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Variances and Covariances for Best-Plane Parameters Including Dihedral Angles

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Equations for the calculation of a number of variance and covariance terms related to best-plane parameters are given. They include expressions for the uncertainties of the orientation of the best plane and allow the calculation of the variances and covariances for the angles between the plane normal and the axes of any chosen coordinate system, as well as for the plane-to-origin distance. Another expression gives the standard deviation of the dihedral angle between two planes; it includes the case in which the two planes share atoms. All expressions are for isotropic positional variances; effects of atomic positional correlations are not included. A numerical example is given with intermediate results, to provide checks for computer programs employing these expressions.

Introduction

The standard deviations of and the covariances between parameters associated with least-squares planes are functions of the positional standard deviations of the atoms to which the planes have been fitted. The pertinent relationships may be derived by applying the standard error propagation formula. In this derivation the methods of Gibbs dyadics can be very helpful (Waser, 1973*a*). Below are given formulas for the standard deviations of the distance of a best plane from the origin and of the direction of the plane normal, as well as for the covariances among these quantities. We also present a formula for the standard deviation of the dihedral angle between two planes, including the case in which these planes have atoms in common. While our results assume that the positional variance–covariance matrices of the individual atoms are isotropic and that there are no correlations among the coordinates of the different atoms, it is possible to generalize the results given so as to take into account anisotropic positional covariances of the atoms as well as correlation among atomic coordinates (Sands, 1966; Waser, 1973*a*). For purposes of checking computer programs we also provide a numerical example concerning a triclinic crystal, giving some of the intermediate results.

Formulation

The parameters of a best plane can be obtained by solving an eigenvalue problem (Schomaker, Waser, Marsh & Bergman, 1959; Hamilton, 1961) in which the plane normal turns out to be parallel to the eigenvector associated with the smallest eigenvalue, which is the weighted sum of the squares of the distances of the atoms from the plane fitted to them, that is, the minimum value of the quantity that is minimized by the least-squares procedure. The other two eigenvectors of the eigenvalue problem are perpendicular to what may be called the worst plane and to an intermediate plane (*i.e.* the sum of the weighted residuals assumes a maximum in the first case and an intermediate stationary value in the second).

It is convenient to introduce an orthogonal coordinate system, referred to as the coordinate system of the plane and described by the unit vectors $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$, which are chosen parallel to the eigenvectors associated with the worst, intermediate and best plane. (In the case that the two larger eigenvalues are equal, $\mathbf{e}_1$ and $\mathbf{e}_2$ are chosen along any two perpendicular directions in the best plane.) In this coordinate system the unit vector $\mathbf{m}$ associated with the best plane has the components $(m_1, m_2, m_3) = (0, 0, 1)$, and we may describe the uncertainty in the orientation of the best plane in terms of the variances and covariances relating to m_1 and m_2, because all variations of $\mathbf{m}$ must be perpendicular to $\mathbf{m}$. In fact the variances of m_1 and m_2 are, respectively, equal to the variances of the angles φ_1 and φ_2 between $\mathbf{m}$ and $\mathbf{e}_1$ and $\mathbf{m}$ and $\mathbf{e}_2$, angles that have expectation values of 90°. For example, $\operatorname{cov}(m_1, m_2) = \operatorname{cov}(\varphi_1, \varphi_2)$. All covariance terms associated with m_3 are zero, and all of the sums used later involving covariance terms of the m_i extend over $i = 1, 2$ only. The situation regarding the orientation of a unit vector such as $\mathbf{m}$ is further illuminated by noting that only two of its components are independent. This implies relationships among the covariances of its three components in any arbitrary coordinate system. Thus if n_j $(j = 1, 2, 3)$ are the components of $\mathbf{m}$ in the framework of the crystal axes $\mathbf{a}_j$ (with $g_{ij} = \mathbf{a}_i \,.\, \mathbf{a}_j$), it can be shown that

$$\sum_{i} \sum n_i g_{ij} \operatorname{cov}(n_k, n_j) = 0 \quad k = 1, 2, 3 \qquad (1)$$

