

The Crystal Structure of Diglycine Sulphate Monohydrate

BY F. H. CANO AND S. MARTÍNEZ-CARRERA

Instituto de Química-Física 'Rocasolano', CSIC, Serrano 119, Madrid-6, Spain

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$\text{SO}_4(\text{NH}_3\text{-CH}_2\text{-COOH})_2 \cdot \text{H}_2\text{O}$. Monoclinic, $P2_1/c$, $a=9.717$ (1), $b=8.481$ (1), $c=13.474$ (2) Å. $\beta=105^\circ 13$ (2)'. $Z=4$. $D_o=1.63$, $D_x=1.582$ g cm⁻³. $\mu(\text{Mo K}\alpha)=3.30$. Colourless prisms of rhombic basis. No evidence for zwitterions has been detected. Quasitetrahedral water and SO_4^{2-} ions are present.

Experimental

The present study was suggested by Dr E. Domínguez (Itto. Torres-Quevedo, CSIC). The cell dimensions were adjusted by least-squares fit from the diffractometer settings of 12 reflexions and their Friedel pairs. 2330 independent reflexions were recorded between 2 and 27° in θ on a PW-1100 diffractometer with graphite monochromator. Bisecting geometry was used for the scans, which were performed in the $\omega/2\theta$ mode at $0.016^\circ \text{ s}^{-1}$ in ω with a constant width of 1.4° . Backgrounds were measured on both sides, fixed settings, during half the scan time. There was no appreciable change in the monitored standard reflexions. Lorentz and polarization corrections were applied but no absorption correction was made. The e.s.d. was calculated as $\sigma^2(I) = \sigma^2_{\text{counts}}(I) + (0.04I)^2$. 307 data were declared unobserved as $F_o < 4\sigma(F_o)$.

The structure was solved by direct methods with the *MULTAN* program (Main, Woolfson & Germain, 1971). The set of phases with highest figure of merit (Germain, Main & Woolfson, 1970, 1971) gave the molecular configuration. Neutral atomic scattering factors were used (*International Tables for X-ray Crystallography*, 1962) and no anomalous scattering correction was applied. The structure was refined by full-matrix least-squares calculations with the X-RAY System (Stewart, Kundell & Baldwin, 1970), to an R value of 0.06. The H atoms were located from a difference synthesis and refined with their thermal parameters kept fixed and equal to the bonded atoms. The weighting scheme was analysed to give a ΔF distribution independent of either F_o or $\sin \theta/\lambda$. In the final cycle the maximum shift/error was 0.9. After an extinction correction ($g=0.7036 \cdot 10^{-5}$) the R value was 0.027 and $R_w=0.025$ for the observed data. Table 1(a) and (b) gives the positional and thermal parameters respectively. Table 2 gives the interatomic distances and bond angles.*

* The table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30458 (11pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion

The mean dimensions of the SO_4^{2-} ion ($1.477, 2.412$ Å; $109.46, 35.27, 60.00^\circ$) indicate a rather symmetric tetrahedron. The two glycine molecules compare quite well with maximum discrepancies of 2.3° [O(1)-O(2)-N] and 0.04 Å [N-O(2)]. The distances from the nitrogen atoms to the least-squares planes through the rest of the atoms are 0.227 and 0.148 Å; with the nitrogen atoms included in the calculations the distances are reduced to 0.068 and 0.044 Å, showing that glycine(II) is more planar than glycine(I) (Fig. 1); the nitrogen atoms deviating significantly from the O(1)O(2)C(1)C(2) planes. The bond lengths involving the hydrogen atoms show the expected short-

