Kitaigorodskii, A. I. (1961). *Organic Chemical Crystallography*, p. 7. New York: Consultants Bureau.
Kitaigorodskii, A. I. (1973). *Molecular Crystals and Molecules*, pp. 11–18. New York: Academic Press.
Jones, D. S. & Karle, I. L. (1974). *Acta Cryst.* **B30**, 624–627.
Mahajan, V. & Sass, R. L. (1974). *J. Cryst. Mol. Struct.* **4**, 15–21.
Marzotto, A., Graziani, R., Bombieri, G. & Forsellini, E. (1974). *J. Cryst. Mol. Struct.* **4**, 253–262.
Oberhänsli, W. E., Wagner, H. P. & Isler, O. (1974). *Acta Cryst.* **B30**, 161–166.
Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
Sivertsen, B. (1972*a*). *STARD*. Tekn. Rapp. 18-RII-72. Inst. for Røntgenteknikk, NTH, Trondheim.
Sivertsen, B. (1972*b*). *FSTAT1*, Tekn. Rapp. 19-RII-72. Inst. for Røntgenteknikk, NTH, Trondheim.
Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. & Hall, S. R. (1972). The X-RAY System, version of June 1972. Technical Report TR-192 of the Computer Science Center, Univ. of Maryland.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
Stout, G. H. & Jensen, L. H. (1968). *X-ray Structure Determination*, pp. 424–425. London: Macmillan.
Svinning, T. (1974). *RIDEX*. Tekn. Rapp. 22-RII-74, Inst. for røntgenteknikk, NTH, Trondheim.
Sørum, H. (1956). *Acta Chem. Scand.* **10**, 1669.
Sørum, H. (1959). *Acta Chem. Scand.* **13**, 345–359.

Acta Cryst. (1975). **B31**, 1586

Comparison of the Results of Two Independent Analyses of the Ethylchlorophyllide A Dihydrate Crystal Structure

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The results of the authors' crystal structure analysis of ethylchlorophyllide A dihydrate are compared with those obtained by Chow, Serlin & Strouse [*J. Amer. Chem. Soc.* In the press]. The agreement between the two sets of positional parameters (except those of the Mg atom) is excellent, as judged by a normal probability plot analysis. However, there appear to be significant differences between the vibrational parameters. Some problems connected with the choice of origin in polar space groups are mentioned.

In the course of a systematic study of chlorophyll derivatives we have determined the crystal structure of ethylchlorophyllide A dihydrate (Fig. 1). The same crystal structure has recently been described elsewhere (Strouse, 1974; Chow, Serlin & Strouse, 1975, hereafter CSS). The opportunity to compare the results of two independent structure analyses, based on experimental data measured under different conditions, does not often occur for a molecule of this complexity. The results of such a comparison may therefore be of interest.

Table 1. *Comparison of measurement conditions and some crystallographic data for the two analyses*

	This analysis	Chow, Serlin & Strouse (1975)
Crystals grown from	acetone/water	acetone/water
Diffractometer	Hilger–Watts Y290	Syntex $P\bar{1}$
Size of crystal specimen used for data collection	$0·4 \times 0·3 \times 0·07$ mm	$0·12 \times 0·12 \times 0·05$ mm
Crystallographic data (cell constants from diffractometer measurements	$a =$ 8·87 (1) Å $c =$ 38·05 (3) space group $P3_1$	$a =$ 8·852 (1) Å $b =$ 38·087 (5) space group $P3_1$
Radiation used (monochromatized)	Mo $K\alpha$, $\lambda = 0·71069$ Å $\mu = 1·14$ cm^{-1}	Cu $K\alpha$, $\lambda = 1·5405$ Å $\mu = 9·65$ cm^{-1}
Scan mode	ω	$\omega/2\theta$
Approximate sin θ/λ limit	0·55 Å^{-1}	0·63 Å^{-1}
Number of reflexions included in refinement	2185	1919
Absorption correction	No	Yes
Number of parameters refined in the last cycles	325	452
Function minimized in least-squares refinement $\sum\omega\|\|F_o\| - \|F_c\|\|^2$ where	$\omega = \exp (r \sin^2 \theta/\lambda^2)$ $r = 6$ Å^2	$\omega = 1/\sigma^2 (F_o)$
Final R	0·048	0·05

Table 1 compares measurement conditions and some crystallographic data for the two analyses. Positional coordinates and vibration parameters from our analysis are listed in Table 2,* and are to be compared with those given by CSS. Although interatomic distances and angles derived from our coordinates show good overall agreement with those obtained by CSS, there are a few apparent discrepancies. Since the statistical significance of these differences depends on their standard deviations, it is important to know if these have been estimated realistically and to what extent errors in the data produce systematic errors in the parameters.