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Moreover, while the standard deviation $\sigma(d)$ of the distance d of the best plane from the origin is often all that is quoted, the covariance terms $\mathrm{cov}\,(d,n_j)$ need not be negligible. These terms satisfy a relationship similar to (1),

$$\sum_i \sum_j n_i g_{ij}\,\mathrm{cov}\,(d,n_j)=0. \tag{2}$$

Relationships similar to (1) and (2) exist when other axes of reference are used, and also among covariances referring to the directional cosines γ_j of $\mathbf{m}$ relative to the $\mathbf{a}_j$ or to any other axes.

The results of the error analysis presented below reflect the direct influence of the (isotropic) positional standard deviations σ_j of the atoms j defining the best plane. They depend on the weights w_j associated with these atoms only inasmuch as these weights are determining elements in defining this plane. These weights need not be governed by the σ_j and may be assigned in any suitable or convenient way, including the frequent practices of choosing them to be inversely proportional to the atomic positional variances in a direction perpendicular to the plane to be fitted or, alternatively, of assigning equal weights to all the atoms that may define the plane, even though the locations of the heavier atoms are usually better determined than those of lighter atoms. The choice of weights is simply a matter of defining the desired 'best' plane and does not affect the error analysis given below. However, as will be seen, some cancellation occurs when the w_j are simply made proportional to σ_j^{-2}.

Our formulas reflect only in a roundabout way [such as the appearance of $\langle X_3^2\rangle$ in denominators, see *e.g.* (7) and (15)] how well the chosen plane fits the atoms. We remark that it is perfectly appropriate to consider a 'best' plane for a severely non-planar array of atoms, such as a puckered ring; the parameters of such a plane are completely defined (except in extreme cases, such as P_4 or cubane) by the positions and weights of the atoms, whereas the variances and covariances of the parameters of the plane depend crucially on the variances in the positions of the atoms. In such a situation the quality of the fit of the plane can be discerned, as in any other case, from a 'chi-squared' test, by evaluating the sum $\sum d_j^2/\sigma_j^2$, where d_j is the distance from atom j to the plane and σ_j is the standard deviation in the position of atom j in the direction parallel to the plane normal.

We now turn to definitions of the symbols not already explained. We denote by x_{1s},x_{2s},x_{3s} the coordinates of atom s with respect to the axes $\mathbf{e}_1,\mathbf{e}_2,\mathbf{e}_3$, the origin being taken at the origin of the unit cell, and by X_{1s},X_{2s},X_{3s} the coordinates of the same atom in a similar coordinate system with the origin at the centroid of the group of atoms under consideration; *i.e.*, $X_{is}=x_{is}-\langle x_i\rangle$. The symbol $\langle\ \rangle$ denotes the mean value of a quantity, as in

$$\langle x_i\rangle=(\sum_s w_s x_{is})/\sum_s w_s\equiv[wx_i]/[w] \tag{3}$$

or

$$\langle X_i^2\rangle=(\sum_s w_s X_{is}^2)/\sum_s w_s\equiv[wX_i^2]/[w] \tag{4}$$

which implicitly define the bracket sum symbol [ ] of Gauss. In particular we have $\langle X_iX_j\rangle=0$ when $i\neq j$, because the coordinate system of the plane is erected by eigenvectors. By { } we abbreviate sums of the kind

$$\{X_i\}=\sum_s w_s^2\sigma_s^2 X_{is} \tag{5}$$

$$\{X_iX_j\}=\sum_s w_s^2\sigma_s^2 X_{is}X_{js}. \tag{6}$$

Note that the last quantity is not necessarily zero when $i\neq j$.