Table 1. *Final positional and thermal parameters*

(a) Final positional parameters given as fractional coordinates ($\times 10^5$). The least-squares e.s.d.'s are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
S	20878 (3)	24105 (3)	3921 (2)
O(1)	31934 (9)	36549 (11)	6985 (7)
O(2)	16845 (10)	19008 (11)	13310 (7)
O(3)	8024 (10)	30879 (12)	-3362 (7)
O(4)	26351 (11)	10792 (12)	-729 (8)
O(1GI)	34439 (10)	70176 (11)	21125 (7)
O(2GI)	18193 (9)	54323 (11)	24889 (8)
C(1GI)	30378 (12)	57213 (13)	24939 (9)
C(2GI)	42671 (12)	46411 (14)	29662 (9)
N(GI)	36875 (12)	31284 (13)	32185 (8)
O(1GII)	44585 (10)	79614 (12)	47167 (8)
O(2GII)	33925 (9)	98283 (11)	35925 (7)
C(1GII)	33502 (11)	87645 (14)	41772 (9)
C(2GII)	19817 (12)	81654 (15)	43657 (9)
N(GII)	7406 (10)	89610 (14)	36653 (9)
O(W)	11982 (10)	87944 (11)	16221 (7)
H(1W)	5041 (257)	83517 (278)	11614 (178)
H(2W)	13351 (230)	97500 (294)	14390 (169)
H(1GI)	27396 (255)	76553 (268)	19018 (180)
H(2GI)	48092 (217)	50901 (256)	35661 (172)
H(3GI)	48424 (219)	44842 (239)	25047 (173)
H(4GI)	31115 (236)	26630 (253)	26490 (176)
H(5GI)	32194 (233)	32608 (255)	36951 (171)
H(6GI)	43903 (245)	24443 (268)	34626 (164)
H(1GII)	51758 (259)	82412 (293)	45415 (177)
H(2GII)	19808 (213)	84139 (257)	50503 (173)
H(3GII)	18875 (216)	70642 (286)	42366 (162)
H(4GII)	8306 (210)	89538 (261)	30336 (191)
H(5GII)	7243 (210)	99435 (301)	38824 (169)
H(6GII)	-501 (252)	84440 (254)	36648 (159)

Table 1 (cont.)

(b) Final thermal parameters ($\times 10^6$) as defined in the expression $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + \dots + 2U_{23}klb^*c^*)]$. In parentheses the least-squares e.s.d.'s affecting the last digits are given. B_{iso} refers to the Hamilton isotropic temperature factor equivalent to the anisotropic values.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{iso}
S	1672 (12)	2077 (14)	1737 (12)	-127 (10)	566 (8)	16 (10)	1.60 (10)
O(1)	2029 (38)	3148 (44)	3397 (45)	-729 (34)	955 (33)	-532 (36)	2.52 (18)
O(2)	3389 (44)	2761 (40)	2455 (40)	-196 (35)	1429 (33)	291 (33)	2.61 (26)
O(3)	2352 (40)	3564 (46)	3369 (46)	-265 (37)	-310 (34)	904 (39)	2.52 (31)
O(4)	4514 (53)	2980 (47)	3843 (52)	126 (41)	2269 (44)	-808 (38)	3.51 (39)
O(1GI)	2702 (40)	2220 (41)	3946 (49)	-72 (35)	1037 (36)	324 (35)	2.63 (20)
O(2GI)	2127 (40)	3206 (47)	4697 (55)	40 (35)	974 (36)	738 (41)	2.93 (19)
C(1GI)	2379 (49)	2126 (50)	2113 (48)	-143 (41)	593 (40)	-298 (41)	1.93 (13)
C(2GI)	2145 (49)	2517 (55)	2454 (56)	-67 (42)	505 (44)	-130 (44)	2.05 (12)
N(GI)	2809 (47)	2378 (47)	2491 (49)	392 (43)	791 (43)	394 (40)	2.25 (16)
O(1GII)	1807 (37)	4441 (54)	3725 (46)	435 (36)	722 (34)	1285 (41)	2.85 (15)
O(2GII)	2415 (40)	2909 (43)	2949 (43)	-192 (33)	908 (32)	297 (35)	2.43 (18)
C(1GII)	2006 (49)	2523 (54)	2125 (49)	30 (41)	647 (39)	-425 (41)	1.94 (14)
C(2GII)	2037 (47)	2745 (58)	2737 (58)	80 (43)	757 (42)	298 (46)	2.20 (16)
N(GII)	1629 (43)	3167 (56)	2849 (53)	30 (39)	753 (36)	154 (42)	2.22 (16)
O(W)	3004 (44)	2269 (44)	2650 (43)	-247 (35)	48 (35)	213 (34)	2.21 (14)

For the hydrogen atoms the parameters are those of the bonded atom.

