

Neutron Diffraction Structure Determination of Bis-(L-histidinato)cadmium Dihydrate

By H. FUESS* AND H. BARTUNIK†

Institut Laue-Langevin, 56X Centre de Tri, F-38042 Grenoble Cédex, France

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A neutron diffraction study of tetragonal bis-(L-histidinato)cadmium dihydrate $\text{Cd}(\text{C}_6\text{H}_8\text{N}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ has been carried out in order to prepare a basis for a methodical study of anomalous phase determination. The structure belongs to space group $P4_32_12$, with $a=b=7.397$ (5), $c=30.53$ (3) Å, $Z=4$. 1027 reflexions measured at $\lambda=1.216$ Å were used in the least-squares refinement including several Bijvoet pairs. The final $R(F^2)=0.069$. The positions of the non-H atoms are in general agreement with a previous X-ray study. Cd is octahedrally surrounded by two amide N atoms at 2.287 (9), two N of two imidazole groups at 2.290 (8), and two carboxyl O at 2.480 (9) Å. The histidine group adopts a closed conformation with the imidazole ring folded back on top of the carboxylate group.

Introduction

Neutron diffraction studies of various histidine compounds have been published: L-histidine (Lehmann, Koetzle & Hamilton, 1972) and L-histidine hydrochloride monohydrate (Fuess, Hohlwein & Mason, 1977). The X-ray structure determinations of several metal-histidine complexes have been reported: Zn L-histidine dihydrate (Kretsinger, Cotton & Bryan, 1963); Zn L-histidine pentahydrate (Harding & Cole, 1963); Ni L-histidine monohydrate (Fraser & Harding, 1967); Co L-histidine monohydrate (Harding & Long,

1968) and Co DL-histidine dihydrate (Candlin & Harding, 1970). We have undertaken a neutron study of Cd L-histidine in order to (1) compare the conformation of histidine in Cd L-histidine to its conformation in other structures, (2) provide a basis for a methodical study of anomalous-dispersion techniques for phase determination with thermal and hot neutrons (Bartunik & Fuess, 1975).

A determination of Cd L-histidine based on two-dimensional X-ray data with a final R of 13.4% has been reported by Candlin & Harding (1967).

Experimental

The crystals were prepared by adding CdCO_3 to a solution (0.4 mmol) of L-histidine in boiling water. Large colourless crystals were obtained. The composition

* Present address: Institut für Kristallographie der Universität, D-6000 Frankfurt/Main, Germany.

† Also at Technische Universität München, Physikdepartment.

Table 1. Fractional coordinates and temperature parameters

The temperature parameters are given as $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + \dots)]$. The β_{ij} 's are multiplied by 10^3 , the fractional coordinates by 10^4 .

