It follows that

$$\mathbf{b} = 4\pi^2\mathbf{B} \tag{17}$$

and that

$$B = \tfrac{4}{3}\mathbf{A}'\mathbf{b}\mathbf{A} = \tfrac{4}{3}\sum_i \sum_j b_{ij}(\mathbf{a}_i \cdot \mathbf{a}_j)\ . \tag{18}$$

If some of the components of the **b** matrix are unknown, for example, if refinement is carried out in two dimensions only, one may still obtain an equivalent isotropic temperature factor by assuming that the unknown components of the anisotropic matrix and the isotropic matrix are identical, i.e., we may set

$$b_{ij} = \frac{B}{4}(\mathbf{A}\mathbf{A}')^{-1}_{ij} \tag{19}$$

$$= \frac{B}{4}(\mathbf{A}^*\mathbf{A}^{*\prime})_{ij} \tag{19a}$$

by virtue of (6).

Suppose we have refined an [001] projection; we may write

$$\mathbf{b} = \begin{pmatrix} b_{11} & b_{12} & \frac{B}{4}a^*c^* \cos\beta^* \\ b_{12} & b_{22} & \frac{B}{4}b^*c^* \cos\alpha^* \\ \frac{B}{4}a^*c^* \cos\beta^* & \frac{B}{4}b^*c^* \cos\alpha^* & \frac{B}{4}c^{*2} \end{pmatrix} \tag{20}$$

and applying (18), we find after some manipulation that the equivalent isotropic temperature factor is

$$B = \frac{4}{1+(cc^*)^2}\,[a^2b_{11}+ab\cos\gamma(2b_{12})+b^2b_{22}]\ . \tag{21}$$

It should be pointed out that the equivalent isotropic temperature factor defined here is not necessarily that which would minimize the least-squares error. This could be found only by taking into account the least-squares error matrix for the individual components.

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A general method for determining film-to-film scaling constants.

By R. E. Dickerson, *M.R.C. Unit, Cavendish Laboratory, Cambridge, England*

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In a recent short communication, Kraut (1958) has proposed a systematic method of scaling a set of mutually intersecting reciprocal lattice planes obtained using zero-level precession camera photographs. The purpose of this paper is to propose an alternative method applicable where not all planes are mutually intersecting, as when upper level photographs are used.

Kraut's method may be briefly summarized as follows: If k_i is the desired scaling constant for reciprocal lattice plane i or film i, and if r_{ij} is the average value of the reciprocal-point-by-point ratio between reflections occurring on films i and j, or $r_{ij} = \langle I_{j(hkl)}/I_{i(hkl)}\rangle$, then the desired constant for film i is given by:

$$k_i = \left[\prod_{j=1}^{n} \frac{r_{ij}r_{jn}}{r_{ji}r_{nj}}\right]^{1/2n} \tag{1}$$

where n is the total number of planes and k_n is arbitrarily chosen to be unity. The criterion leading to this equation is the minimization of the following function with respect to all log k_j's

$$F(k_i, r_{ij}) = \sum_{i=1}^{n} \sum_{j=1}^{n} \left(\log\frac{k_i}{k_j} - \log r_{ij}\right)^2 . \tag{2}$$

This approach is inapplicable to upper level photographs, in which case there are planes which do not intersect, for here r_{ij} and r_{ji} are indeterminate quantities. It is not correct simply to omit such terms from the product, for this implicitly assumes that $r_{ij}/r_{ji} = 1$, which could be true only if the scaling constants for the two planes were identical.

In the process of obtaining data for a Fourier synthesis of myoglobin with 2 Å resolution we collect twenty-two sets of zero and upper level precession photographs, of the type h, n, l (n = 0 to 6), h, k, n (n = 0 to 6), and $h, k, k-n$ (n = 0 to 7). We have found the following to be a convenient method of scaling these films so as to make the maximum possible use of film intersection. Define J_{ij} as the sum of all reflections on film i which are common to film j, and J_{ji} as a similar sum on film j. Because of reciprocal-space symmetry these may lie on more than one row. If i and j do not intersect, then $J_{ij} = J_{ji} = 0$, but both may be considered formally as present. Define k_j as the desired scaling constant for film j. If there were no experimental errors then the 'residual' for one pair of planes would be zero when proper scaling constants were used: $e_{ij} = k_iJ_{ij} - k_jJ_{ji} = 0$. This is never realized, but the best set of k's will be that minimizing the sum of squares of residuals, the sum being taken over all pairs of intersecting films. From a formal viewpoint the sum may be taken over all possible combinations of planes with the above stipulation about J values of non-intersecting planes.

$$E = \sum_{i=1}^{n} \sum_{j=1}^{n} (k_iJ_{ij} - k_jJ_{ji})^2\ . \tag{3}$$

Differentiation with respect to a particular k_i yields:

$$\sum_{j=1}^{n} (k_iJ^2_{ij} - k_jJ_{ji}J_{ij}) = 0\ . \tag{4}$$

For convenience, J_{ii} may be defined as zero, since the terms with $j = i$ cancel.