Table 2. Lengths (Å) and angles (°) with e.s.d.'s in parentheses

(a) The sulphate ion

S—O(1)	1.482 (1)	S—O(2)	1.487 (1)
S—O(3)	1.479 (1)	S—O(4)	1.460 (1)
O(1)—O(2)	2.402 (1)	O(1)—O(3)	2.411 (1)
O(1)—O(4)	2.417 (1)	O(2)—O(3)	2.397 (1)
O(2)—O(4)	2.422 (2)	O(3)—O(4)	2.420 (1)
O(1)—S—O(2)	107.98 (5)	O(1)—S—O(3)	109.00 (5)
O(1)—S—O(4)	110.44 (6)	O(2)—S—O(3)	107.89 (6)
O(2)—S—O(4)	110.57 (6)	O(3)—S—O(4)	110.87 (6)
O(1)—O(2)—S	35.95 (3)	O(1)—O(3)—S	35.55 (3)
O(1)—O(4)—S	35.08 (3)	O(2)—O(3)—S	36.17 (4)
O(2)—O(4)—S	35.08 (4)	O(3)—O(4)—S	34.82 (3)
S—O(1)—O(2)	36.07 (3)	S—O(1)—O(3)	35.45 (3)
S—O(1)—O(4)	34.48 (4)	S—O(2)—O(3)	35.94 (3)
S—O(2)—O(4)	34.35 (3)	S—O(3)—O(4)	34.31 (4)
O(1)—O(2)—O(3)	60.31 (4)	O(3)—O(1)—O(2)	59.76 (4)
O(2)—O(3)—O(1)	59.94 (4)	O(1)—O(2)—O(4)	60.13 (4)
O(4)—O(1)—O(2)	60.36 (4)	O(2)—O(4)—O(1)	59.52 (4)
O(2)—O(3)—O(4)	60.37 (4)	O(4)—O(2)—O(3)	60.28 (4)
O(3)—O(4)—O(2)	59.35 (4)	O(1)—O(3)—O(4)	60.04 (4)
O(4)—O(1)—O(3)	60.17 (4)	O(3)—O(4)—O(1)	59.79 (4)

(b) The glycine molecules

	Glycine (I)	Glycine (II)	$d/\sigma \leq$
O(1)—O(2)	2.234 (1)	2.241 (1)	7
O(1)—C(1)	1.319 (2)	1.314 (1)	2.5
O(1)—C(2)	2.350 (1)	2.330 (2)	10
O(1)—N	3.601 (1)	3.605 (1)	4
O(2)—C(1)	1.207 (2)	1.206 (2)	0.5
O(2)—C(2)	2.385 (1)	2.394 (2)	4.5
O(2)—N	2.666 (1)	2.707 (1)	41
C(1)—C(2)	1.503 (2)	1.508 (2)	2.5
C(1)—N	2.419 (2)	2.446 (1)	14
C(2)—N	1.477 (2)	1.477 (1)	0.1
O(1)—O(2)—C(1)	29.16 (6)	28.51 (6)	11
O(1)—O(2)—C(2)	61.07 (4)	60.25 (4)	20
O(1)—O(2)—N	94.15 (5)	93.05 (5)	22
O(1)—C(1)—C(2)	112.69 (10)	111.08 (10)	32
O(1)—C(1)—N	147.38 (9)	145.31 (9)	21
O(1)—C(2)—N	139.19 (8)	141.51 (10)	23
O(2)—C(1)—C(2)	122.96 (11)	123.39 (10)	4.3
O(2)—C(1)—N	88.03 (8)	88.95 (7)	14
O(2)—C(2)—N	83.79 (7)	85.27 (8)	18

Table 2 (cont.)