| | <i>x</i> | <i>y</i> | <i>z</i> | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|-------|-----------|-----------|------------|--------------|--------------|--------------|--------------|--------------|--------------|
| Cd | 1989 (14) | 1989 (14) | 0 | 111 (23) | 111 (23) | 5 (1) | 5 (1) | 18 (4) | 18 (4) |
| C(1) | 1716 (4) | 5787 (4) | 487.8 (8) | 103 (6) | 85 (6) | 6 (1) | 7 (6) | 1 (1) | 2 (1) |
| C(2) | 334 (5) | 5808 (4) | 114.8 (7) | 130 (7) | 80 (6) | 5 (1) | 1 (1) | 1 (1) | 8 (1) |
| C(3) | 8506 (5) | 5079 (5) | 287.0 (10) | 100 (7) | 112 (7) | 8 (1) | 27 (6) | 0 (1) | 7 (1) |
| C(4) | 8661 (4) | 3451 (4) | 573.1 (8) | 87 (6) | 114 (6) | 5 (1) | 7 (6) | 6 (1) | 3 (1) |
| C(5) | 9365 (5) | 754 (5) | 789.4 (9) | 117 (7) | 97 (7) | 7 (1) | 9 (6) | 2 (1) | 3 (1) |
| C(6) | 8002 (5) | 3237 (5) | 986.2 (10) | 111 (1) | 158 (8) | 7 (1) | -6 (7) | 10 (1) | 4 (1) |
| N(1) | 4703 (3) | 953 (4) | 256.5 (6) | 150 (5) | 129 (5) | 4 (1) | 3 (5) | 3 (1) | 1 (1) |
| N(2) | 9522 (3) | 1867 (3) | 452.4 (6) | 118 (4) | 97 (4) | 5 (1) | 3 (4) | 4 (1) | 1 (1) |
| N(3) | 8446 (4) | 1527 (4) | 1117.7 (7) | 152 (6) | 153 (5) | 6 (1) | 35 (5) | 8 (1) | 7 (1) |
| O(1) | 2796 (5) | 4480 (5) | 507.1 (10) | 157 (8) | 115 (7) | 6 (1) | 29 (8) | 11 (1) | 2 (1) |
| O(2) | 1650 (6) | 7050 (5) | 757.2 (10) | 175 (9) | 132 (8) | 8 (1) | 21 (8) | 4 (2) | 7 (2) |
| O(3) | 5319 (9) | 7961 (9) | 884 (2) | 263 (15) | 257 (14) | 8 (1) | 76 (13) | 11 (2) | 9 (2) |
| H(1) | 123 (9) | 7211 (8) | 20 (2) | 230 (17) | 113 (13) | 11 (1) | 5 (13) | 4 (3) | 11 (3) |
| H(2) | 7820 (11) | 6130 (11) | 472 (2) | 208 (18) | 188 (18) | 14 (1) | 66 (16) | 11 (3) | -2 (4) |
| H(3) | 7663 (9) | 4794 (10) | 0 (3) | 112 (12) | 234 (18) | 12 (1) | 5 (13) | 8 (3) | 11 (3) |
| H(4) | -82 (11) | -607 (9) | 800 (2) | 240 (19) | 118 (14) | 13 (1) | 9 (16) | 4 (3) | 6 (3) |
| H(5) | 7253 (13) | 4146 (13) | 1187 (2) | 309 (24) | 262 (21) | 12 (1) | 40 (18) | 23 (4) | 8 (4) |
| H(6) | 5294 (12) | 2115 (11) | 381 (2) | 267 (21) | 203 (18) | 10 (1) | 60 (16) | -7 (3) | -17 (3) |
| H(7) | 4746 (11) | 21 (11) | 501 (2) | 265 (20) | 213 (16) | 7 (1) | 37 (17) | -2 (3) | 9 (3) |
| H(8) | 8211 (11) | 958 (11) | 1423 (2) | 242 (18) | 234 (18) | 9 (1) | -43 (18) | 14 (3) | 5 (3) |
| H(9) | 4152 (16) | 7519 (13) | 889 (3) | 279 (24) | 213 (20) | 12 (1) | -43 (21) | -17 (4) | 8 (4) |
| H(10) | 5740 (12) | 8088 (11) | 1181 (2) | 272 (20) | 233 (19) | 10 (1) | -78 (17) | -10 (3) | 5 (3) |

was checked by X-ray fluorescence and microanalysis.

The crystal used for data collection was a plate, $1.3 \times 1.1 \times 0.7$ mm along **a**, **b** and **c**, with a volume of 0.97 mm³. Data were collected on the D8 facility at the high flux reactor at ILL, Grenoble. Neutrons with a wavelength of 1.216 Å from the (200) plane of a Cu monochromator were used. The flux at the sample position was approximately 10^7 n cm⁻² s⁻¹. Integrated intensities were measured in θ - 2θ step scans for 1027 independent reflexions including about 50 Bijvoet pairs.

The data set was corrected for absorption with the program *ABSORB* of the X-RAY system involving a Gaussian-grid method. The neutron absorption coefficient was determined in transmission measurements to be $\mu = 8.2$ (3) cm⁻¹. The transmission coefficients vary between 0.37 and 0.58. The cell dimensions were redetermined from measurements at two wavelengths (1.216 and 0.912 Å).