The variances and covariances referred to earlier are then given by the following expressions:

$$\sigma^2(m_i)\equiv\mathrm{cov}\,(m_i,m_i)$$
$$=\frac{1}{[w]^2}\,\frac{\{X_i^2\}+\{X_3^2\}}{(\langle X_i^2\rangle-\langle X_3^2\rangle)^2}\quad i=1,2 \tag{7a}$$

$$\mathrm{cov}\,(m_1,m_2)=\frac{1}{[w]^2}\,\frac{\{X_1X_2\}}{(\langle X_1^2\rangle-\langle X_3^2\rangle)(\langle X_2^2\rangle-\langle X_3^2\rangle)} \tag{7b}$$

$$\sigma^2(d)=\sum_{i,j}\langle x_i\rangle\langle x_j\rangle\,\mathrm{cov}\,(m_i,m_j)$$
$$+\frac{1}{[w]^2}\left([w^2\sigma^2]-2\sum_i\frac{\langle x_i\rangle\{X_i\}}{\langle X_i^2\rangle-\langle X_3^2\rangle}\right) \tag{8}$$

$$\mathrm{cov}\,(d,m_i)=\sum_k\langle x_k\rangle\,\mathrm{cov}\,(m_i,m_k)$$
$$-\frac{1}{[w]^2}\,\frac{\{X_i\}}{\langle X_i^2\rangle-\langle X_3^2\rangle} \tag{9}$$

where the sums in (8) and (9) cover just the indices 1 and 2.

When the weights w_s are taken to be proportional to σ_s^{-2} there is some simplification. In this case $\{\ldots\}=[w]\langle\ldots\rangle$, and since $\langle X_1\rangle=\langle X_2\rangle=\langle X_1X_2\rangle=0$, we have $\mathrm{cov}\,(m_1,m_2)=0$. Moreover some terms in all formulas involving d become zero.

It may be of interest to calculate the covariance matrix of the direction cosines γ_{3i} of the plane normal $\mathbf{m}$ relative to any set of three axes $\mathbf{c}_i$ (which may but need not be the crystallographic axes $\mathbf{a}_i$ or their reciprocals $\mathbf{b}_i$), as well as the covariance terms among the γ_{3i} and d. If the quantities γ_{ij} are the cosines of the angles between the directions $\mathbf{e}_i$ and $\mathbf{c}_j$ then

$$\mathrm{cov}\,(\gamma_{3i},\gamma_{3j})=\sum_{k,l}\gamma_{ki}\gamma_{lj}\,\mathrm{cov}\,(m_k,m_l);\quad i,j=1,2,3 \tag{10}$$

and

$$\mathrm{cov}\,(d,\gamma_{3j})=\sum_k\gamma_{kj}\,\mathrm{cov}\,(d,m_k). \tag{11}$$

[Here and in (12) and (13) the sums over k and l extend over 1 and 2 only.] Similarly, if the quantities n_{ij} are the components of the unit vectors $\mathbf{e}_i$ along the axes $\mathbf{c}_j$, so that $\mathbf{e}_i=\sum n_{ij}\mathbf{c}_j$, then

$$\mathrm{cov}\,(n_{3i},n_{3j})=\sum_{k,l} n_{ki}n_{lj}\,\mathrm{cov}\,(m_k,m_l) \tag{12}$$

$$\mathrm{cov}\,(d,n_{3j})=\sum_{k} n_{kj}\,\mathrm{cov}\,(d,m_k). \tag{13}$$

These quantities satisfy the relationships (1) and (2) with $n_i \equiv n_{3i}$ and $g_{ij}=\mathbf{c}_i\,.\,\mathbf{c}_j$.

Next, we consider two planes and the angle θ_0 between the two plane normals. We designate all quantities specifically associated with the second plane by primes. Examples are the unit vectors $\mathbf{e}'_j$ $(j=1,2,3)$ of the coordinate system of the second plane, the weights w'_j, the coordinates X'_{js}, *etc.*, and the variance–covariance matrix $\mathrm{cov}\,(m'_1,m'_2)$ pertaining to the plane normal $\mathbf{m}'$. The formula for the standard deviation of θ_0 includes contributions from the covariance matrix $\mathrm{cov}\,(m_i,m'_j)$ $(i,j=1,2)$, which is non-zero when the two planes considered have atoms in common. In the formula for $\mathrm{cov}\,(m_i,m'_j)$ we use the subscript c to denote summation over common atoms, as in

$$\{X_iX'_j\}_c=\sum_{\substack{\text{common}\\ \text{atoms } s}} w_s w'_s \sigma_s^2 X_{is} X'_{js}. \tag{14}$$