C(1)—C(2)—N	108.54 (9)	110.04 (7)	15
C(1)—O(1)—O(2)	26.50 (6)	25.97 (6)	9
C(2)—O(1)—O(2)	62.64 (4)	63.13 (5)	10
C(2)—O(1)—O(3)	36.14 (6)	37.16 (4)	17
C(2)—O(2)—C(1)	31.91 (7)	31.74 (6)	2
N—O(2)—C(1)	65.06 (7)	64.61 (7)	6.5
N—O(2)—C(2)	33.43 (6)	32.94 (4)	8
N—C(1)—C(2)	35.38 (6)	34.56 (6)	13.5
O(2)—C(1)—O(1)	124.34 (11)	125.52 (11)	10.5
O(2)—C(2)—O(1)	56.30 (4)	56.62 (4)	8
C(1)—C(2)—O(1)	31.17 (6)	31.75 (5)	10
C(1)—C(2)—O(2)	25.13 (6)	24.87 (5)	4.5
C(1)—N—O(2)	26.91 (4)	26.44 (4)	12
C(2)—N—O(2)	62.79 (6)	61.79 (7)	14.5
C(2)—N—C(1)	36.08 (6)	35.40 (4)	11.5

ening in comparison with neutron diffraction studies (Jönsson & Kvik, 1972). They form nearly perfect tetrahedra with mean angular values of 109.65 and 109.35° in the CH₂ groups and 109.44 and 109.47° in the NH₃⁺ groups. No oscillatory correction has been made but it has been estimated to be about 1.5 to 2σ, without taking into account errors in the scattering factors and the few data used. This means a possible bias of up to 6σ.

The distortions in the SO₄²⁻ ion from $\bar{3}$ symmetry could be due to the neglect of thermal corrections and to the different H-bonding. The carboxylic features of the glycine molecules are defined by the differences in the C—O lengths and in the angles around C(1) (*Molecular Structures and Dimensions*, 1972). The distortions that push the nitrogen atoms out of the carboxylic planes are small enough to exclude effects other than packing being involved. Moreover the H-bond distribution on the oxygen atoms tends to stabilize the carboxylic structure. Thus we think that the difference in the C—O length is more significant than the nitrogen-plane separation as a test of the zwitterion character. From other studies (Marsh,

1958; Koch & Germain, 1970; Almlöf, Kvik & Thomas, 1973; Destrada, Forel & Garrigan-Lagrange, 1973; Mohana & Viswamitra, 1972; and references therein) it seems that the NH₃⁺ group is formed if there is something capable of donating a proton, and the remaining H atoms subsequently fill the convenient chemical sites. The NH₃⁺ and CH₂ groups form a staggered configuration with minimal overlapping. The water molecule is engaged in a tetrahedral hydrogen-

bond system with two donor triangles of the normal type (Donohue, 1968). The carboxylic oxygen atoms are involved in only two doubtful bifurcated H-bond systems.

There is no doubt about the H-bond systems around the nitrogen atoms, apart from H(6GI) and H(6GII), which again distinguish both glycines. H(6GII) has three neighbours O(2)XI, O(3)XI and O(2GI)XI, the first giving the best geometry; thus we think that there

