
020	2·178	6	14	2·178	12
202	2·045	9	20	2·044	24
120	2·007	17	13	2·009	12
212	1·851	12	20	1·853	20
022	1·825	15	6	1·828	4
300	1·722	18	25	1·722	16
122	1·721				
004	1·673	6	6	1·681	5
220	1·665	5	5	1·665	5
310	1·602	11	10	1·597	8
104	1·591				
014	1·561	5	5	1·567	5
302	1·531	6	4	1·531	5
114	1·495	24	24	1·493	20
222	1·491				
030	1·452	3	1	—	Abs.
312	1·445	8	12	1·443	7
204	1·404	8	7	1·403	5
130	1·398				
320	1·351	4	4	—	Abs.
214	1·336	8	11	1·335	16
032	1·332				
024	1·327	2	4	—	Abs.
400	1·292	20	11	1·290	8
132	1·290				
124	1·285				
230	1·266	3	3	1·268	5
322	1·253	4	4	1·253	5
410	1·238	2	3	1·238	4
402	1·205	5	5	1·202	5
304	1·200				
232	1·184	6	6	1·184	6
224	1·180				
412	1·161	8	5	1·161	7
314	1·157				
006	1·115	1	0	—	Abs.
420	1·111	3	4	1·110	4
330	1·110				
034	1·097				
106	1·090	1	2	—	Abs.
040	1·089	1	1	—	Abs.
016	1·080	2	2	—	Abs.
134	1·073	2	3	1·074	3
140	1·066	1	1	1·064	3
422	1·054	8	8	1·053	6
116	1·054				
332	1·054				

is the correct one, and that structure I can be eliminated. Because of the almost complete predominance of the scattering of mercury as compared with that of chlorine, it would be of interest to investigate the possibility that $HgNH_2Br$ and $HgNH_2I$ might have closely related structures.

The comparative structural chemistry of the compounds $Hg_2NCl.H_2O$, $HgNH_2Cl$ and $Hg(NH_3)_2Cl_2$ is interesting because of their easy production and interconversions in the presence of ammonia and ammonium chloride of various concentrations. The chloride of Millon's base, $Hg_2NCl.H_2O$, consists of an infinite three-dimensional framework, that of $HgNH_2Cl$ (infusible precipitate) of infinite one-dimensional chains, and that of $Hg(NH_3)_2Cl_2$ (fusible precipitate) (MacGillavry & Bijvoet, 1936) could well be described in terms of finite linear groups $^+H_3N\text{–}Hg\text{–}NH_3^+$ placed at random along the directions of the three crystallographic axes in the cubic unit cell with Cl^- at 0, 0, 0 and NH_3^+ at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Thus in each of these structures mercury forms bonds at 180° angles, while nitrogen forms tetrahedral bonds, to 4 Hg in $Hg_2NCl.H_2O$, to 2 Hg and 2 H in $HgNH_2Cl$, and to 1 Hg and 3 H in $Hg(NH_3)_2Cl_2$.

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Forbidden Reflections in the Harker–Kasper Inequalities*

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Two variations of the standard method of sign determination, using the Harker–Kasper inequalities, are discussed with specific illustrations from the structure of *p*-di-tertiary-butylbenzene. The first instance is the use in the left-hand side of the inequality of planes whose intensities are zero, owing to space-group extinctions. The second, more interesting, instance involves half odd-integer planes in the same position.

Some of the limitations of the Harker–Kasper‡ inequalities can be circumvented by the use of reflections forbidden either by the space group, or even by the lattice itself (i.e. non-integral indices may be used).

In all of the inequalities it is necessary to use the largest available U's. (This is the notation for the unitary structure factor introduced by Gillis (1948).) Indeed, the best results are obtained by using the more complicated inequalities with combinations of large U's on the right-hand side. Even then the signs of the U's often remain indeterminate, especially for crystals with large unit cells containing many atoms, such as many organic crystals.

The two applications discussed here are sometimes successful when previously described methods fail.

1. Space-group extinctions

The Harker–Kasper 'sum and difference' inequality,

$$|\,U(h0l) \pm U(h'0l')\,|^2 \leqslant 1 + \tfrac{1}{2}\,U(2h.0.2l) + \tfrac{1}{2}\,U(2h'.0.2l') \pm [U(h-h'.0.l-l') + U(h+h'.0.l+l')], \qquad (1)$$

provides relationships between signs of different U's. When zeros occur on the left side, the inequality remains useful if the following is satisfied:

$$|\,U(h-h'.0.l-l')\,| + |\,U(h+h'.0.l+l')\,| > 1 + \tfrac{1}{2}\,|\,U(2h.0.2l)\,| + \tfrac{1}{2}\,|\,U(2h'.0.2l')\,|.$$

Although a zero value on the left may reduce the effectiveness of the inequality, greater flexibility is gained in the choice of planes on the right.

It is unnecessary to insure observable reflections on the left and thus limit the planes used on the right. In fact, for the space group Pn, in order to have $h-h'$, $l-l'$ and $h+h'$, $l+l'$ all odd, h must be odd, l even and h' even, l' odd, or conversely. This condition requires the use of planes forbidden by space-group symmetry.

An example from the structure of *p*-di-tertiary-butylbenzene, with space group $P2_1/n$, illustrates this

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‡ All of the inequalities used here are given in the paper by Harker & Kasper (1948).