

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 $\text{Hg}_2\text{NCl}\cdot\text{H}_2\text{O}$, HgNH_2Cl and $\text{Hg}(\text{NH}_3)_2\text{Cl}_2$ is interesting because of their easy production and inter-conversions in the presence of ammonia and ammonium chloride of various concentrations. The chloride of Millon's base, $\text{Hg}_2\text{NCl}\cdot\text{H}_2\text{O}$, consists of an infinite three-dimensional framework, that of HgNH_2Cl (infusible precipitate) of infinite one-dimensional chains, and that of $\text{Hg}(\text{NH}_3)_2\text{Cl}_2$ (fusible precipitate) (MacGillavry & Bijvoet, 1936) could well be described in terms of finite linear groups $^+\text{H}_3\text{N}-\text{Hg}-\text{NH}_3^+$ 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 $\text{Hg}_2\text{NCl}\cdot\text{H}_2\text{O}$, to 2 Hg and 2 H in HgNH_2Cl , and to 1 Hg and 3 H in $\text{Hg}(\text{NH}_3)_2\text{Cl}_2$.

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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,

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

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

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

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).

application. With the data from Table 1, the signs of $U(103)$ and $U(30\bar{5})$ can be related by means of

$$|U(20\bar{1}) \pm U(10\bar{4})|^2 \leq 1 + \frac{1}{2}U(40\bar{2}) + \frac{1}{2}U(20\bar{8}) \\ \pm [U(103) + U(30\bar{5})]$$

or

$$|0 \pm 0|^2 \leq 1 + 0.331S + 0.098S \pm [0.695S + 0.877S],$$

where $S = \pm 1$, and is the sign of the structure factor. For the most unfavorable case, $S(40\bar{2}) = S(20\bar{8}) = +1$,

$$0 \leq 1.429 \pm [0.695S + 0.877S],$$

which must be true for both signs in front of the bracket. Clearly, if $S(103) = S(30\bar{5})$ this is not the case. Hence, $S(103) = -S(30\bar{5})$.

Table 1. Observed $U(hkl)$ values from p-di-tertiary-butylbenzene

| hkl | $U(hkl)_o$ |
|--------------|---------------------|
| 103 | 0.695 |
| 208 | 0.195 |
| 30 $\bar{5}$ | 0.877 |
| 40 $\bar{2}$ | 0.661 |
| 430 | 0.717 |
| 440 | 0.577 |
| 70 $\bar{7}$ | 0.190 |
| 870 | 0 |
| $h0l$ | 0 when $h+l$ is odd |
| $0k0$ | 0 when k is odd |

2. Half odd-indices

In cases where the use of space-group extinctions does not yield signs for a sufficient number of U 's, unobservable reflections with half-integral indices are frequently helpful on the left side of (1). In fact, if the relative signs are to be determined at all for

$$U(h-h'.0l-l') \quad \text{and} \quad U(h+h'.0l+l'),$$

when $h-h'$ and $h+h'$, $l-l'$ and $l+l'$ differ by odd numbers, fractional indices must occur on the left of (1). Although, under the terms of Bragg's law, reflections from such planes are not observable, their use is justifiable. The applicability of the Schwarz or Cauchy

inequalities to the structure factors depends only on the general algebraic form of $U(hkl)$ and the positivity, respectively, of the electron-density function everywhere, or of the atomic f 's. The derivation does not in any way restrict (hkl) to integers.

An example of the application of such planes follows. Consider, for instance,

$$|U(3\frac{1}{2}0.3\frac{1}{2}) \pm U(\frac{1}{2}0.1\frac{1}{2})|^2 \leq 1 + \frac{1}{2}U(70\bar{7}) + \frac{1}{2}U(103) \\ \pm [U(30\bar{5}) + U(40\bar{2})].$$

The left-hand side of the inequality is not necessarily equal to zero but has a real positive, as yet unknown, value R , even though these intensities cannot be observed. Then, substituting from Table 1,

$$R \leq 1 + 0.095S + 0.348S \pm [0.877S + 0.661S].$$

Thus even if $S(70\bar{7}) = S(103) = +1$, it is necessary that $S(30\bar{5}) = -S(40\bar{2})$. This follows from the fact that the inequalities

$$R \leq 1.443 \pm 1.538$$

cannot both be satisfied.

For a set of $(hk0)$ planes,

$$|U(4.3\frac{1}{2}0) \pm U(0.\frac{1}{2}0)|^2 \leq 1 + \frac{1}{2}U(870) + \frac{1}{2}U(010) \\ \pm [U(430) + U(440)].$$

Equating the left-hand side to a real positive number, R , then

$$R \leq 1 + 0 + 0 \pm [0.717S + 0.577S].$$

From this it follows that $S(430) = -S(440)$.

Although specific examples of forbidden reflections in the inequalities are discussed here, the generality of this approach can be extended to all space groups. If unobservable planes are helpful on the right of (1), fractional indices other than $\frac{1}{2}$ can also be used on the left.

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