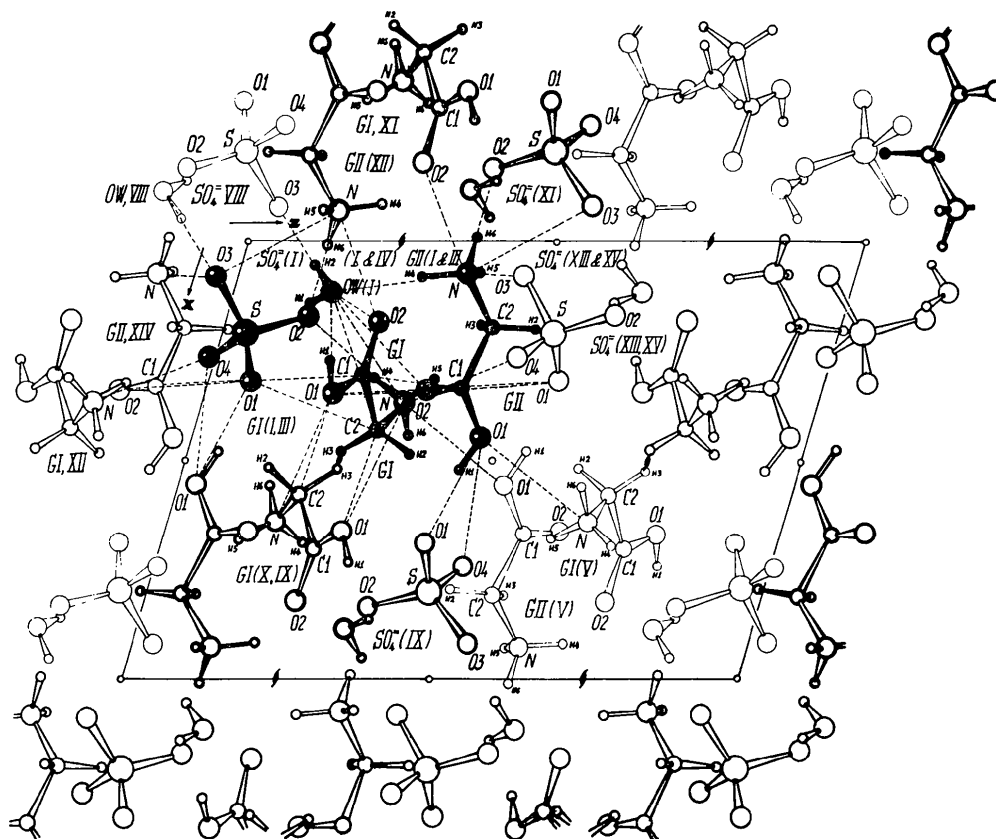


Fig. 1. (010) projection.

Table 3. Hydrogen bonds, short X-H---Y van der Waals contacts and group features (X_a, Y_a are the atoms bonded to X and Y respectively: distances are in Å and angles in degrees, with the e.s.d. from least squares in parentheses)

Distances							
X _a	X	H	Y	Y _a	X···Y	X-H	H···Y
-	O(W)	H(2W)	O(2I)	SI	2.724 (1)	0.868 (25)	1.868 (25)
-	O(W)	H(1W)	O(3)VIII	SVIII	2.738 (1)	0.868 (21)	1.890 (22)
C(1GI)	O(1GI)	H(1GI)	O(W)	-	2.586 (1)	0.858 (23)	1.735 (24)
C(1GII)	O(1GII)	H(1GII)	O(1)IX	SIX	2.561 (1)	0.829 (27)	1.737 (27)
C(2GI)	N(GI)	H(4GI)	O(2)	S	2.941 (1)	0.908 (21)	2.038 (20)
C(2GI)	N(GI)	H(5GI)	O(4)XV	SXV	2.842 (1)	0.889 (26)	1.976 (25)
C(2GI)	N(GI)	H(6GI)	O(2GII)III	C(1GII)III	2.672 (2)	0.888(22)	2.447 (23)
C(2GI)	N(GI)	H(6GI)	O(1GII)V	C(1GII)V	3.019 (1)	0.888 (22)	2.428 (20)
C(2GI)	N(GI)	H(6GI)	O(1GI)X	C(1GI)X	3.087 (1)	0.888 (22)	2.459 (26)
C(2GII)	N(GII)	H(4GII)	O(W)	-	2.909 (2)	0.879 (27)	2.033 (27)
C(2GII)	N(GII)	H(5GII)	O(3)XIII	SXIII	2.834 (1)	0.885 (25)	1.964 (25)
C(2GII)	N(GII)	H(6GII)	O(2)XI	SXI	2.935 (1)	0.884 (24)	2.054 (24)
C(2GII)	N(GII)	H(6GII)	O(3)XI	SXI	3.114 (2)	0.884 (24)	2.568 (24)
C(2GII)	N(GII)	H(6GII)	O(2GI)XI	C(1GI)XI	2.839 (1)	0.884 (24)	2.600 (21)

Table 3 (cont.)