Table 2. *Ethylchlorophyllide A dihydrate: fractional atomic coordinates and vibrational tensor components* ($Å^2$) *of the non-hydrogen atoms* ($\times 10^4$)

The temperature factors have the form (*a*) for atoms refined isotropically $T = \exp[-(8\pi^2 U_{\text{iso}} \sin^2\theta/\lambda^2)]$; (*b*) for atoms refined anisotropically $T = \exp[-2\pi^2(h^2a^{*2}u_{11} + \ldots + 2hka^*b^*u_{12} + \ldots)]$. Standard deviations (in parentheses) are in units of the last significant figure.

	x	y	z	U_{iso}
Mg^{2+}	2954 (3)	4328 (3)	1997 (0)	364 (5)
N(1)	4185 (7)	2986 (7)	1847 (1)	375 (11)
N(2)	3590 (7)	5600 (7)	1513 (1)	373 (11)
N(3)	1061 (7)	4987 (7)	2021 (1)	381 (12)
N(4)	1533 (6)	2318 (6)	2393 (1)	326 (11)
C(1)	4231 (8)	1694 (8)	2031 (2)	386 (13)
C(2)	5419 (8)	1233 (8)	1863 (2)	425 (14)
C(3)	6072 (8)	2263 (8)	1576 (2)	422 (14)
C(4)	5290 (8)	3375 (8)	1565 (2)	408 (13)
C(5)	5540 (9)	4584 (9)	1308 (2)	421 (14)
C(6)	4762 (8)	5639 (8)	1280 (2)	391 (13)
C(7)	5034 (9)	6819 (9)	992 (2)	463 (15)
C(8)	3967 (9)	7482 (9)	1053 (2)	441 (14)
C(9)	3070 (8)	6721 (8)	1381 (2)	406 (13)
C(10)	1838 (8)	7038 (8)	1539 (2)	419 (14)
C(11)	851 (8)	6224 (8)	1841 (2)	389 (13)
C(12)	−479 (8)	6465 (8)	1996 (2)	399 (14)
C(13)	−1095 (8)	5281 (8)	2280 (2)	370 (13)
C(14)	−86 (8)	4459 (8)	2280 (2)	370 (13)
C(15)	−527 (8)	3216 (8)	2555 (2)	377 (13)
C(16)	258 (8)	2230 (7)	2612 (2)	344 (12)
C(19)	2098 (8)	1276 (8)	2512 (2)	367 (13)
C(20)	3313 (8)	949 (8)	2342 (2)	383 (13)