Structure refinement

The refinement was started with the parameters given by Candlin & Harding (1967). After refinement on the

heavy atoms alone $R(F^2)$ was 0.28. A subsequent Fourier synthesis allowed the location of all the H atoms. The final refinement was by full-matrix least squares with the program *ORXFLS3* (Busing *et al.*, 1971) first with isotropic, then anisotropic temperature factors for all atoms. Neutron scattering lengths were $b_{\text{O}} = 0.5804$, $b_{\text{N}} = 0.937$, $b_{\text{C}} = 0.6648$ and $b_{\text{H}} = -0.3741$ (all in 10^{-12} cm) (Koester, 1975). The real and imaginary part of the scattering length of Cd were calculated from a single-level Breit-Wigner formula. These values for Cd varied little when included in the refinement procedure. We therefore used the calculated values in the final steps of the refinement ($b_{\text{O}} + b' = 0.404$; $b'' = 0.101$). The quantity minimized was $\sum w(F_o^2 - F_c^2)^2$;

Table 3. Bond lengths and angles around cadmium

| | | | |
|---------------|-------------|---------------|-----------|
| Cd-N(1) | 2.287 (9) Å | N(1)-Cd-N(2) | 88.5 (3)° |
| Cd-N(2) | 2.290 (8) | N(1)-Cd-O(1) | 69.0 (3) |
| Cd-O(1) | 2.480 (9) | N(2)-Cd-O(1) | 81.1 (2) |
| N(1)-Cd-N(1') | 134.9 (5)° | N(1)-Cd-N(2') | 118.7 (2) |
| N(2)-Cd-N(2') | 107.5 (4) | N(1)-Cd-O(1') | 79.9 (2) |
| O(1)-Cd-O(1') | 91.8 (3) | N(2)-Cd-O(1') | 168.0 (4) |

Table 2. Intramolecular distances (Å) and angles (°)

| | | | |
|----------------|------------|-----------------|-----------|
| C(1)-O(1) | 1.256 (5) | C(1)-C(2)-C(3) | 109.1 (2) |
| C(1)-O(2) | 1.246 (5) | H(1)-C(2)-N(1) | 111.7 (4) |
| C(1)-C(2) | 1.530 (4) | H(1)-C(2)-C(3) | 107.3 (5) |
| C(2)-N(1) | 1.471 (4) | N(1)-C(2)-C(3) | 109.9 (3) |
| C(2)-C(3) | 1.548 (5) | C(2)-N(1)-H(6) | 107.8 (5) |
| C(3)-C(4) | 1.492 (5) | C(2)-N(1)-H(7) | 109.7 (5) |
| C(4)-N(2) | 1.384 (4) | H(6)-N(1)-H(7) | 106.3 (6) |
| N(2)-C(5) | 1.323 (4) | C(2)-C(3)-C(4) | 114.4 (3) |
| C(5)-N(3) | 1.339 (4) | C(2)-C(3)-H(2) | 109.6 (5) |
| N(3)-C(6) | 1.367 (5) | C(2)-C(3)-H(3) | 107.0 (5) |
| C(6)-C(4) | 1.361 (4) | C(4)-C(3)-H(2) | 108.0 (5) |
| N(1)-H(6) | 1.037 (9) | C(4)-C(3)-H(3) | 110.9 (5) |
| N(1)-H(7) | 1.017 (8) | H(2)-C(3)-H(3) | 106.7 (6) |
| C(2)-H(1) | 1.089 (7) | C(3)-C(4)-N(2) | 124.3 (2) |
| C(3)-H(2) | 1.087 (9) | C(3)-C(4)-C(6) | 127.5 (3) |
| C(3)-H(3) | 1.096 (9) | N(2)-C(4)-C(6) | 108.2 (3) |
| C(5)-H(4) | 1.087 (8) | C(4)-N(2)-C(5) | 106.2 (2) |
| C(6)-H(5) | 1.065 (9) | N(2)-C(5)-N(3) | 111.2 (3) |
| N(3)-H(8) | 1.037 (7) | C(5)-N(3)-C(6) | 107.3 (3) |
| O(3)-H(9) | 0.923 (13) | N(3)-C(6)-C(4) | 107.1 (3) |
| O(3)-H(10) | 0.963 (8) | N(2)-C(5)-H(4) | 124.5 (4) |
| O(1)-C(1)-O(2) | 124.9 (3) | N(3)-C(5)-H(4) | 124.3 (4) |
| O(1)-C(1)-C(2) | 117.9 (3) | C(5)-N(3)-H(8) | 125.8 (5) |
| O(2)-C(1)-C(2) | 117.2 (3) | C(6)-N(3)-H(8) | 126.8 (5) |
| C(1)-C(2)-H(1) | 107.7 (4) | N(3)-C(6)-H(5) | 122.7 (5) |
| C(1)-C(2)-N(1) | 111.1 (3) | C(4)-C(6)-H(5) | 130.3 (5) |
| | | H(9)-O(3)-H(10) | 108.9 (9) |