Changing to a more convenient nomenclature, let:

$$a_{ij} = -J_{ij}J_{ji} = a_{ji} \quad \text{and:} \quad a_{ii} = \sum_{k=1}^{n} J_{ik}^2 .$$

Then equations (4) reduce to:

$$\sum_{j=1}^{n} a_{ij}k_j = 0, \quad i = 1 \text{ to } n .$$

As these n equations in n unknowns are not linearly independent, one can arbitrarily specify the value of one variable and reject one equation as redundant. Let us define $x_j = k_j/k_n$ and reject the nth equation. Then the new set of $n-1$ independent equations is:

$$\sum_{j=1}^{n-1} a_{ij}x_j = -a_{in}, \quad i = 1 \text{ to } n-1 . \tag{5}$$

These equations may be solved by various standard methods; for our work this is done with an existing Edsac II computer subroutine.

If it is inconvenient to solve the simultaneous equations directly and if trial values of the scaling constants are known, then the constants can be quickly refined using a variant of equation (4):

$$k_i = \frac{\sum_{j=1}^{n} k'_j J_{ij} J_{ji}}{\sum_{j=1}^{n} J_{ij}^2} \tag{6}$$

where the primed k's are the trial values and the new values are 'normalized' after each cycle by dividing through by some k_n.

It is of interest to compare the functions minimized in the two methods. Kraut uses as the ratio between two planes the average value of the ratios between individual reflections, thus emphasizing the contributions of weak reflections. We use the ratio of the sums of all corresponding reflections on the two films, emphasizing the strong reflections. (This can be compensated for by some weighting method such as rejecting the strongest intensities for scaling or using scattering amplitudes instead of intensities, thus producing an effective weighting factor of $I^{-\frac{1}{2}}$.) If only medium intensities are used the two types of ratio will be quite similar in value. If one uses the latter ratio in Kraut's equations (1) and (2) above, then:

$$r_{ij} = J_{ji}/J_{ij} = (r_{ji})^{-1}$$

$$k_i = \prod_{j=1}^{n} (r_{ij}/r_{nj})^{1/n} \tag{1'}$$

and the quantity minimized is:

$$F(k_i, J_{ij}) = \sum_{i=1}^{n} \sum_{j=1}^{n} (\log k_iJ_{ij} - \log k_jJ_{ji})^2 . \tag{2'}$$

Thus we minimize the difference between two quantities and Kraut effectively minimizes the difference between the logarithms of these same quantities.

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The crystal structure of tetramethylammonium tetrachlorozincate and tetrachlorocobaltate. (II).

By B. Morosin and E. C. Lingafelter, *Department of Chemistry, University of Washington, Seattle 5, Washington, U.S.A.*

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Introduction

The crystal structure of Cs_2CoCl_4 has been reported by Poraj-Koshitz (1956) and Cs_2ZnCl_4 has been shown to be isomorphous by Brehler (1957). In connection with our study of the configuration of $CuCl_4^{--}$ in $[N(CH_3)_4]_2CuCl_4$ (Morosin & Lingafelter, 1959) it was considered of interest to investigate the corresponding compounds of other bivalent metals. The present report includes the isomorphous pair, $[N(CH_3)_4]_2ZnCl_4$ and $[N(CH_3)_4]_2CoCl_4$.

Experimental

Crystals of both compounds were grown by evaporation at room temperature of aqueous solutions containing the stoicheiometric proportions of $N(CH_3)_4Cl$ and $M^{II}Cl_2$. The crystals of both the colorless zinc compound and the blue cobalt compound were short rod-like prisms bounded by (011) and terminated by (100).

Precession and Weissenberg photographs taken with copper radiation (λ = 1·5418 Å) indicated the two compounds to be isomorphous. The following cell dimensions were obtained; for the zinc compound, results were standardized by superimposing NaCl (a_0 = 5·6280 Å) photographs on the same films.

	Zincate	Cobaltate
a_0	12·268 ± 0·007 Å	12·24 ± 0·03 Å
b_0	8·964 ± 0·007	8·92 ± 0·02
c_0	15·515 ± 0·012	15·39 ± 0·03

Systematic absences of ($0kl$) for $k+l$ odd and of ($hk0$) for h odd indicate the space group to be *Pnma* or $Pn2_1a$. Number of molecules per cell = 4. Calculated density, 1·38 g.cm.$^{-3}$; observed, 1·34 g.cm.$^{-3}$.

($h0l$) intensity data were collected for $[N(CH_3)_4]_2ZnCl_4$ with an integrating precession camera (Stewart, 1958) using Mo radiation and partial three-dimensional data (i.e., $0kl$ through $6kl$) were collected by means of a non-integrating Weissenberg camera. The number of observed reflections was 540. Intensities were scanned by means of a photometer and relative peak heights were obtained and used as intensities, being placed on an absolute scale by comparison with calculated values at a later stage of the structure determination.

Lorentz and polarization factors were applied and structure factors calculated using Thomas & Umeda (1957) scattering factors. Calculations were carried out on an IBM type 650 computer.

Determination of the structure

The similarity of the axial ratios of the $[N(CH_3)_4]_2ZnCl_4$ (1·368:1·000:1·731) and Cs_2ZnCl_4 (1·317:1·000:1·755; Brehler, 1957) and the identity of their space-group extinctions suggest that the structures are probably similar. Therefore the space group *Pnma* was initially assumed and later verified by the final structure.

A Harker Section $P(x, \frac{1}{2}, z)$ established the positions