Table 2 (*cont.*)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	−3398 (6)	4971 (7)	2667 (1)	495 (27)	586 (29)	542 (27)	362 (25)	29 (22)	28 (22)
O(2)	−179 (7)	4858 (9)	3253 (1)	387 (30)	1058 (47)	463 (29)	173 (30)	−38 (23)	−197 (29)
O(3)	−3020 (7)	3190 (8)	3325 (1)	438 (28)	812 (38)	452 (28)	227 (27)	51 (22)	−24 (26)
O(4)	−4053 (10)	−954 (12)	3505 (2)	901 (49)	1456 (68)	600 (36)	833 (50)	40 (34)	−55 (39)
O(5)	−1851 (7)	−973 (7)	3780 (1)	639 (31)	710 (33)	500 (28)	409 (28)	28 (24)	−44 (24)
O(6)	4587 (6)	6038 (6)	2365 (1)	448 (25)	482 (25)	484 (25)	268 (22)	−47 (20)	−41 (20)
O(7)	3297 (8)	7102 (11)	2924 (2)	559 (34)	1202 (59)	768 (40)	360 (37)	39 (30)	−293 (41)
C(17)	−140 (8)	911 (8)	2905 (2)	410 (31)	410 (30)	264 (30)	210 (26)	19 (24)	19 (25)
C(18)	1338 (9)	486 (9)	2862 (2)	436 (36)	454 (35)	472 (35)	223 (30)	28 (28)	117 (28)
C(21)	5859 (10)	−88 (10)	1995 (2)	596 (42)	511 (40)	632 (43)	395 (35)	−106 (34)	−96 (34)
C(22)	7324 (11)	2235 (11)	1325 (2)	607 (46)	752 (51)	544 (43)	430 (43)	2 (37)	−11 (38)
C(23)	8526 (13)	3487 (14)	1146 (2)	713 (56)	852 (65)	628 (54)	433 (53)	153 (45)	107 (48)
C(24)	6244 (11)	7175 (11)	688 (2)	629 (47)	695 (48)	478 (40)	252 (40)	131 (35)	151 (36)
C(25)	3669 (10)	8652 (10)	822 (2)	601 (45)	570 (44)	509 (39)	284 (38)	100 (34)	163 (34)
C(26)	2084 (14)	7674 (14)	583 (2)	937 (66)	873 (66)	536 (45)	432 (55)	−147 (44)	110 (44)
C(27)	−1042 (9)	7726 (9)	1882 (2)	512 (37)	515 (37)	506 (38)	300 (31)	−52 (29)	17 (30)
C(28)	−2293 (8)	4626 (8)	2568 (2)	361 (31)	454 (34)	392 (33)	238 (28)	−52 (26)	−21 (27)
C(29)	−1974 (8)	3248 (8)	2763 (2)	341 (31)	449 (34)	400 (31)	217 (28)	−9 (26)	−3 (27)
C(30)	−1949 (9)	−722 (9)	2873 (2)	431 (34)	379 (32)	392 (34)	129 (28)	20 (28)	47 (27)
C(31)	−2376 (10)	−1928 (9)	3188 (2)	584 (41)	435 (37)	474 (40)	232 (33)	177 (32)	90 (30)
C(32)	2693 (11)	1289 (15)	3154 (2)	507 (42)	1334 (86)	454 (40)	525 (51)	30 (33)	243 (46)
C(33)	−1571 (9)	3859 (9)	3138 (2)	426 (38)	430 (36)	425 (35)	235 (32)	−2 (30)	26 (28)
C(34)	−2933 (13)	3808 (15)	3676 (2)	776 (57)	1099 (73)	420 (42)	462 (54)	26 (39)	21 (42)
C(35)	−2866 (10)	−1241 (10)	3505 (2)	482 (40)	535 (42)	545 (43)	237 (34)	132 (34)	150 (34)
C(36)	−2241 (13)	−319 (13)	4100 (2)	865 (60)	843 (60)	615 (47)	542 (52)	9 (44)	−116 (43)
C(37)	−939 (14)	−1 (14)	4365 (3)	775 (61)	764 (57)	769 (57)	386 (51)	−131 (47)	−195 (46)

Normal probability plot

Abrahams & Keve (1971) have drawn attention to the usefulness of the normal probability plot for this kind of problem. Any two sets of measured or derived quantities can be analysed with respect to their errors by plotting the weighted differences between corresponding pairs

$$\delta m_i = \frac{p_i(1) - p_i(2)}{\{\sigma^2[p_i(1)] + \sigma^2[p_i(2)]\}^{1/2}}$$

against their statistically expected values. The points of such a plot are scattered about a straight line with zero intercept and unit slope provided $p_i(1)$ and $p_i(2)$ contain only random errors and their standard deviations $\sigma[p_i(1)]$ and $\sigma[p_i(2)]$ have been estimated correctly.

To make our positional coordinates comparable

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30950 (16 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

with those of CSS, they have to be transformed as follows: $x'=x-\frac{1}{3}$, $y'=y-\frac{2}{3}$, $z'=z-\Delta z$.

The origin along **c** was defined in both analyses by fixing the z coordinate of the Mg atom (which was thus assigned zero standard deviation). With $\Delta z=z(\mathrm{Mg})-z^{\mathrm{CSS}}(\mathrm{Mg})=-0{\cdot}3587$ the normal probability plot of the z coordinates has unit slope but an intercept of about 0·8. We therefore redetermined Δz by minimizing the expression

$$\sum_i \frac{(z_i-z_i^{\mathrm{CSS}}+\Delta z)^2}{\sigma^2[z_i]+\sigma^2[z_i^{\mathrm{CSS}}]}$$

with all atoms except Mg included in the summation to obtain $\Delta z=-0{\cdot}35895$. The corresponding normal probability plot for all positional coordinates [except z(Mg)] has unit slope and zero intercept [Fig. 2(*a*)].