Other sums, in the denominators, extend over all atoms in one or the other plane, depending on whether or not a prime appears. For example, in $[w]$ and $\langle X_i^2\rangle$ the sums extend over all atoms on the first plane, and in $[w']$ and $\langle X_i'^2\rangle$ over all atoms of the second plane. With these abbreviations we find the following expression for $\mathrm{cov}\,(m_i,m'_j)$:

$$\mathrm{cov}\,(m_i,m'_j)=\frac{\{X_3X'_3\}_c(\mathbf{e}_i\,.\,\mathbf{e}'_j)+\{X_3X'_i\}_c(\mathbf{e}_i\,.\,\mathbf{e}'_3)+\{X_jX'_3\}_c(\mathbf{e}_3\,.\,\mathbf{e}'_j)+\{X_iX'_j\}_c(\mathbf{e}_3\,.\,\mathbf{c}'_3)}{[w]\,[w']\,(\langle X_i^2\rangle-\langle X_3^2\rangle)\,(\langle X_j'^2\rangle-\langle X_3'^2\rangle)}\,. \tag{15}$$

For the variance of the angle θ_0 between $\mathbf{m}$ and $\mathbf{m}'$ we obtain

$$\begin{aligned}\sigma^2(\theta_0)=\frac{1}{\sin^2\theta_0}\sum_{i,j}(&\mathrm{cov}\,(m_i,m_j)\,(\mathbf{e}_i\,.\,\mathbf{e}'_3)\,(\mathbf{e}_j\,.\,\mathbf{e}'_3)\\ &+\mathrm{cov}\,(m'_i,m'_j)\,(\mathbf{e}_3\,.\,\mathbf{e}'_i)\,(\mathbf{e}_3\,.\,\mathbf{e}'_j)\\ &+2\,\mathrm{cov}\,(m_i,m'_j)\,(\mathbf{e}_i\,.\,\mathbf{e}'_3)\,(\mathbf{e}_3\,.\,\mathbf{e}'_j)).\end{aligned} \tag{16}$$

In the case that θ_0 is zero this expression becomes an undetermined 0/0. Moreover, the linearization involved in the derivation of the results given becomes untenable when the magnitude of θ_0 is comparable with that of $\sigma(m_i)$ or $\sigma(m'_i)$, $i=1,2$. That is to say, when θ_0 is large compared to these standard deviations, the difference between the actual θ and its mean θ_0 is approximately normally distributed, assuming that this is the case for the quantities m_i and m'_i. When θ_0 becomes comparable to the standard deviations cited, the distribution of θ about its mean is no longer approximately normal, and indeed this mean is no longer θ_0 but larger; we have not been able to find a closed expression for $\langle\theta\rangle$ in the circumstances described. However, an upper bound for $\sigma^2(\theta)$ that should be satisfactory for most purposes is given by the expression

$$\begin{aligned}\sigma^2(\theta)=\langle\theta^2\rangle-\langle\theta\rangle^2 &\ge \langle\theta^2\rangle-\theta_0^2\\ &=\sum_i(\sigma^2(m_i)+\sigma^2(m'_i))\\ &\quad-2\sum_{i,j}\mathrm{cov}\,(m_i,m'_j)\mathbf{e}_i\,.\,\mathbf{e}'_j.\end{aligned} \tag{17}$$