Angles X-H...Y	H-X...Y	X...Y...H	YXX _a	HXX _a	XYY _a	HYY _a	Torsion angles			
							X _a XY XHY	XHY X _a XH	XYX _a XHY	XHY XYX _a
168.23 (221)	8.04 (151)	3.73 (71)	—	—	120.00 (5)	116.47 (76)	—	—	19.57	18.90
165.30 (219)	10.09 (152)	4.62 (68)	—	—	121.31 (6)	116.78 (69)	—	—	11.58	11.08
170.63 (264)	6.28 (171)	3.10 (86)	105.33 (8)	110.99 (171)	—	—	26.74	27.71	—	—
172.28 (230)	5.23 (155)	2.49 (75)	113.89 (8)	108.67 (157)	113.38 (6)	115.67 (80)	2.80	2.70	23.44	23.90
172.38 (195)	5.28 (135)	2.35 (60)	108.21 (7)	111.66 (148)	111.55 (5)	112.02 (72)	48.54	49.96	78.14	79.07
164.32 (191)	10.83 (132)	4.85 (62)	102.98 (8)	111.00 (140)	114.71 (6)	111.28 (64)	42.14	44.43	46.61	45.10
109.82 (176)	53.28 (151)	16.92 (52)	161.64 (9)	110.46 (156)	150.07 (8)	144.08 (48)	30.21	9.74	82.39	57.48
124.29 (191)	41.64 (147)	14.07 (57)	107.97 (6)	110.46 (156)	149.60 (9)	135.69 (59)	79.69	85.23	9.69	7.00
128.10 (198)	38.81 (163)	13.09 (50)	79.41 (7)	110.46 (156)	133.50 (8)	128.17 (53)	36.86	39.00	71.35	60.95
174.54 (189)	3.18 (132)	1.65 (57)	105.91 (8)	109.67 (130)	—	—	6.71	6.86	—	—
167.48 (210)	8.64 (145)	3.28 (64)	101.06 (7)	107.70 (121)	124.27 (6)	126.05 (56)	38.43	39.84	2.55	2.30
170.26 (209)	6.82 (145)	2.92 (64)	104.09 (8)	109.40 (132)	103.05 (5)	101.51 (64)	35.51	36.77	65.59	62.11
120.78 (213)	45.08 (138)	14.12 (47)	84.23 (8)	109.40 (132)	95.65 (5)	81.62 (48)	55.10	59.89	6.28	6.32
96.43 (148)	65.54 (133)	18.03 (54)	172.95 (9)	109.40 (132)	143.53 (9)	128.53 (58)	45.22	5.29	39.64	28.99

is no so-called bifurcated bonding but merely a single H bond. H(6GI) has another three neighbours, O(2GI)III, O(1GI)V and O(1GI)X, with similar geometry, and it seems that there are no H bonds but only weak electrostatic interactions. In Table 3 one should note the X-H...Y angular values, all around 165° (Hamilton, 1968).

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References

- ALMLÖF, J., KVICK, Å. & THOMAS, J. O. (1973). 1st European Crystallographic Meeting, Group B3. Bordeaux.
- DESTRADA, C., FOREL, M. & GARRIGAN-LAGRANGE, C. (1973). 1st European Crystallographic Meeting, Group B6. Bordeaux.
- DONOHUE, J. (1968). *Structural Chemistry and Molecular Biology*, edited by A. RICH & N. DAVIDSON, pp. 443–465. San Francisco: Freeman.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* **B26**, 274–285.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- HAMILTON, W. C. (1968). *Structural Chemistry and Molecular Biology*, edited by A. RICH & N. DAVIDSON, pp. 466–483. San Francisco: Freeman.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- JÖNSSON, P. G. & KVICK, Å. (1972). *Acta Cryst.* **B28**, 1827–1833.
- KOCH, M. H. J. & GERMAIN, G. (1970). *Acta Cryst.* **B26**, 410–417.
- MAIN, P., WOOLFSON, M. M. & GERMAIN, G. (1971). *MULTAN: A Computer Program for the Automatic Solution of Crystal Structures*. Univ. of York. (Not published.)
- MARSH, R. E. (1958). *Acta Cryst.* **11**, 654–663.
- MOHANA RAO, J. K. & VISWAMITRA, M. A. (1972). *Acta Cryst.* **B28**, 1484–1496.
- Molecular Structures and Dimensions* (1972). Vol. A1, edited by O. KENNARD *et al.* Univ. Chem. Lab. Crystal Data Centre, Cambridge, England.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). *The X-RAY System*. Computer Science Center, Univ. of Maryland, U.S.A.