A normal probability plot for 179 vibrational parameters is shown in Fig. 2(*b*). In our refinement, the temperature factors of 23 atoms were taken as spherical, whereas CSS used anisotropic temperature factors for all non-hydrogen atoms. To make the results comparable, the CSS vibration tensors for these 23 atoms were contracted into scalars. There is evidently a systematic difference between the two sets of vibrational parameters since the plot does not pass through the origin. Our vibrational parameters are systematically smaller (by the order of half a standard deviation) than those of CSS. The difference might be attributable to a number of possible causes: different weighting schemes, neglect of absorption correction for our data, overcompensation for absorption errors in the CSS data, a genuine difference in temperature factors depending on choice of crystal specimen and experimental conditions *etc.*, and it is almost impossible to decide between them. In any case, the difference is rather small and disappears when an isotropic increment $\Delta U=0{\cdot}004$ Å^2 is applied to our vibrational parameters.

There is a problem concerning the arbitrary choice of origin along **c**. If the origin is chosen by fixing the z coordinate of the Mg atom (as was done in both analyses) then there appears to be a systematic difference between the z coordinates of the light atoms relative to the fixed coordinate.

We mentioned above that a normal probability plot of the z coordinates has intercept 0·8 for $\Delta z=z(\mathrm{Mg})-z^{\mathrm{CSS}}(\mathrm{Mg})=-0{\cdot}3587$ and intercept zero for $\Delta z=-0{\cdot}35895$. The value of $\Delta\Delta z$ is $2{\cdot}5\times10^{-4}$ (corresponding to a shift of about 0·01 Å) and has standard deviation $\sigma(\Delta\Delta z)\sim3{\cdot}8\times10^{-5}$. We might conclude that the two analyses show a highly significant difference between the relative position of the Mg atom with respect to the rest of the molecule. However, the origin could have been chosen in other ways. In particular, it could have been chosen by fixing the mean z coordinate of some group of atoms, say, the atoms of the organic moiety. The value of $\sigma[z(\mathrm{Mg})]$ that would have been obtained can be estimated to lie in the range 7×10^{-5} $\{$corresponding to $\sigma[x(\mathrm{Mg})]\sim\sigma[y(\mathrm{Mg})]\sim0{\cdot}0027$ Å$\}$ to 10^{-4} $\{$half $\sigma[z(\mathrm{C})]\}$ *i.e.* two to three times larger than

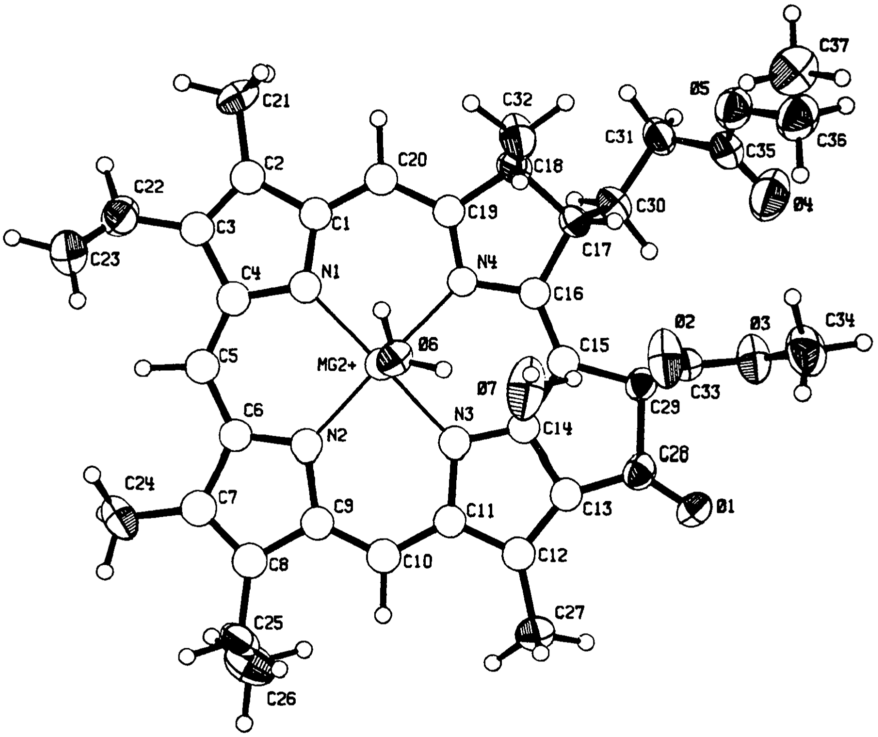

Fig. 1. Ethylchlorophyllide A dihydrate structure, showing atom numbering.