It can be shown that in special situations equations (7), (15), and (16) yield results that are identical with results obtained in other ways. One of these relates to the torsion angle associated with a sequence of atoms *ABCD*, that is, the angle between the normals upon the planes *ABC* and *BCD*. In the case of equal bond distances *A–B*, *B–C*, and *C–D*, but arbitrary bond angles and (isotropic) positional standard deviations the present results are algebraically identical with those derived by Stanford & Waser (1972); the establishment of algebraic identity looks cumbersome in more general cases, but both approaches have yielded identical numerical results in a number of tests. Another special situation is that of two planes defined by the rectangles $A_1A_2B_1B_2$ and $B_1B_2C_1C_2$, which share the corners B_1 and B_2. Let the positional standard deviations for the two 'atoms' in each pair A_1–A_2, B_1–B_2, and C_1–C_2 be equal. Then the variance for the dihedral angle between the two planes is found to be equal to one-half the variance of the 'bond angle' $A_1B_1C_1$; the factor $\frac{1}{2}$ reflects that twice as many atoms are involved in defining the dihedral angle. An analogous result is obtained for a 'butterfly' arrangement of four 'atoms' in two isoceles triangles AB_1B_2 and B_1B_2C.

It should be emphasized that our assumptions of isotropic positional variances and of the absence of covariances may not be justified; more general formulas that apply in such situations are available (Waser, 1973*a*). A particular problem arises in polar space groups, where one or more coordinates of the origin are arbitrary. It is the usual custom to define these coordinates by holding fixed the cooresponding coordinates of one atom; as a result, the variances and covariances involving these fixed coordinates are zero, while variances and covariances involving the remaining atoms may be larger than normal (Sands, 1966). Even in these cases, we expect that the formulas in this paper will yield good approximations to the correct results, provided that reasonable values are assigned to the standard deviations (Templeton, 1960; Waser, 1973*b*).

A numerical example

As an example we choose the joined five- and six-membered rings of the indole portion of indomethacin

(Kistenmacher & Marsh, 1972). The triclinic crystals of this compound contain two molecules in the unit cell in space group $P\overline{1}$. Full-matrix least-squares refinements were carried out with 3678 counter-collected Ni-filtered Cu $K\alpha$ reflections, with a final value of 0·059 for R. In the following we report intermediate as well as final computational results, and include, for purposes of checking computer programs, more significant figures than we necessarily believe to be significant. The values of the σ_i used are averages of σ_{xi}, σ_{yi}, and σ_{zi} given by the least-squares refinement, while the weights w_i were to some extent chosen arbitrarily; they are very roughly equal to const/$\sigma^2_{i\perp}$, where the $\sigma_{i\perp}$ are positional standard deviations in a direction perpendicular to the plane considered. (A calculation of *exact* values of the $\sigma_{i\perp}$ would require a knowledge of positional covariances as well as variances; see, *e.g.*, Hamilton, 1961.)

It would hardly have made a difference, in the present example, if we had used w_i=const/σ^2_i, but we chose otherwise so as to illustrate all aspects of our

Table 1. *Unit-cell dimensions*

a=	9·295 (2) Å	α=	69·38 (1)°
b=	10·969 (1)	β=	110·79 (1)
c=	9·742 (1)	γ	92·78 (1)

Table 2. *Atomic coordinates, assigned weights, and average isotropic standard deviations* (Å)

The five-ring comprises atoms N(1), C(2), C(3), C(4) and C(9); the six-ring comprises C(4)–C(9); there are two common atoms, C(4) and C(9).

	x	y	z	w	$\sigma\times10^5$
N(1)	0·4331	0·7923	0·4599	4755	153
C(2)	0·5732	0·7309	0·4793	2921	190
C(3)	0·5972	0·6103	0·5918	3087	186
C(4)	0·4746	0·5926	0·6520	3265	180
C(5)	0·4478	0·4881	0·7711	2770	197
C(6)	0·3193	0·5011	0·8052	2508	213
C(7)	0·2200	0·6166	0·7244	1975	227
C(8)	0·2461	0·7202	0·6077	2268	217
C(9)	0·3729	0·7063	0·5694	3262	183

Table 3. *Atomic coordinates in plane system* ($\mathbf{e}_1,\mathbf{e}_2,\mathbf{e}_3$) *relative to crystal origin* (x_i) *and to plane centroid* (X_i)