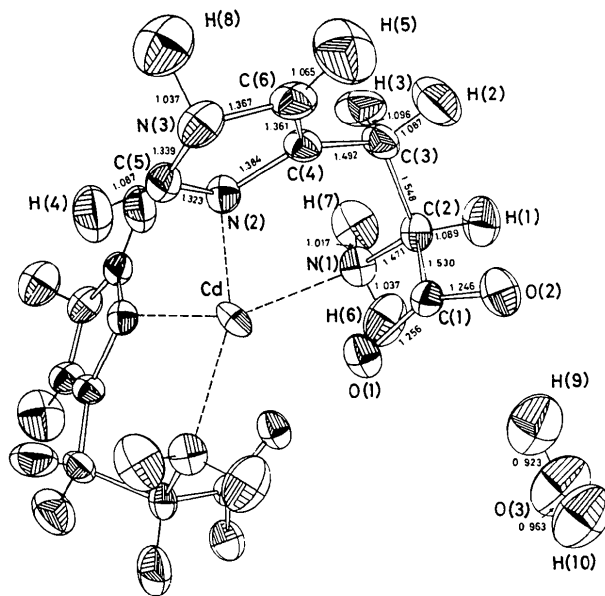


Fig. 1. The molecular structure of bis-(L-histidinato)cadmium dihydrate. Two histidine molecules and their coordination to cadmium are shown.

Table 4. Hydrogen-bond distances (Å) and angles (°)

| A | H | B | C | A...B | H...B | A-H...B | C-B...H |
|------|-------|-------|--------|-----------|------------|-----------|-----------|
| N(1) | H(7) | O(3') | | 2.963 (7) | 1.967 (3) | 165.6 (7) | |
| O(3) | H(9) | O(2) | C(1) | 2.823 (8) | 1.926 (13) | 163.6 (9) | 103.6 (8) |
| O(3) | H(10) | O(2') | C(1') | 2.800 (7) | 1.845 (7) | 170.9 (8) | 125.9 (4) |
| N(3) | H(8) | O(1') | C(1'') | 2.815 (5) | 1.796 (7) | 166.4 (7) | 107.0 (3) |

Positions of primed atoms

| | | | |
|-------|----------------------------|--------|--------------------------|
| O(3') | -0.20381, 0.5319, -0.08841 | O(1') | 0.7796, 0.0520, 0.19929 |
| O(2') | 0.6650, 0.7950, 0.17428 | C(1'') | 0.6716, -0.0787, 0.20122 |
| C(1') | 0.6716, 0.9213, 0.20122 | | |

the weights were $w = 1/\sigma^2(F_o^2)$ with $\sigma^2(F_o^2) = \sigma_c^2(F_o^2) + (0.03F_o^2)^2$, where σ_c is based on counting statistics. In the last stage of the refinement isotropic extinction was introduced. A subsequent run with anisotropic extinction parameters did not give further improvement. The final extinction parameter was $g = 2.7 \times 10^{-4}$. Only two reflexions showed more than 10% extinction. The final $R(F^2) = [\sum(F_o^2 - F_c^2)^2 / \sum F_o^4]^{1/2} = 0.069$; $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w F_o^4]^{1/2} = 0.0665$. The final positional parameters are listed in Table 1 with anisotropic temperature factors.* Bond distances and angles are listed in Table 2.

The molecular geometry

Two histidine molecules are linked by the Cd atom to form the complex. The environment of the metal is formed in a way similar to that in the other metal-histidine complexes by N(1) of the amide group, N(2) of the imidazole ring and one O of the carboxyl group (Fig. 1). The Cd-N distances are considerably shorter than the Cd-O distances (Table 3), while for the Ni and Co compounds the equivalent distances are almost equal. On the other hand, the metal-oxygen distances are even longer in the Zn (Table 6) than in the Cd compound.