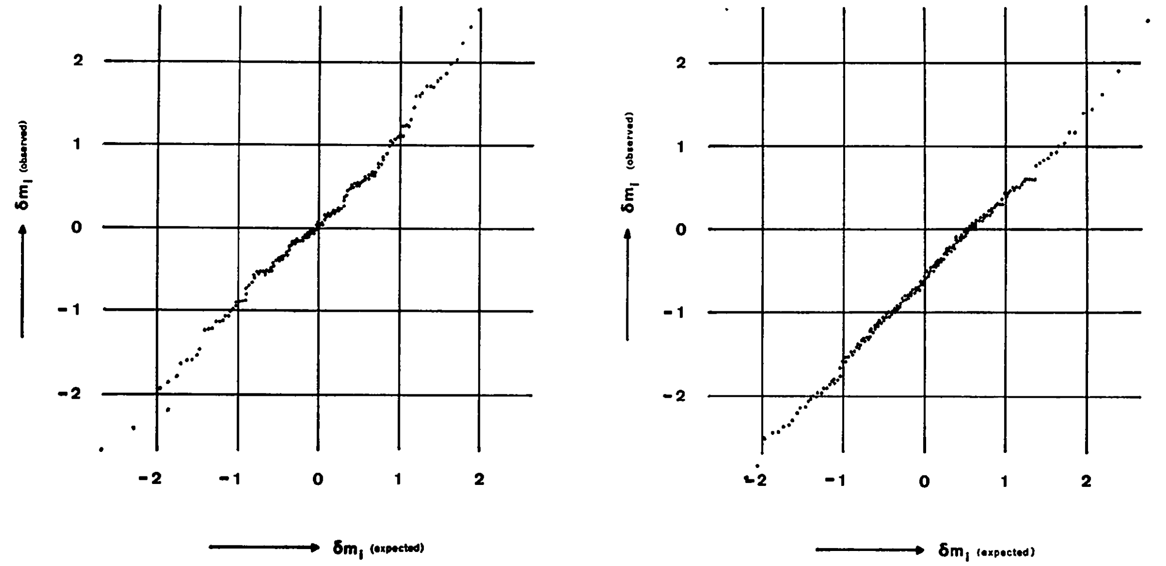

Fig. 2. Normal probability plots (*a*) of δm_i from 146 positional coordinates, (*b*) of δm_i from 179 vibrational parameters.

$\sigma(\Delta\Delta z)$. Waser (1974) has shown that apparent discrepancies of this kind arise by neglect of covariance terms. The value of $\sigma(\Delta\Delta z) \sim 3{\cdot}8 \times 10^{-5}$ is too low because the covariance terms ignored in our discussion are larger when the origin is fixed at a single atom than when it is fixed at the centroid of a group of atoms. Covariance terms do not affect comparison of individual parameters but they have to be taken into account when comparing quantities that depend on more than one parameter. This should be borne in mind in the interpretation of normal probability plots.

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References

Abrahams, S. C. & Keve, E. T. (1971). *Acta Cryst.* A**27**, 157–165.

Chow, H. C., Serlin, R. S. & Strouse, C. E. (1975). *J. Amer. Chem. Soc.* In the press.

Strouse, C. E. (1974). *Proc. Nat. Acad. Sci. U.S.* **71**, 325–328.

Waser, J. (1974). *Acta Cryst.* A**30**, 261–264.

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Die Kristallstrukturen zweier Addukte des Hexamethylentetramins mit Jod

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Hexamethylenetetramine-1-diiodine $C_6H_{12}N_4.I_2$ crystallizes in the space group $Cmc2_1$, $Z=4$ with the unit-cell parameters $a=9{\cdot}307$ (2), $b=7{\cdot}603$ (2), $c=15{\cdot}577$ (3) Å. Hexamethylenetetramine-2-diiodine $C_6H_{12}N_4.2I_2$ crystallizes in the space group $P2_1/c$, $Z=4$ with the unit-cell parameters $a=6{\cdot}097$ (2), $b=16{\cdot}754$ (3), $c=14{\cdot}771$ (3) Å, $\beta=91{\cdot}91$ (2)°. The two crystal structures were determined from three-dimensional diffractometer data and refined to conventional R values of 0·034 and 0·053 respectively. Both compounds belong to the class of n–σ^* donor–acceptor complexes and show the structural features of this group.

Einleitung

In den bisher bekannten Strukturen von Donor–Akzeptor Komplexen des Jods mit Aminen (Hassel, Rømming & Tufte, 1961; Strømme, 1959) wurden kurze Stickstoff–Jod Abstände (2,27; 2,31 Å) gefunden. Im Stickstofftrijodid-1-Dijod-1-Hexamethylentetramin (Pritzkow, 1974) bildet sich zwischen dem Jodmolekül