Plane 1	x_1	x_2	x_3	X_1	X_2	X_3
C(4)	−2·3165	−0·1728	10·1524	1·0510	−0·7049	0·0024
C(9)	−3·6561	−0·5843	10·1545	−0·2886	−1·1164	0·0045
N(1)	−4·4502	0·5879	10·1433	−1·0827	0·0558	−0·0067
C(2)	−3·5820	1·7067	10·1629	−0·2145	1·1746	0·0130
C(3)	−2·3034	1·2600	10·1407	1·0641	0·7279	−0·0092
Plane 2						
C(4)	2·0014	1·3926	10·1253	0·1721	−1·2010	0·0073
C(9)	3·0860	2·2799	10·1045	1·2567	−0·3137	−0·0135
C(8)	2·8796	3·6503	10·1315	1·0503	1·0567	0·0135
C(7)	1·5781	4·1063	10·1198	−0·2511	1·5127	0·0017
C(6)	0·4856	3·2242	10·1085	−1·3436	0·6305	−0·0095
C(5)	0·6820	1·8640	10·1218	−1·1472	−0·7296	0·0038

Table 4. *Second-moment matrix* [wX_iY_i]

Diagonal elements are eigenvalues. Off-diagonal elements differ from zero because of round-off-errors.

Plane 1			Plane 2		
13082	−0·00146	−0·00009	16049	0·00269	0·00006
−0·00146	11368	−0·00035	0·00269	14554	0·00073
−0·00009	−0·00035	1·0520	0·00006	0·00073	1·4563

Table 5. *Direction cosines of worst, intermediate, and best-plane normals, relative to crystal axes* **a**, **b**, **c** (j= 1,2,3)

	Plane 1			Plane 2		
	j=1	j=2	j=3	j=1	j=2	j=3
γ_{1j}	0·25110	−0·74184	0·22009	0·11868	0·66838	−0·45133
γ_{2j}	0·93388	−0·03503	−0·63995	−0·94992	0·33644	0·53468
γ_{3j}	0·25458	0·66967	0·73622	0·28908	0·66338	0·71443

Table 6. *Components of these plane-system unit vectors in orthogonalized crystal system*

This system is defined by the unit vectors **i**, **j**, **k**, where **i** is in the (001) plane and perpendicular to **b**; **j**=**b**/b; **k**=**i**×**j**. The direction cosines (and components) of $\mathbf{m}_1$, $\mathbf{m}_2$, and $\mathbf{m}_3$ are denoted by μ_{1j}, μ_{2j}, and μ_{3j}, where j= 1, 2, 3 refers to the orthogonalized axes.

	Plane 1			Plane 2		
μ_{1j}	0·21537	−0·74184	0·63505	0·15128	0·66838	−0·72828
μ_{2j}	0·93328	−0·03503	−0·35743	−0·93470	0·33644	0·11462
μ_{3j}	0·28740	0·66967	0·68480	0·32163	0·66338	0·67563

Table 7. *Intermediate sums*

	Plane 1	Plane 2		Plane 1	Plane 2
$[w]$	17290	16048			
$\langle x_1\rangle$	−3·3675	1·8293	$\{X_1\}$	−2·8156	−1·3839
$\langle x_2\rangle$	0·5321	2·5936	$\{X_2\}$	−1·0003	−0·3924
$\langle x_3\rangle=d$	10·1500	10·1180	$\{X_1X_2\}$	0·47134	−1·19039
$\langle X_1^2\rangle$	0·75664	1·00004	$\{X_1^2\}$	141·91	176·00
$\langle X_2^2\rangle$	0·65748	0·90690	$\{X_2^2\}$	121·70	153·56
$\langle X_3^2\rangle$	$6·0843\times10^{-5}$	$9·0747\times10^{-5}$	$\{X_3^2\}$	0·011279	0·015842

Table 8. *Variances and covariances* ($\times10^8$) *of* d, m_1, m_2, *in* Å², Å × rad, *and* rad²

	Plane 1			Plane 2		
	d	m_1	m_2	d	m_1	m_2
d	1020·74	−277·89	49·57	781·65	124·25	187·32
m_1	−277·89	82·940	0·317	124·25	68·354	−0·510
m_2	49·57	0·317	94·200	187·32	−0·510	72·520

Standard deviations.