The water molecule takes part in the hydrogen-bonding scheme as an acceptor for H(7) of the amide group and as a donor *via* the two H atoms which are linked to O(2) of two different molecules (Table 4). It is doubtful whether the short distance of 2.706 Å between N(1) and O(1) can be described as a hydrogen bridge since the nearest amide H(6) is 2.574 Å from O(1) and the N(1)-H(6)-O(1) angle is 108.4°. The existence of such a hydrogen bond had been postulated

by Kretsinger *et al.* (1963) from their X-ray structure investigation of Zn histidine dihydrate. The H attached to N(3) bonds to O(1) of a neighbouring molecule. The H on N(3) of that second molecule is bonded to O(1) of the first.

The imidazole ring and the carboxyl group are planar (Table 5), and the torsion angle between them shows that the molecule is in the closed form (Kistenmacher, Hunt & Marsh, 1972). N(1), however, sticks out of the plane of the carboxyl group, because of its bond to the Cd atom; H(2) lies in this plane. The conformation of the whole molecule is essentially the same as in other metal-histidine complexes as shown by the torsion angles. The conformation angles of Table 6 show that the Zn histidine investigated by Kretsinger *et al.* (1963) was in fact the D-form. The Co histidine dihydrate has one molecule in the D- and one in the L-form; all the other complexes are L-forms.

Table 5. Atom deviations from the least-squares planes (Å)

| | | | |
|-------|--------|-------|--------|
| C(3) | -0.003 | C(1) | -0.01 |
| C(4) | 0.003 | C(2) | 0.003 |
| C(5) | 0.001 | O(1) | 0.004 |
| C(6) | 0.004 | O(2) | 0.004 |
| N(2) | 0.001 | N(1)* | -0.510 |
| N(3) | 0.005 | | |
| H(8)* | 0.05 | | |
| H(4)* | 0.012 | | |
| H(5)* | -0.005 | | |

* Atom not included in least-squares calculation.

The difference in the metal environment does not result in different torsion angles (Table 6). The open form found in L-histidine (Madden, McGandy & Seemann, 1972) is characterized by the torsion angle C(1)-C(2)-C(3)-C(4) of about 180° as compared to about -40 to -50° in the complexes. The water molecules link two molecules together *via* hydrogen bonds between the carboxyl groups. An additional bond is formed between the water and the amide group.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31826 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester, CH1 1NZ, England.

Table 6. Conformation angles and metal environment in various histidine compounds

| | Co. H ₂ O ^b | | Co. 2H ₂ O ^c | | Zn. 5H ₂ O ^d | Zn. 2H ₂ O ^e | Cd. 2H ₂ O ^f | L-Histidine ^g | Histidine. HCl ^h |
|---------------------|-----------------------------------|-------|------------------------------------|--------|------------------------------------|------------------------------------|------------------------------------|--------------------------|-----------------------------|
| | Ni. H ₂ O ^a | I | II | I | | | | | |
| M-N(1) | 2.106 | 2.19 | 2.11 | 2.116 | 2.141 | 2.000 | 2.041 | 2.287 | |
| M-N(2) | 2.091 | 2.19 | 2.17 | 2.139 | 2.077 | 2.049 | 2.049 | 2.290 | |
| M-O(1) | 2.113 | 2.12 | 2.12 | 2.152 | 2.067 | 2.912 | 2.79 | 2.480 | |
| C(1)-C(2)-C(3)-C(4) | -56.5 | -47.8 | -53.0 | 50.8 | -58.1 | -49.3 | 48.3 | -42.9 | 181.4 |
| C(2)-C(3)-C(4)-C(6) | 159.1 | 145.3 | 156.5 | 139.4 | 164.9 | 139.8 | -133.7 | 125.2 | -123.2 |
| C(2)-C(3)-C(4)-N(2) | -20.6 | -26.7 | -21.5 | 36.1 | -18.6 | -42.1 | 45.9 | -55.2 | 56.8 |
| C(3)-C(2)-C(1)-O(1) | 109.0 | 113.9 | 98.9 | -105.1 | 107.7 | 118.5 | -109.9 | 98.2 | 94.4 |
| C(3)-C(2)-C(1)-O(2) | -71.1 | -73.7 | -82.4 | 71.8 | -69.9 | -61.9 | 68.1 | -79.9 | 83.8 |
| N(1)-C(2)-C(1)-O(1) | -14.1 | -9.8 | -20.8 | 15.3 | -15.3 | -3.6 | 10.0 | -23.8 | -26.8 |
| N(1)-C(2)-C(1)-O(2) | 165.8 | 162.6 | 157.9 | -167.3 | 167.2 | 176.1 | 172.0 | 158.1 | 155.1 |
| C(1)-C(2)-N(1)-H(1) | | | | | | | | -63.1 | 45.8 |
| C(1)-C(2)-N(1)-H(2) | | | | | | | | 179.6 | 163.5 |
| C(1)-C(2)-N(1)-H(3) | | | | | | | | | -76.4 |

References: (a) Fraser & Harding (1967). (b) Harding & Long (1968). (c) Candlin & Harding (1970). (d) Harding & Cole (1963). (e) Kretsinger, Cotton & Bryan (1963). (f) This work. (g) Madden, McGandy & Seemann (1972); Lehmann, Koetzle & Hamilton (1972). (h) Fuess, Hohlwein & Mason (1977).

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A Neutron Diffraction Study of 1,2-Diaminobenzene Monohydrochloride

BY CLAES STÅLHANDSKE

Division of Inorganic Chemistry 2, Chemical Center, The Lund Institute of Technology, P.O. Box 740, S-220 07 Lund 7, Sweden

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The structure of $C_6H_4(NH_2)_2 \cdot HCl$ has been refined from single-crystal neutron diffraction data. Full-matrix least-squares calculations based on F^2 converged to a final R of 0.039 for the 782 observed reflexions. The crystals are orthorhombic, space group $P2_12_12_1$, with $a=9.312$ (2), $b=4.920$ (1), $c=16.155$ (3) Å, $Z=4$. The structure is composed of $C_6H_4N_2H_5^+$ and Cl^- ions. Three cations are coordinated to one Cl^- ion through hydrogen bonds $N-H \cdots Cl^-$. All H atoms of the NH_3^+ group and one H of the NH_2 group are involved in hydrogen bonds.

The structures of 1,2-diaminobenzene monohydrochloride, dihydrochloride and dihydrobromide have been solved from X-ray data (Stålhandske, 1972*a*, *b*, 1974). Only approximate positions of the H atoms were obtained for the monohydrochloride and dihydrobromide. Neutron diffraction studies were therefore performed in order to determine the H positions and to reveal the hydrogen-bonding systems. The present article deals with the structure of the monohydrochloride.

Experimental

Large colourless crystals were grown, by slow evaporation at room temperature, from an aqueous solution containing equimolar quantities of 1,2-diaminobenzene and HCl.

Crystal data

1,2-Diaminobenzene monohydrochloride, $C_6H_4N_2H_5^+ Cl^-$, F.W. 144.60, orthorhombic, $P2_12_12_1$, $a=9.312$ (2), $b=4.920$ (1), $c=16.155$ (3) Å, $V=740.13$

Å³, $Z=4$, $D_x=1.30$, $D_m=1.31$ g cm⁻³ (floatation). Cell parameters were determined from powder photographs taken in a Guinier-Hägg focusing camera with Cu $K\alpha_1$ radiation and KCl as an internal standard.

A crystal, 3.5 × 3.5 × 4.0 mm, packed in thin Al foil, was used for data collection. The crystal was mounted with **b** parallel to the ϕ axis on an automatic Hilger-Ferranti four-circle diffractometer, located at the DR3 reactor at the Danish Atomic Energy Commission Research Establishment, Risø, Denmark. The wavelength of the monochromatized neutron beam was 1.025 Å and the flux at the specimen 0.9×10^6 n cm⁻² s⁻¹. The reflexions were measured by the ω -scan and the step-scan technique.

The total scan range for a reflexion was 3.36° with the peak-scan (2.40°) in steps of 0.04° and background scans (0.48°) in steps of 0.08°. In the range $0.07 < \sin \theta/\lambda < 0.618$, 1916 reflexions were recorded in sequence of increasing $\sin \theta/\lambda$. A standard reflexion, 321, was measured after every 15 reflexions. Background corrections were made (Lehmann & Larsen, 1974). The peak is separated from the background in such a way