	Plane 1	Plane 2
$\sigma(d)$	0·00320 Å	0·00280 Å
$\sigma(m_1)$	0·000911 rad = 0·0522°	0·000827 rad = 0·0474°
$\sigma(m_2)$	0·000971 rad = 0·0556°	0·000852 rad = 0·0488°

Table 9. *Variances and covariances* ($\times10^6$) *among d and the direction cosines* γ_{3j} *of the plane normal relative to the crystal axes* **a**,**b**,**c** ($j=1,2,3$)

	Plane 1			Plane 2		
	γ_{31}	γ_{32}	γ_{33}	γ_{31}	γ_{32}	γ_{33}
d(Å)	−0·23488	2·04410	−0·92879	−1·63196	1·46070	0·44079
γ_{31}	0·87534	−0·18753	−0·51700	0·66516	−0·17451	−0·40745
γ_{32}	−0·18753	0·45776	−0·11282	−0·17451	0·38515	−0·07679
γ_{33}	−0·51700	−0·11282	0·42506	−0·40745	−0·07679	0·34902

Table 10. *Variances and covariances* ($\times10^6$) *among d and the direction cosines* μ_{3j} *of the plane normal relative to the orthogonal axes* **i**,**j**,**k** ($j=1,2,3$)

	Plane 1			Plane 2		
	μ_{31}	μ_{32}	μ_{33}	μ_{31}	μ_{32}	μ_{33}
d(Å)	−0·13590	2·04410	−1·94189	−1·56296	1·46070	−0·69020
μ_{31}	0·86024	−0·16553	−0·19916	0·65067	−0·15602	−0·15656
μ_{32}	−0·16553	0·45776	−0·37817	−0·15602	0·38515	−0·30390
μ_{33}	−0·19916	−0·37817	0·45340	−0·15656	−0·30390	0·37292

equations. Another point to note is that if, *e.g.*, the common practice of setting $w_i=\text{const}/\sigma_{i\perp}^2$ is employed, atoms common to two different planes may have different weights in the two-plane calculations. In the example below the common atoms were assigned the same weights for both plane determinations. The parameters involved are given in Tables 1–11.

We remark that neither the five-ring nor the six-ring is satisfactorily planar in the example given, since the r.m.s. deviations of the individual atoms from the least-squares planes are appreciably larger than their positional standard deviations. Accordingly, the dihedral angle between the two best planes, and the standard deviation of this angle, do not by themselves constitute an adequate description of the relationships among the atoms in the two rings. They describe the relationship between the best planes of the two sets of atoms, while saying nothing about how 'good' these planes are.

Table 11. *Cosines of angles between the two plane coordinate systems*

$\mathbf{e}_i\,.\,\mathbf{e}'_j=$	−0·92574	−0·37810	0·00621
	0·37808	−0·92509	0·03544
	−0·00766	0·03516	0·99935

Angle between plane normals $\theta_0=2·065°$ $[=\cos^{-1}(\mathbf{e}_3\,.\,\mathbf{e}'_3)]$
Common atom sums

$\{X_iX'_j\}_c=$	−6·67676	−40·37188	0·40302
	−54·18548	41·71748	0·36173
	0·21579	−0·14989	−0·001569

Covariance matrix for the two plane normals.

$10^8\text{cov}\,(m_i,m'_j)=$	−3·179	−21·187
	−29·685	25·209

$\sigma^2(\cos\theta_0)$, disregarding common atom correlations,
$=0·2156\times10^{-8}$

$\sigma^2(\cos\theta_0)$, including common atom correlations,
$=0·2856\times10^{-8}$

$\sigma(\theta_0)=0·085°$.

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The Crystal and Molecular Structure of Di-μ-(*N*,*N*-diethylnicotinamide-*O*,*N*)-tetraisothiocyanatodizinc

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The title compound, $Zn_2(C_{10}H_{14}N_2O)_2(NCS)_4$, is triclinic, space group $P\bar{1}$, with $a = 10{\cdot}387$ (6), $b = 12{\cdot}436$ (6), $c = 7{\cdot}835$ (5) Å, $\alpha = 108{\cdot}4$ (1), $\beta - 117{\cdot}2$ (1), $\gamma - 97{\cdot}8$ (1)°, $Z = 1$. The structure has been determined from X-ray intensities collected on an automated diffractometer. The structure, solved by Patterson and Fourier methods and refined by least squares, consists of centrosymmetric dimers with tetrahedral coordination around zinc. The two tetrahedra of the dimer are held together by *N*,*N*-diethylnicotinamide molecules acting as bridges through pyridine N and amide O. Packing of the dimers is determined by van der Waals interactions only.

Introduction

Structural studies on metal complexes of *N*,*N*-diethylnicotinamide (DENA) were undertaken in order to define the ligand properties of this respiration stimulant. The structures of the following complexes have been determined so far: Cd(DENA)(SCN)$_2$, (I) [μ-(*N*,*N*-diethylnicotinamide-*O*,*N*)-di-μ-thiocyanatocadmium; Bigoli, Braibanti, Pellinghelli & Tiripicchio (1972)], Mn(DENA)$_2$(NCS)$_2$, (II) [di-μ-(*N*,*N*-diethylnicotinamide-*O*,*N*)-diisothiocyanatomanganese; Bigoli, Braibanti, Pellinghelli & Tiripicchio (1973*a*)], Zn(DENA)$_2$(NCS)$_2$(H$_2$O)$_2$, (III) [diaquobis-(*N*,*N*-diethylnicotinamide)diisothiocyanatozinc; Bigoli, Braibanti, Pellinghelli & Tiripicchio (1973*b*)]. In these compounds the complexes are octahedral but differ from one another in the disposition of the donor atoms and in the type and number of bridges. In (I) and (II) the DENA ligand forms one and two bridges respectively through pyridine N and amide O; in (III) the organic ligand is bound to the metal through pyridine N only. Crystals of (III), when left to stand in the presence of the mother liquor, change, with a complete transformation of the metal complex, into crystals of the title compound, Zn$_2$(DENA)$_2$(NCS)$_4$, (IV). The coordination of the metal changes from octahedral to tetrahedral.

In the present paper the results of the crystal structure determination of (IV) are given.

Experimental

Preparation

Crystals of Zn(DENA)$_2$(NCS)$_2$(H$_2$O)$_2$ remain unaltered in the mother liquor for many days, then transform rapidly into the stable Zn$_2$(DENA)$_2$(NCS)$_4$.

Crystal data

Compound: di-μ-(*N*,*N*-diethylnicotinamide-*O*,*N*)-tetraisothiocyanatodizinc, $Zn_2(C_{10}H_{14}N_2O)_2(NCS)_4$.
F.W. 719·54.

Unit cell: the parameters, determined from rotation and Weissenberg photographs and refined with data obtained on an automated single-crystal diffractometer (Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å), are:
$a = 10{\cdot}387$ (6), $b = 12{\cdot}436$ (6), $c = 7{\cdot}835$ (5) Å;
$\alpha = 108{\cdot}4$ (1), $\beta = 117{\cdot}2$ (1), $\gamma = 97{\cdot}8$ (1)°;
$V = 805{\cdot}7$ Å^3; $Z = 1$;
$D_x = 1{\cdot}483$, $D_m = 1{\cdot}485$ g cm^{-3};
μ(Cu $K\alpha$) = 44·96 cm^{-1}; $F(000) = 368$.

Space group: $P\bar{1}(C_i^1$, No. 2) from the structure determination.